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Eprints ID : 15993

To link to this article : DOI : 10.1002/slct.201600335
URL : http://dx.doi.org/10.1002/slct.201600335

To cite this version : Nistico, Roberto and Evon, Philippe and Labonne, Laurent and Vaca Medina, Guadalupe and Montoneri, Enzo and Francavilla, Matteo and Vaca-Garcia, Carlos and Magnacca, Giuliana and Franzoso, Flavia and Negre, Michèle *Extruded Poly(ethylene–co–vinyl alcohol) Composite Films Containing Biopolymers Isolated from Municipal Biowaste*. (2016) ChemistrySelect, vol. 1 (n° 10). pp. 2354-2365. ISSN 2365-6549

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DOI: 10.1002/slct.201600335

Extruded Poly(ethylene–co–vinyl alcohol) Composite Films Containing Biopolymers Isolated from Municipal Biowaste

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Single-screw extrusion allows obtaining composite films containing poly(ethylene-co-vinyl alcohol), hereinafter EVOH, and water-soluble lignin-like biopolymers (SLP) isolated from the alkaline hydrolysate of two materials sampled from an urban waste treatment plant. During extrusion, a condensation reaction occurs between the EVOH and SLP. The products are heterogeneous. They contain a mix of EVOH-SLP copolymers with different composition and solubility properties. The films were characterized for tensile strength and water sorption properties. Young modulus and strain at break, respectively, were 2.8 GPa and 14% for neat EVOH vs. 2.1-0.9 GPa and 17–4% for the blends containing 2–15% SLP, with values decreasing upon increasing the % SLP. The blends were more hydrophilic than neat EVOH; their water sorption capacity was found to increase upon increasing the SLP content. Compared to previously reported similar blends obtained by twin-screw extrusion and solvent casting, the data for the single-screw extruded films allows discussing several aspects connected to the valorisation of blends obtained from fossil and biowaste sourced polymers.

Introduction

The experimental work reported here was undertaken with three intents: i.e. (i) to manufacture new composite bio-based films by extruding biopolymers isolated from municipal biowastes and poly(ethylene-co-vinyl alcohol); (ii) to compare the properties of the extruded films with those previously published for films obtained by solvent casting the same blend components; (iii) to evaluate the neat effect of the different manufacturing technologies on the products properties. More than this, for the nature of reported products and sourcing materials, the work addresses two current important issues: (iv) the management of biowastes and (v) the substitution of synthetic polymers with biopolymers.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/slct.201600335

Bio-waste management has become a major technical and social issue. Solid bio-waste originates from industrial, agriculture and urban activities. It has two opposite faces. On one hand, it represents an economic and environmental burden. On the other hand, it contains valuable chemical exploitable energy. Thus, waste recycling and utilization is considered an essential element in efforts to make countries more resource efficient.[1] In principle, technology is available to recover and utilize the chemical energy contained in biowaste from any source. However, any technical approach has to account for process/product sustainability. In this respect, municipal biowaste are favored compared to all other biowaste sources. The environmental impact of municipal biowaste has grown dramatically, due to the increase of population urbanization and consumption habits. This has generated higher costs for society due to the need to dispose higher amounts of wastes. On the other hand, the population urbanization has resulted in the creation of a low entropy source of chemical energy by concentrating the bio-wastes in confined spaces. As taxpayers have already paid collection costs, municipal bio-wastes are a negative cost source of chemical energy.[2]

Recently, municipal biowastes have been demonstrated a cost effective source of water-soluble biobased lignin-like polymers (SLP).[3] The SLP are obtained by low temperature alkaline hydrolysis of the recalcitrant lignin fraction of urban biowastes.[4] They have been shown to perform as ecofriendly chemical auxiliaries in diversified fields; e.g. in the formulation of flocculants, dispersants and binding agents for ceramics manufacture,[3] detergents,[5] textile dyeing baths,[6] as emulsifiers,[7] auxiliaries for soil/water remediation[8–10] and enhanced oil recovery,[11] nanostructured materials for chemical[12,13] and biochemical catalysis,[14] plastic materials,[15–18] soil fertilizers and

plant biostimulants for agriculture,[19–21] and animal feed supplements.[22,23] The wide range of applications arises from the fact that SLP are a mix of polymeric molecules containing organic C and N distributed over a variety of aliphatic and aromatic C moieties substituted by acid and basic functional groups which are bonded to several mineral elements.[3,4] These chemical features represent the memories of the protein, fats, polysaccharide, and lignin proximates constituting the pristine biowaste. They are associated to the SLP properties as surfactants, agents for sequestering or carrying small molecules and mineral ions in solution, photosensitizers and reactive biopolymers.

Biopolymers have also become a major matter of research. Biopolymers are investigated mainly in the attempt to replace synthetic polymers, in order to reduce fossil sources depletion and CO_2 emission.[24] Biopolymers are macromolecular substances derived from renewable resources. They can be divided in three categories, i.e. polymers directly extracted/removed from biomass, polymers made by classical chemical synthesis using monomers from renewable resources, polymers obtained with the help of microorganisms or genetically modified bacteria. The use of biopolymers is not the only way to reduce the environmental impact caused by the increasing consumption of synthetic polymers. For most popular synthetic polymers, such as polyolefins, poly(vinyl chloride), polyurethane, poly(ethylene terephthalate), recycling is pursued. However, this practice still remains a major challenge. There are both technological and economic issues, which restrain the progress in this field.[25] The biopolymers alternative faces several criticalities too. So far, bio-based polymers have not found extensive applications in industries to replace conventional plastic materials, reasons being their high production costs and sometimes their underperformed properties. Compared to traditional resins costs, which run below 2 € kg^{-1},[26] current biopolymers are from about 2.0 to 7.0 times more expensive.[27] The difference depends on the fluctuation of oil prices and on the type of bioplastics, whether they are from dedicated crops, such as starch, or from fermentation, such as polyhydroxylalkanoates. In the case of biopolymers extracted from dedicated crops, the use of land to cultivate plants for energy or chemicals production raises much socio-environmental and moral concern.[28] Negative impacts on land, water and biodiversity, and food production count among the most discussed side effects of this practice.[29–30] Using corn as non-food feedstock may cause food price increase and thus can be controversial.

Bio-wastes, as sources of bio-based polymers, have not been much investigated so far. Yet, their valorization for this scope can potentially overcome some of the critical drawbacks faced by biopolymers extracted from dedicated crops or obtained by fermentation and/or chemical polymerization of monomers from renewable sources. In this context, investigation on SLP as potential candidates for the manufacture of bio-based consumer articles is undoubtedly a praiseworthy approach. The SLP production cost has been estimated 0.1-0.5 € kg^{-1}, depending on the nature of the biowaste.[3] Contrary to the case of dedicated crops, the exploitation of biowastes to obtain the SLP falls within the newest waste management technologies, which are expected to yield economic and environmental benefits, and at the same time to encounter social acceptance.[31–33]

A major technological draw back of SLP is the fact that they decompose without melting and do not have film forming properties.[3,4] They are complex mixtures of molecules with weight-average molar masses (Mw's) of 67–463 kDa. As obtained by low temperature alkaline hydrolysis of the recalcitrant lignin fraction of urban biowastes, the SLP save the memory of the aromatic rigid chemical structure of the parent lignin, a though not ductile material. Thus, neat SLP cannot be processed to obtain useable objects by the available conventional technologies, such as solvent casting or melt extrusion. Under these circumstances, the only possibility is compounding them with other polymeric materials to obtain processable blends. Franzoso et al. have indeed obtained blend films made from SLP and synthetic polyethylene copolymers,[15–17] such as poly(ethylene-co-vinyl alcohol) (EVOH) and polyethylene-co-acrylic acid (PEEA). These commercial polymers derived from fossil sources are used for the manufacture of a great variety of articles of every day life. Blends of synthetic polymers and biopolymers of agricultural sources are well known. Several blends of poly(vinyl alcohol), ethylene-vinyl alcohol copolymers, and polysaccharides, such as starch[34–36] or lignocellulosic materials including corn fiber[37] and sugar cane bagasse[38–41] have been reported. These products have been proposed for the manufacturing of mulch films for use in agriculture. In these films, the synthetic polymer provides the required mechanical properties and is compatible with the lignocellulosic fillers by virtue of its hydroxyl and carboxyl groups. In the case of the SLP composites, considering the SLP properties as biostimulants for plant cultivation,[19–21] the manufacturing of blended SLP mulch films offers the intriguing perspective to perform a dual function with the same material, i.e. assure protection of the cultivation soil and, during and/or at the end of its service life, to promote soil fertilization.

Franzoso et al. work demonstrated that the EVOH-SLP[15] and PEAA-SLP[16] blends, which contain not more than 10% SLP, have similar or higher mechanical strength as the pristine synthetic polymer. Blends with higher biopolymers content were found to have poor unacceptable mechanical properties. The results indicated that it is possible to enhance the mechanical strength of the tested synthetic polymers. However, this occurs with some loss of the elongation capacity. Most recent work[18] has demonstrated that the mixtures of EVOH and SLP could be processed by twin-screw extrusion to obtain articles in rod form. The results encouraged the present work reporting the manufacture of EVOH-SLP blends in film form by single-screw extrusion.

The reason for undertaking the present work on the extruded EVOH-SLP blends in film form was that, although recently solvent casting has gained much industrial importance,[42] extrusion is still a more industrially relevant technique, particularly for the manufacture of articles in film form. Being carried out in the absence of solvents,[43] extrusion is a potentially greener process alternative. Moreover, extrusion occurs with the blend constituents in the melt state, resulting

Table 1. Analytical data[a] for mineral elements, organic c and n, functional groups, and weight ($\bar{M}_w$) and number ($\bar{M}_n$) average molecular weights for digestate (D) and compost (CP) SLPs.

SLP	pH	Volatile Solids, w/w %[b]	C, w/w %[b]	N, w/w %[b]	C/N
D	6.4	84.6	45.07 ± 0.12	7.87 ± 0.12	5.73
CP	8.2	72.1	38.25 ± 0.09	4.01 ± 0.03	9.54

	Mineral elements: Si, Fe, Al, Mg, Ca, K, Na as % w/w;[b] Cu, Ni, Zn, Cr, Pb, Hg as ppm[b]												
	Si	Fe	Al	Mg	Ca	K	Na	Cu	Ni	Zn	Cr	Pb	Hg
D	0.36 ±0.03	0.16 ±0.00	0.78 ±0.04	0.18 ±0.01	1.32 ±0.05	9.15 ±0.06	0.39 ±0.01	100 ±1	27 ±1	185 ±4	11 ±0	44 ±2	0.23 ±0.01
CP	2.55 ±0.01	0.77 ±0.04	0.49 ±0.04	1.13 ±0.06	6.07 ±0.38	3.59 ±0.21	0.16 ±0.01	202 ±4	92 ±1	256 ±1	19 ±1	85 ±1 ($\bar{M}_w$)	0.15 ±0.02 ($\bar{M}_w/\bar{M}_n$)
	C types and functional groups[c] concentration as C mmol per g of product												
	Af	NR	OMe	OR	OCO	Ph	PhOH	PhOY	COOH	CON	C=O		
D	16.1	3.7	1.5	3.7	1.1	3.7	0.75	0.37	2.6	3.4	0.37	188	1.4
CP	11.8	2.2	0.0	4.4	1.3	4.1	1.6	0.64	3.8	0.32	1.5	66	4.7

[a]Data obtained according to previously reported analytical methods:[44] volatile solids calculated from the sample weight losses after heating to 105 and 650 °C, organic C and N by microanalysis, mineral elements by atomic absorption spectroscopy, C types and functional groups by potentiometric titration and solid-state ^{13}C NMR spectroscopy, molecular weights by multi-angle light scattering detector online to size exclusion chromatography system. [b]Concentration values referred to dry matter: averages and standard deviation calculated over triplicates. [c]Aliphatic (Af), aromatic (Ph), methoxy (OMe), amide (CON), ammine (NR), alkoxy (RO), phenoxy (PhOY) and anomeric (OCO), carboxylic acid (COOH), phenol (PhOH), and ketone (C=O) C atoms.

in large differences in temperature but also in residence time and applied shear rate compared to the solvent cast technique. To the authors of the present work, these facts pointed out that, to acquire further knowledge on the full potential and process/product sustainability of the EVOH-SLP blends, it was necessary to compare the blends with the same formulation, but obtained by the two different manufacturing technologies. Indeed, the data reported here in after demonstrate that the different fabrication processes do affect differently the films mechanical properties. Moreover, for the extruded films the water sorption properties were investigated in order to assess perspectives for potential uses of these materials in a wider range of applications than the fabrication of mulch films only.

Results and Discussion

Preparation, and chemical and physical characterization of neat SLPs

The SLPs used in this work were available from previous work.[15–18] These materials, hereinafter named with the acronym D SLP and CP SLP were sourced from municipal biowastes sampled from two different streams of a waste treatment plant located in Pinerolo (TO), Italy. The sourcing biowastes were the digestate (D) recovered from the plant biogas production reactor fed with the organic humid fraction from a separate source collection of urban refuse, and the compost (CP) obtained from home gardening and park trimming residues aged for 230 days under aerobic conditions. The two SLPs were isolated from the alkaline hydrolysates of the digestate and compost, and were characterized as previously reported.[44] According to Table 1 data, they contain either organic and mineral matter, the latter constituted mainly by silicates containing Ca, Mg, Al, Fe, Na and K cations present in 15–28 wt.% concentration relatively to the dry matter content. The organic matter is polymeric. The weight ($\bar{M}_w$) and number ($\bar{M}_n$) average molecular weights are 66 ($\bar{M}_w$) and 14 ($\bar{M}_n$) kDa for the compost (CP) SLP, and 188 ($\bar{M}_w$) and 134 ($\bar{M}_n$) for the digestate (D) SLP, with polydispersity indexes ($\bar{M}_w/\bar{M}_n$) of 4.7 for the compost (CP) SLP and 1.4 for the digestate (D) SLP. Table 1 reports also relative concentration data for aliphatic and aromatic C types, and acid and basic functional groups, which were identified and measured by using ^{13}C NMR spectroscopy, potentiometric titration, and C and N microanalysis. The C types and functional groups are likely to constitute C moieties, which are reminiscent of the pristine polysaccharide, protein and lignin matter present in the starting biowastes as collected, before anaerobic and/or aerobic fermentation. Due to their biological origin, the molecules constituting the SLPs are most likely not homogeneous. The $\bar{M}_w/\bar{M}_n$ index shows that a mix of molecules with different weight is present. Moreover, these molecules have probably different chemical nature. They do not necessarily contain the same C types and functional groups, and the same mineral elements bonded to the functional groups. Under these circumstances, the body of analytes reported in Table 1 does not allow to assess a definite chemical structure for SLP as for single synthetic molecules. Nevertheless, it gives valuable information on differences in the chemical nature of the two SLPs. The data shows that, compared to the digestate (D), the compost (CP) SLP contains more aromatic lignin-like matter, acid functional groups, and ash content. This is the likely reflection of the different nature (the organic humid fraction versus gardening waste) and biological processes (anaerobic versus aerobic fermentation) of the D and CP pristine biowastes. The data points out the higher oxidation degree of the compost SLP. Evidence for this is obtained from the following two parameters calculated from Table 3 data for the D and CP SLP, respectively: i.e. (i) the VS/(C + N) values resulting 1.59 and 1.71, and (ii) the total O content, calculated from the C types and functional groups concentration values, resulting 17.5 and 21.5 mmol per g of product. The 1.71 VS/(C + N) points out a higher amount of H and O in the CP SLP than in the D SLP. The 21.5 C mmol

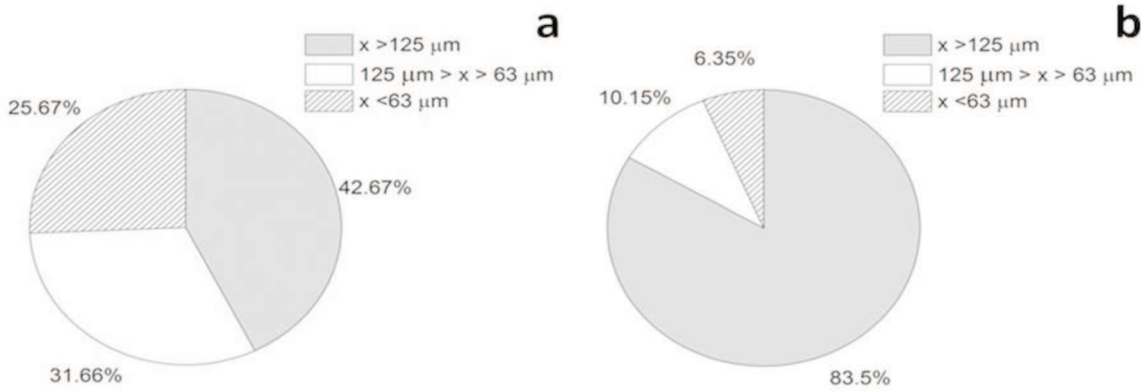


Figure 1. Overall particle size distribution for the entire grinding process of neat digestate (a) and compost (b) SLP.

Table 2. Blend sheet films[a] dimensional data, and recorded pressure and temperature of the extruded material during single-screw extrusion.

Sample	Length (m)	Width (cm)	Thickness (μm)	Weight (kg)	Pressure (bar)	Temperature (°C)
E0	9.07	2.9	130 ± 44	0.040	104 ± 1	198 ± 1
ED2	8.44	3.2	223 ± 25	0.066	116 ± 1	202 ± 1
ED5	8.55	3.5	250 ± 17	0.082	128 ± 6	203 ± 1
ED10	8.35	4.5	450 ± 35	0.078	116 ± 3	203 ± 1
ED15	8.58	4.4	330 ± 35	0.078	112 ± 3	202 ± 1
EC5	8.30	2.8	200 ± 32	0.036	104 ± 2	199 ± 1
ED/C2/3	8.78	3.4	304 ± 36	0.068	116 ± 4	203 ± 1
ED/C5/5	9.07	4.0	508 ± 61	0.076	131 ± 1	201 ± 1

[a]Neat EVOH (E0), EVOH containing 2, 5, 10, 15% digestate (D) SLP (ED2, ED5, ED10 and ED15, respectively), EVOH containing 5% compost (CP) SLP (EC5), and EVOH containing both digestate (D) and compost (CP) SLP in the same sample at 2% D and 3% CP (ED/C2/3), and at 5% D and 5% CP (ED/C5/5).

per g of product confirms that the CP SLP organic matter has higher oxygen content that the D SLP.

Before use, the neat SLPs were ground and sieved (see Supporting Information). Figure 1 reports the overall D and CP particle size distribution for the entire grinding process. The $125\mu m > x > 63\mu m$ fraction was kept and used for the blend film preparation.

Preparation, and chemical and physical characterization of SLP blend films

The composition of the blend films, produced in this work by single-screw extrusion was chosen based on previous work reporting the fabrication of the EVOH blends containing the digestate (D) and the compost (CP) SLP produced in film form by solvent casting.[15] The digestate (D) SLP at 5.9% content in the EVOH blend was found[15] to enhance the blend film Young modulus, compared to the neat EVOH film. At SLP concentration > 15%, the blend films exhibited poorer mechanical properties than neat EVOH. In all cases, the D filler performed better than the CP one, either for its higher compatibility with EVOH and for its effects on the blend mechanical properties.

Based on the above findings, the films listed in Table 2 were produced according to the experimental details reported in the Supplementary Information. In essence, sheet film production was carried out in a Scamex (France) 30–26 single-screw extruder with a 26 length/diameter ratio and a 30 mm screw diameter, operated under the following conditions: 25 rpm screw speed, 10 m min^{-1} calendar speed and 0.84 ± 0.05 mm lip height, in essence cancel (B) ambient temperature at the inlet, 165 °C in the conveying zone, 195 °C in the melting zone, 185 °C in the kneading zone and 175 °C at the outlet die. These conditions were much different from those used for the production of the solvent cast films,[15] were the operating temperature was never above 120 °C. The extruded products were the films of neat EVOH (E0), EVOH containing 2, 5, 10, 15% D SLP (ED2, ED5, ED10 and ED15, respectively), EVOH containing 5% CP SLP (EC5), and EVOH containing both D and CP SLP at 2% D and 3% CP (ED/C2/3), and 5% D and 5% CP (ED/C5/5). For the most promising D filler, the four films containing 2, 5, 10 and 15% D SLP were fabricated to investigate the effect of the D content on the film thermal and mechanical behaviour. The other films in Table 2 were fabricated to assess if the lower performance of the CP SLP filler previously observed for the solvent cast films[15] was still confirmed or not under single-screw extrusion conditions, and to discover eventual synergism from the presence of both D and CP SLPs in the same blend.

The chemical nature of the blends was assessed, based on the solubility properties of the starting reagents. Neat EVOH is insoluble in water. The SLPs are soluble in water at pH > 4, but precipitate at lower pH. As in previous work,[15] selective extraction (see Supplementary Information) of the blends was carried out with 1 M aqueous NaOH at room temperature and at 60 °C. This procedure allows identifying the following three types of SLP in the blend: (i) SLP not bonded to EVOH, soluble

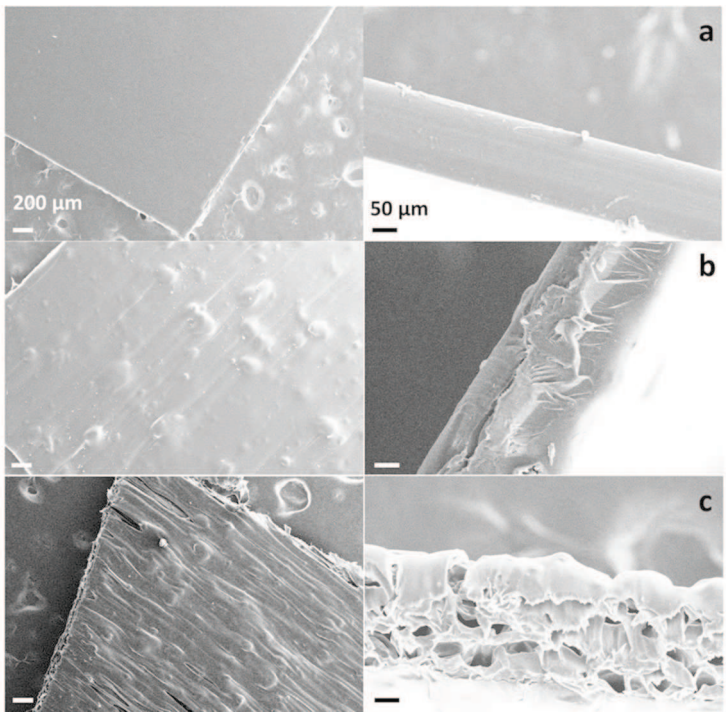


Figure 2. Scanning electron microscopy images of surface (left) and cross section (right) of neat EVOH (a) and its blend films containing 5 (b) and 15 (c) % digestate (D) SLP: samples E0, ED 5 and ED10, respectively, in Table 2.

in aqueous NaOH at room temperature; (ii) SLP bonded to EVOH by hydrolysable ester bonds, becoming soluble only upon hydrolysis of the EVOH-SLP copolymer carried out in 60 °C NaOH, and (iii) SLP bonded to EVOH by not hydrolysable covalent bonds, not released into the alkaline solution even after treatment at 60 °C. The results of the above NaOH treatments showed average 34 ± 5% weight loss of the starting SLP amount in the blends containing 5 and 15% SLPs, respectively, either at room temperature or 60 °C. The recovered precipitate from the acidified water phase accounted well for the weight loss of the blend sample. This indicated that most of the SLP contained in the blend was bonded to EVOH with not hydrolysable covalent bonds.

The amount of SLP in the films recovered from the NaOH treatment was estimated from the amount of N. This element was present only in the SLP filler (Table 1). Thus, assuming that the N containing molecules were representative of the entire SLP filler, in principle one could calculate the % SLP in the blend from its N content. For example, the ED5 pristine film contained 0.31% N, which corresponded to 3.96% D in the blend, based on the N content in neat D (Table 1). The ED5 films recovered from the NaOH treatment at 30 and 60 °C were 0.31 and 0.28% respectively. The data allows calculating that 90% of the total D amount present in the blend was bonded to EVOH with not hydrolysable covalent bonds forming a new EVOH–D copolymer. By comparison, the ED15 pristine film contained 0.83% N, which corresponded to 10.6% D in the blend. The ED15 films recovered from the NaOH treatment at 30 and 60 °C were 0.55 and 0.59% respectively. The data allows calculating that 71% of the total D amount present in the blend was bonded to EVOH with not hydrolysable covalent bonds. The remaining D was not bonded to EVOH, but simply present as a separate phase mixed with the EVOH–D copolymer.

The above results of the films NaOH treatments suggest that the blend chemical composition was heterogeneous over the entire sample, and that the degree of heterogeneity increased upon increasing the filler content. The presence of different phases in the blends was also demonstrated by scanning electron microscopy. Figure 2 shows that the surface and cross section of the neat EVOH are homogeneous and/or not porous. The ED5 film is also non-porous. However, it shows some heterogeneity. The ED15 film has also non-porous surface. However, the surface is more heterogeneous than that of the ED5 film. In addition, the cross section exhibits several internal cracks. The films were also analysed by BET and BJH measurements (see Supplementary Information). The results showed that the ED films had surface areas decreasing from ca. 2.01 to ca. 1.37 $m^2 g^{-1}$ upon increasing the filler content, and that the pore volume ranged from 0.006 to 0.010 $cm^3 g^{-1}$. The measured low surface area does not allow applying correctly the BET method, since the measured values are below the instrumental limit.[45] The data only suggests that the films were not porous, in accordance with the scanning electron microscopy images in Figure 2. The results of NaOH treatments are well consistent with those obtained in previous work for the solvent cast EVOH films[15] containing the same SLPs. The presence of different EVOH-SLP copolymers with different composition and solubility properties had been reported for the solvent cast films.[15] The data reported in the present work confirms that, also during the blend production using single-screw extrusion, a chemical condensation reaction occurs between the EVOH hydroxyl functional groups and the SLP phenol functional OH groups (Table 1) with formation of aralkyl ether bonds.

Table 3. Films* DSC and crystallinity data: glass transition (T_g), melting (T_m) and recrystallization (T_c) temperatures, melting (ΔH_m) and recrystallization (ΔH_c) enthalpies, X_c and CrI crystallinity degrees calculated according to Eq (1) and Eq (2), respectively.

Sample	T_g (°C)$^+$	T_c (°C)$^+$	T_m (°C)$^+$	ΔH_c (J/g)$^+$	ΔH_m (J/g)$^+$	X_c (%)	CrI (%)
E0	46.7 ± 0.0a	145.3 ± 0.8a	170.8 ± 1.1a,b	58.5 ± 0.4a	62.6 ± 0.0a,b	37	68
ED2	50.5 ± 3.4a	145.4 ± 1.3a	170.5 ± 0.3a,b	56.9 ± 1.0a,b	63.8 ± 0.2a	38	60
ED5	42.5 ± 5.2a	141.5 ± 2.2a	167.7 ± 3.5a,b	52.4 ± 1.8a,b	59.6 ± 1.8a,b	37	59
ED10	50.7 ± 7.2a	145.1 ± 3.1a	170.4 ± 0.6a,b	50.9 ± 2.3a,b	59.0 ± 0.3a,b	39	61
ED15	47.6 ± 0.8a	145.1 ± 2.1a	169.8 ± 0.0a,b	48.1 ± 0.8b	50.1 ± 1.3b	35	58
EC5	43.1 ± 2.2a	141.5 ± 1.6a	167.3 ± 2.3b	53.7 ± 0.9a,b	52.1 ± 0.5b	32	68
ED/C2/3	50.0 ± 0.1a	145.6 ± 1.0a	171.9 ± 0.3a	55.5 ± 2.1a,b	59.5 ± 3.2a,b	37	63
ED/C5/5	49.6 ± 1.0a	146.7 ± 0.8a	171.4 ± 0.2a,b	53.6 ± 0.0a,b	59.7 ± 0.1a,b	39	58

*Neat EVOH (E0), EVOH containing 2, 5, 10, 15% digestate (D) SLP (ED2, ED5, ED10 and ED15, respectively), EVOH containing 5% compost (CP) SLP (EC5), and EVOH containing both digestate (D) and compost (CP) SLP in the same sample at 2% D and 3% CP (ED/C2/3), and at 5% D and 5% CP (ED/C5/5). $^+$Values are means of two measurements ± standard deviation; values followed by the same letters in each column are not significantly different ($P \leq 0.05$; Tukey tests).

No other techniques or procedures were found suitable for supporting the formation of the above covalent bonds. The filler content was too low for its presence to be appreciated by IR or ^{13}C NMR spectroscopy. In addition, as shown in Table 1, ether bonds are already present in the neat SLP. This adds difficulty to the selective identification of new ether bonds formed through the reaction of SLP with EVOH. The reaction might involve also participation of the mineral fraction present in the SLP. Assessing the effect of the mineral fraction on the SLP reactivity implies demineralization of SLP and comparing the reactivity of the demineralized SLP with that of the pristine SLP. Attempts to demineralize SLP by HCl and HF metal ion stripping were found to cause important changes in the residual organic fraction composition relatively to that in the pristine SLP. This pointed out that new biopolymers could potentially be obtained by further acid treatment of SLP. Under these circumstances, further testing of the reactivity of the demineralized SLP with EVOH was planned for being carrying out in future work in order to comprise the full characterization of both the new acid treated SLP biopolymers and the corresponding blends.

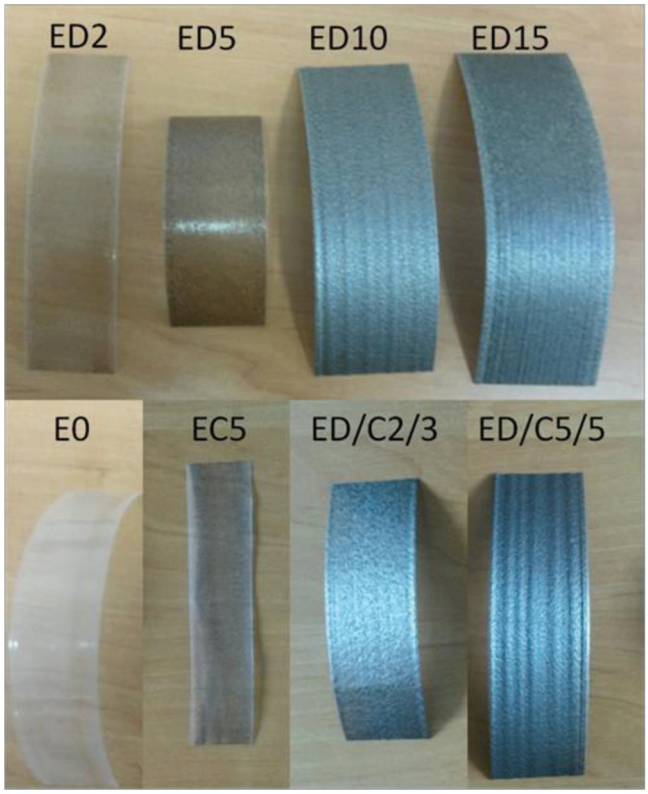


Figure 3. Blend sheet films at different filler contents. Sample abbreviations as in Table 2.

Blend film physico–chemical characterization

Figure 3 shows the aspect of the investigated films. Table 2 reports the dimensional data and the recorded pressure and temperature of the extruded materials during single-screw extrusion. The data shows that upon increasing the filler content up to 15%, the film becomes increasingly dark colored (Figure 3), and the film thickness (Table 2) tends to gradually increase. All films could be bent at 180 degrees angle or rolled over. However, they tended to become more and more rigid upon increasing the filler content. The blends containing both the digestate (D) and the compost (CP) SLPs in the same sample (ED/C 2/3 and ED/C 5/5 in Table 2) are always thicker than the blends made with one filler, i.e. only D or CP (as in ED2-15 and EC5 Table 2 samples, respectively). Electron microscopy scans (images not shown) demonstrated that the blends containing both the digestate (D) and the compost (CP) SLPs in the same sample (ED/C 2/3 and ED/C 5/5 in Table 2) were more heterogeneous than the blends containing the single SLPs at equal total SLP content. It is important to notice that the blend containing the compost SLP (EC5) and the blends containing the mix of digestate (D) and compost (CP) SLP (ED/C 2/3 and ED/C 5/5 in Table 2) presented many friction problems during the extrusion process. The problem was probably due to the high ash content contributed by the compost (CP) SLP. It may lead to wear phenomena by abrasion of the metal parts of the single-screw extrusion line (i.e. the plasticizing cylinder, the screw and the die) on the long term. Samples made with demineralized SLPs might be more easily flexible for industrial applications (see above subsection).

Table 3 reports the data obtained from the DSC scans and X-ray diffraction of neat EVOH and the EVOH-SLP blend films. These samples gave measurable values for all reported parameters. On the contrary no values could be measured for the neat

SLPs. For the latter ones, no glass transition or melting up to 220 °C was evidenced by DSC. At this temperature, both CP and D SLP started to decompose. XRD analysis showed that the neat SLPs are mostly amorphous. For the blends, the data in Table 3 shows no significant difference or trend of the reported phase transition temperatures and X_c crystallinity degrees, by increasing the filler contents in the blend. However, the values for melting (ΔH_m) and cold crystallization (ΔH_c) enthalpies of the blends are lower than the values for neat EVOH. This behavior is different from that reported for the twin-screw extruded blends.[18] Relatively to neat EVOH, the twin-screw extruded blends containing 2–14% SLP exhibited significantly lower T_m, T_c and T_g values, while ΔH_m and ΔH_c showed opposite trend. In addition, the enthalpy and crystallinity values for the single-screw extrudates are remarkably lower than the ones calculated for the twin-screw extrudates. For example, the melting and cold crystallization enthalpies of single-screw neat EVOH and blend films containing 2–15% D (ED2-15 in Table 3) range from 62.6 to 50.1 J g^{-1}, and from 58.5 to 48.1 J g^{-1}, respectively. By comparison, the enthalpy values for the twin-screw extrudates[18] with the same composition range from 100 J g^{-1} for neat EVOH to 125 J g^{-1} for the blend containing 5% D.

The crystallinity degree % X_c and CrI % values in Table 3 were calculated, respectively, from the enthalpy data in Table 3 according to eq. (1) and from the X-ray diffraction patterns shown in Figure 4 according to eq. (2):

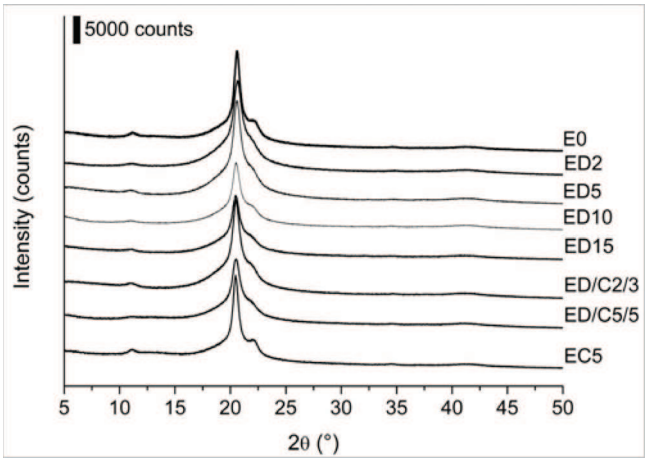


Figure 4. X-ray diffraction patterns relative to extruded blend sheet films. Comparison between neat EVOH (E0), and its blends containing the digestate (D) and the compost (CP) SLP. Samples abbreviations as in Table 2.

$$\%X_c = 100\ \Delta H_m/(w\ \Delta H^\circ_m) \quad (1)$$

$$\%CrI = 100\ (I_f - I_s)/I_f \quad (2)$$

In eq. (1), ΔH_m is the melting enthalpy of the blend sample (J/g), ΔH°_m is the melting enthalpy (169.2 J/g) of the EVOH sample assuming 100% crystallinity as in pure polyvinyl alcohol (PVOH),[46] and w is the EVOH mass fraction in the composite. In eq. (2),[47] I_f is the peak intensity of the fundamental band at $2\theta = 20.1^\circ$, and I_s is the peak intensity of the secondary band at $2\theta = 22.1^\circ$, both bands present in the X-ray diffraction patterns represented in Figure 4. The raw I_s and I_f measured values are reported in the Supporting Information file. The calculated values for the crystallinity degree of the single-screw blends (Table 3) are in the 39–35% X_c and 68–58% CrI ranges. The corresponding values for the twin-screw extrudates[18] are comprised in the 60–80% range. These differences can be explained. Before opening the twin-screw extruder to recover the test specimens, samples were cooled slowly (ca. 9 min). Thus, the EVOH macromolecules had enough time to organize themselves in an orderly manner. Conversely, the single-screw extrusion procedure adopted in this work resulted in remarkably lower cooling time scale as for industrial level (order of seconds). Thus, macromolecules were still in the disordered state and the resulting extruded films were more amorphous.

The crystallinity of the single-screw extruded sheet films may be appreciated better from the X-ray diffraction patterns represented in Figure 4. Poly(ethylene-vinyl alcohol) copolymers[48] are known to be crystalline irrespectively of composition. They show a polymorphic behaviour depending on composition and thermal treatment. The copolymers with relatively high vinyl alcohol content (68-71%), such as the Soarnol copolymer used in the present and in the previous[15,17–18] works, crystallize from the melt into a monoclinic or orthorhombic lattice, depending on the cooling rate. The two lattices give similar patterns, i.e. a fundamental high intensity band at $2\theta = 20^\circ$ and a smaller band at $2\theta = 21\text{-}22^\circ$. However for the monoclinic lattice the fundamental band is split into two well distinct signals, falling at $2\theta = 19\text{-}20^\circ$ and at $2\theta = 20\text{-}21^\circ$, respectively. For the orthorhombic lattice these signals collapse into one broad band. These copolymers crystallize in the monoclinic lattice upon slow cooling, and in the orthorhombic lattice upon quenching. For the semi crystalline EVOH co-polymer used in the present work, Figure 4 shows sharp well-defined and broad peaks due to small crystallites. In agreement with literature data,[49] the peaks are centred at $2\theta = 10.8^\circ$, 20.1° and 22.1°. The broad fundamental band at $2\theta = 20.1^\circ$ resembles that reported for the copolymer crystallized in the orthorhombic lattice.[49] In contrast, the patterns for the SLPs (not reported), have very broad features consistent with incoherent scatter from an amorphous solid. Figure 4 also shows that, in all analysed blends, the characteristic EVOH peaks are in the same position as those for the neat EVOH extruded sample. Moreover, upon increasing the SLP content in the blend, one can observe a slight decrease of the EVOH signals intensity, no change in the relative ratios between the peaks and no new signal arising from a new crystalline phase. This behaviour is reflected in the % CrI values (Table 3), showing the trend for crystallinity to slightly decrease upon increasing the filler content in the blend.

Table 4. Mechanical properties for neat EVOH and EVOH-SLP extruded films,* and for starch based (MB) and low density polyethylene (MP) mulch films.

Samples	Young modulus G (MPa) [+]	Stress at yield (MPa) [+]	Max stress (MPa) [+]	Stress at break (MPa) [+]	Strain at break (%) [+]
E0	2823 ± 479a	41.2 ± 5.0a	54.2 ± 4.5a	46.8 ± 5.1a	14.1 ± 1.8a,b
ED2	2067 ± 180b,c	41.7 ± 2.5a	53.7 ± 2.9a	44.3 ± 2.6a,b	17.0 ± 5.2a
ED5	2112 ± 169b	34.8 ± 0.1b	42.1 ± 1-0b	30.1 ± 8.8c	7.2 ± 2.8b
ED10	970 ± 148e	15.3 ± 0.6c,d	16.1 ± 0.7d,e	13.9 ± 1.8d	4.9 ± 0.1b
ED15	1005 ± 129e	11.2 ± 1.0d	13.4 ± 1.5e	12.7 ± 1.2d	5.9 ± 0.2b
EC5	1730 ± 99b,c	38.8 ± 2.0a,b	39.5 ± 1.7b,c	35.0 ± 1.1b,c	9.1 ± 0.6b,c
ED/C2/3	1058 ± 121d,e	20.1 ± 1.4c	20.2 ± 1.5d	18.6 ± 1.7d	5.7 ± 0.7c
ED/C5/5	906 ± 53d	14.1 ± 0.9cd	14.5 ± 1.2d,e	14.1 ± 1.2d	4.2 ± 1.0c
MB	247 ± 70			15 ± 1	413 ± 200
MP	160 ± 25			15 ± 1	230 ± 70

*Neat EVOH (E0), EVOH containing 2, 5, 10, 15% digestate (D) SLP (ED2, ED5, ED10 and ED15, respectively), EVOH containing 5% compost (CP) SLP (EC5), and EVOH containing both digestate (D) and compost (CP) SLP in the same sample at 2% D and 3% CP (ED/C2/3), and at 5% D and 5% CP (ED/C5/5). [+]Values are means of three measurements ± standard deviation; values followed by the same letters (a-e) in each column are not significantly different ($P \leq 0.05$; Tukey tests). Data for MB and MP taken from literature (see Relevance of Results section below) are not included in the statistical comparison of EVOH and EVOH-SP extruded films.

Blend film mechanical characterization

Table 4 reports data relative to the mechanical properties of the films. For the blends containing the digestate (D) SLP (ED2-15 in Table 4), the Young modulus of the neat EVOH film decreases significantly already at only 2% filler content. The Young modulus for the blend containing the compost (CP) SLP (EC5) and the mix of digestate (D) and compost (CP) SLP (ED/C 2/3 and ED/C 5/5) is even lower than that of the EVOH blends containing the digestate (D) SLP only. The other mechanical indicators of the neat EVOH films are not significantly affected at 2% filler content. Significant decreases appear at higher filler content.

Similar trends are reported for the flexural strength at break and bending modulus of the twin-screw extruded EVOH-SLP blends, upon increasing the SLP content.[18] It is particularly interesting however to observe that the Young modulus values for the single-screw extruded films from this work are much higher than those reported for the solvent cast films containing the same components,[15] while the strain at break values are much lower. For the solvent cast films, the strain at break and Young modulus values of the neat EVOH film were 86.2%, and 352 MPa, respectively. By comparison, the film containing 5.9% digestate (D) SLP exhibited 42.3% strain at break and 1082 MPa Young modulus. Several factors may cause the above differences between the solvent cast and the single-screw extruded films. These may be the higher processing temperature and higher applied shear rate of the extruded films, and the presence of residual dimethylsulfoxide solvent in the solvent cast films. The higher processing temperature and higher applied shear rate of the extrudates may be responsible of higher crystallinity. On the other hand, the residual solvent in the cast films may act as compatibilizer, and thus modify the blend morphology-property connections.

Blend film water sorption

An important property, which was not addressed in the previous work by Franzoso et al.[15–18] is the blend vapor and liquid water sorption. This property, coupled to the thermal and mechanical properties of the films, might disclose interesting perspectives for use of the EVOH-SLP blends in the separation of gases,[50,51] in the textile industry,[52] in reverse osmosis,[53] in ion exchange[54] or proton conduction[55] technology. Other uses may be envisaged in cases requiring water insoluble materials which can work in humid and aqueous environment, and be mechanically, chemically and dimensionally stable in water, and at the same time exhibit water permeability. The chemical features of the SLP fillers (Table 1) encourage these expectations. By virtue of the presence of lipophilic and hydrophilic C moieties, these products exhibit interesting surfactant properties.[56] For the same features, they can interact in different ways with molecules of different polarity. In principle, water sorption may occur due to physical entrapment of water into porous structure or to chemical interactions between water and the solid phase. The latter are more favored as the hydrophilicity of the solid phase increases. In the case of the non-porous EVOH-SLP blends listed in Table 2, the physical entrapment of water by the blends may be reasonable excluded.

Water vapor sensitivity of the neat SLPs was estimated by DVS analysis. For both the neat digestate (D) and the neat compost (CP) SLP samples, water vapor uptake increased upon increasing relative humidity (Figure 5). For high relative humidity

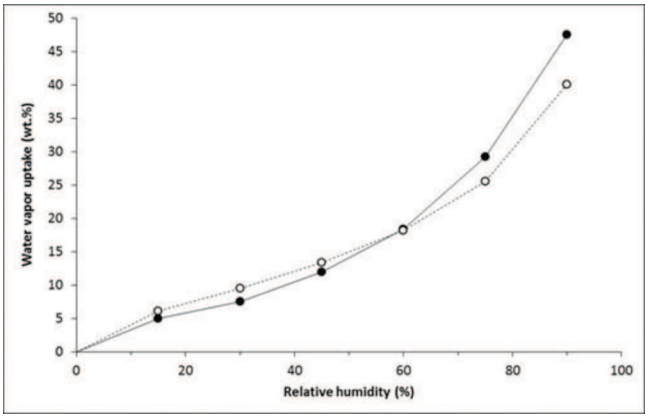


Figure 5. Water vapour sensitivity evaluation by DVS analysis for the neat digestate (D; black solid line, black circles) and the neat compost (CP, black dotted line, white circles) SLP.

levels ≥ 75%, the compost (CP) SLP was less water vapor sensitive, and this could be correlated to its chemical composition revealing more aromatic lignin-like matter than the digestate (D) SLP (Table 1). The EVOH-SLP blends (Figure 6 and 7) exhibit

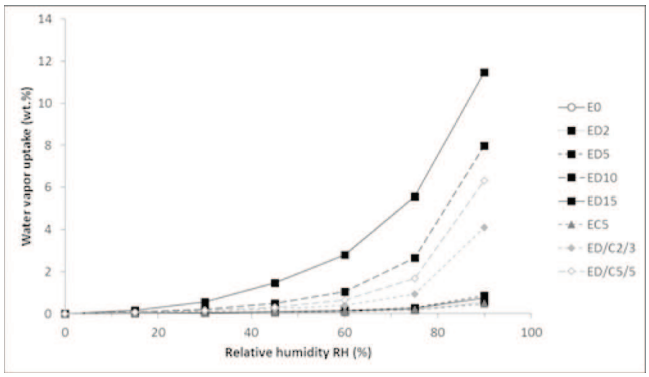


Figure 6. Water vapour sensitivity evaluation by DVS analysis for neat EVOH and blend films. Legends: E0 (black solid line, white circles),ED2 (black dotted line, black squares), ED5 (black short-dashed line, black squares), ED10 (black long-dashed line, black squares), ED15 (black solid line, black squares), EC5 (dark-grey short-dashed line, dark-grey triangles), ED/C2/3 (light-grey short-dashed line, light-grey diamonds), ED/C5/5(light-grey long-dashed line, white diamonds). Samples abbreviations as in Table 2.

the following behavior. For ED and EC blends with no more than 5% filler content (ED2, ED5 and EC5 samples), the water vapor uptake is roughly comparable to that of neat EVOH (E0 sample), with uptakes all situated between 0.5 and 0.9% at 90% RH. For the blends containing the digestate (D) SLP (ED2-15 samples), the water vapor uptake increases progressively upon increasing the D content in the film. As an example, at 90% RH conditioning, it increases from 0.6% with only 2% D filler content to 11.5% with 15% D filler content. Thus, the more the D filler content in the blend, the more the water vapor sensitivity of the EVOH–D blend.

The water uptake depends also on the filler type. As an example, for a 5% filler content, water vapor uptake at 90% RH is only 0.5% for the EC5 blend containing 5% of compost (CP) SLP, 0.9% for the ED5 blend containing 5% of digestate (D) SLP, and it reaches 4.1% for the ED/C2/3 blend containing 2 and 3% of D and CP SLP, respectively, in the same sample. The performance of the blends containing the single SLP (ED5 and EC5) are consistent with the data obtained for the neat D and CP SLP (Figure 5), which indicates that the D SLP is more water vapor sensitive than the CP SLP. Moreover, it may observed that the presence of both fillers in the blend at total 5% filler content leads to synergic water vapor absorption. In essence, the water vapor sorption by the ED/C2/3 film sample is from 4.5 to 8 times higher than that by the ED5 and EC5 blend samples, respectively (see Figure 7). On the contrary, this synergic effect is no more observed from the ED/C5/5 blend sample, its water vapor uptake at 90% RH (6.3%) being significantly lower than that of the ED10 blend (8.0%). Both samples contain the same 10% amount of total filler. However, the ED10 sample contains 10% of digestate (D) SLP only, while the ED/C5/5 sample contains 10% of a mix of equal quantities of digestate (D) and compost (CP) SLP.

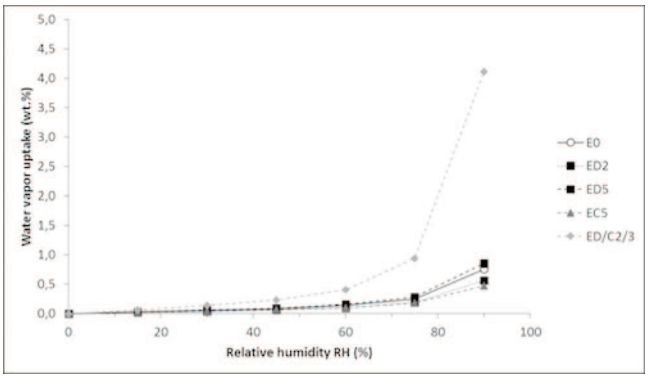


Figure 7. Same as Figure 6 but with a 0–5% zoom along the ordinate-axis (i.e. ≤ 5%). Legends: E0 (black solid line, white circles),ED2 (black dotted line, black squares), ED5 (black short-dashed line, black squares), EC5 (dark-grey short-dashed line, dark-grey triangles), ED/C2/3 (light-grey short-dashed line, light-grey diamonds). Samples abbreviations as in Table 2.

Figure 8 reports the liquid water absorption by the films listed in Table 2. The water uptake (y) values for all films, except

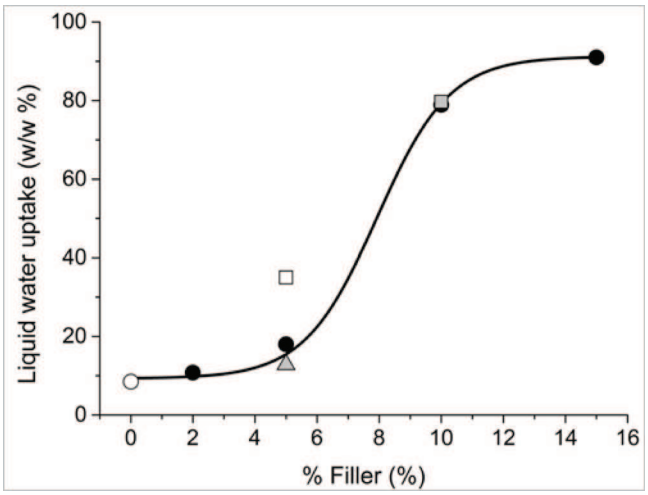


Figure 8. Liquid water uptake as a function of the filler content for neat EVOH (E0, white circle ○), and its blends containing 2–15% digestate (D) SLP (black circles ●), 5% compost (CP) SLP (EC5, grey triangle ▲), and the blends containing both D and CP SLP in the same sample at total SLP concentration of 5% (ED/C2/3, white square □) and 10% (ED/C5/5, grey square ■). Samples abbreviations as in Table 2.

the EVOH blend containing both 2% D and 3% CP SLP in the same sample (ED/C2/3), well correlate with the total % filler (x) in the blend according to eq. (3):

$$y = A_2 + (A_1 + A_2)/[1 + 10^{(\log x_o - x)p}] \quad (3)$$

The data regression gives the following values for the constants, their standard error, and the correlation coefficient (R):

$A_1 = 9.28 \pm 1.76$, $A_2 = 91.2 \pm 2.4$, log $x_o = 7.93 \pm 0.28$, $p = 0.37 \pm 0.04$, $R = 0.9982$. For $x = 5$, eq. (3) allows calculating the maximum and minimum y values at 99% confidence level 21.2 and 15.3, respectively. The experimental y value for the ED/C2/3 sample, as average of duplicates, was found 35.0 ± 1.7. The results indicate that the film water uptake depends both on the total content and on the composition of the filler. Indeed, at 5% total filler content, a remarkable synergic effect by the presence of both the digestate (D) and the compost (CP) SLP in the blend is evident. The ED/C2/3 sample exhibits almost 2 x higher water uptake than the ED5 and EC5 samples at equal 5% total filler content. The same does not occur at 10% total filler content. The blend containing 10% digestate SLP (ED10) and the blend containing 5% digestate and 5% compost SLP in the same sample (ED/C5/5) exhibit nearly the same water uptake. The effects observed by the DVS and liquid water sorption measurement are well consistent with each other. The data offers interesting scope for investigating further blend formulations containing both SLPs with variable relative and total fillers' contents, and their performance in the above[13-18] technologies.

Relevance of the results

This work addresses well-known issues, such as the management of waste management and bio-based material development, and deals with well-known technologies, such as fermentation, hydrolysis, solvent casting and extrusion, and readily available materials, such as the commercial EVOH copolymer and municipal biowastes. Nevertheless, it proposes process/product innovation by properly integrating the above technologies and sourcing materials. For biobased polymers, two important facts are assessed in the present work: (i) the possibility of processing the EVOH-SLP blends for obtaining sheet films by single-screw extrusion, and (ii) for lower amount of SLP (2-5 wt.%) in the blend mix, the absence of significant or great deterioration of the mechanical properties of the blend compared to the neat EVOH film. The possibility to substitute part of the synthetic polymer with a low cost waste derived biopolymer, while still maintaining the same mechanical properties of the neat synthetic polymer, is a step forward in the research of new bio-based materials. This would allow reducing material production costs. The EVOH copolymer is a special high cost polymer, with a 2016 market price[57] of about 5.80 and 8.00 € kg^{-1} for standard and special grade, respectively. The production cost of SLP is estimated 0.1-0.5 € kg^{-1}.[3] It would also allow reducing the exploitation of chemicals from fossil sources, and of dedicated crops as source of biobased materials.

For the attainment of the above perspectives, the data reported in the present work propose wide research potential for obtaining the EVOH-SLP in a variety of physical forms. The possible effect of DMSO determining the different mechanical properties of the solvent cast films[15] suggests that a variety of formulations should be tested for the EVOH-SLP blends, including plasticizers for EVOH polymer but also additives to improve the compatibility of the interface between the synthetic copolymer and the biopolymer. This would optimize their performance in the intended application. The possibility to process the EVOH-SLP composites with different technologies and with different formulations offers several alternatives for further product development. A wide range of municipal biowastes is potentially available. A wide range of SLPs may be obtained by integrating biochemical and chemical technologies for the treatment of municipal wastes, as well as agricultural and agro-industrial wastes. A wide range of synthetic polymers is also available. Thus, a wide range of formulations comprising synthetic polymers blended with waste sourced biopolymers may be obtained. The valorisation of municipal[3,4] and agricultural[16,58] biowastes as sources of SLP has been reported in many previous papers. A green process has been developed comprising hydrolysis of the sourcing biowaste in water and complete recycling of solvent and reagents.[4,19] The process does not require secondary waste treatment. The performance of the above SLP has been studied in diversified fields[3–23] of the chemical industry, agriculture and animal husbandry.

With specific reference to the performance of SLP in the blend EVOH-SLP films, the results obtained in this work prospect a number of possible applications. The data in Table 4 have shown that at 2–5% D SLP the blends have significantly lower Young modulus than neat EVOH. Moreover, the Young Modulus tends to decrease upon increasing the SLP content. To predict the impact of these findings on applications of these blends, it should be taken in consideration that all blend films listed in Table 4 exhibit Young modulus values in the range of the values published for many multipurpose polymers,[59] which are used for manufacturing a wide range of consumer products, and for most commercial plastic bags.[60] Moreover, for use in specific application requiring higher strength, the SPP blends exhibiting lower modulus could be fabricated with higher thickness to achieve the same strength and assure the same performance as the higher modulus materials during service. In this context, taking in consideration the properties of the SLP as biostimulant for plant growth,[19–21] the most intriguing application and potentially most feasible application of the SLP blends appears the manufacture of mulch films.

Table 4 reports the vis-à-vis comparison of the mechanical data for the SLP blend film and for some typical commercial starch based (MB) and low density polyethylene (MP) mulch films.[61] It may be observed that, compared to the MB and MP films, all SLP blend films listed in Table 4 have higher Young modulus, and lower strain at break. It is obvious that each application has specific material property requirements. Rarely, one polymer has all needed properties. Specific formulations are necessary for each intended applications. In the case of the SLP blends, the film elongation property may need improvement, depending on the application. Nevertheless, considering the SLP source availability, low process cost, plant growth biostimulant properties, and processability through solvent casting and melt extrusion, further development of blended SLP mulch films is a worthwhile scope to pursuit. More generally, the development of new biobased polymers, as proposed in this work, widens the perspectives to realize a cost-effective bio-

refinery processing municipal biowastes to obtain value-added marketable products.

Conclusions

Amorphous lignin-like soluble biopolymers (SLP) obtained from fermented municipal biowastes mixed with EVOH can be processed by single-screw extrusion to obtain sheet films for industrial applications. For SLP amount no more than 5 wt.% in the blend, the physico-chemical characteristics of the blend films seem to be not critically influenced by the filler content. Thus, their behaviour is similar to that of the neat EVOH film. Increasing the filler content in the blend deteriorates its mechanical properties, but increases its hydrophilicity. Improvement of mechanical properties, while still maintaining the water sorption property, would allow widening the range of applications of the blends. This might be achieved by working out formulations to include some other auxiliaries like plasticizers or compatibilizers, which should improve the interaction between the blend components. The data indicate potential for new worthwhile research aiming to the development of materials that contain biopolymers isolated from different wastes, in different physical forms, through different manufacture technologies, and using different formulations.

Supporting Information

The experimental section is provided.

Acknowledgments

This work was carried out also within the framework of the COST-European Cooperation in Science and Technology EUBis Action TD1203, specifically through the COST-STSM-TD1203-26977. The authors would like to thank William Tapia (Laboratoire de Chimie Agro-industrielle, INP-ENSIACET, Université de Toulouse, France) for the precious help in the EVOH grinding procedure. Extrusion experiments and mechanical characterizations were conducted in AGROMAT platform (Tarbes, France), the technological transfer hall of LCA laboratory dedicated to agromaterial production. For the collection of part of the analytical and product characterization, evaluation of experimental results and writing this paper, the authors acknowledge the contribution of the funds obtained within the BIORG project given by Regione Piemonte within Programma Operativo Regionale "Competitività regionale e occupazione" F.E.S.R. 2007/2013.

Keywords: Biomaterials · biopolymers & renewable polymers · blend films · composites · extrusion

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