

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Post-harvest tomato plants and urban food wastes for manufacturing plastic films

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1658233> since 2018-01-19T14:23:08Z

Published version:

DOI:10.1016/j.jclepro.2017.08.160

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

Post-harvest tomato plants and urban food wastes for manufacturing plastic films

Roberto Nisticò^a, Philippe Evon^b, Laurent Labonne^b, Guadalupe Vaca-Medina^b, Enzo Montoneri^{*c}, Carlos Vaca-Garcia^b, Michèle Negre^d

^a*Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia DISAT, C.so Duca degli Abruzzi 24, 10129 Torino, Italy*

^b*Laboratoire de Chimie Agro-industrielle (LCA), Université de Toulouse, INRA, INPT, 4 Allée Emile Monso, BP 44362, 31030 Toulouse Cedex 4, France*

^c*Biowaste Processing, Via XXIV Maggio 25, 37126 Verona, Italy*

^d*Università degli studi di Torino, Dipartimento di Scienze Agrarie, Forestali e Alimentari, Largo P. Braccini 2, 10095 Grugliasco (TO), Italy*

ABSTRACT

Poly(vinyl alcohol-*co*-ethylene) was compounded with 2-10% post-harvest tomato (PHT) plant powder and processed by single-screw extrusion to yield composite films. Upon increasing the filler content, the values of the mechanical properties indicators were found to decrease as follows: Young's modulus from 1797 to 750 MPa, stress at yield from 36 to 15 MPa, maximal stress from 39 to 15 MPa, stress at break from 35 to 14 MPa, and strain at break from 6.6 to 4.3%. The results are discussed in comparison with other composite films containing poly(vinyl alcohol-*co*-ethylene) and water soluble biopolymers obtained by alkaline hydrolysis of fermented municipal biowastes, and with other commercial materials, such as starch based and low density polyethylene mulch films. Depending on the intended application, the post-harvest tomato blend films may be competitive for cost, performance and sustainability.

Keywords: Biomaterials, biopolymers, blend films, extrusion, municipal food wastes, post-harvest tomato plants

*Corresponding author.

E-mail address: enzo.montoneri@gmail.com (E. Montoneri).

Abbreviations

Post-harvest tomato (PHT)

Soluble biopolymers (BPs)

Polyethylene-*co*-vinyl alcohol (EVOH)

1. Introduction

The valorisation of biowastes from municipal and agriculture sources as feedstock for the production of added-value biobased products is a topic currently addressed by the European Commission calls for research proposals (EU commission, 2017). In this context, several papers have reported the manufacture, properties and performance of soluble biopolymers (BPs) obtained from the above biowastes (Franzoso et al., 2015 and 2016). The BPs are high molecular weight biopolymers, which are isolated from the acid or alkaline hydrolysates of the sourcing biowastes. In essence, they are soluble fragments of the pristine biowaste lignocellulosic proximates. They are constituted by C moieties, which save the chemical memory of the native polysaccharide, protein, fat and lignin proximates present in the parent biowaste.

The BPs have been demonstrated multipurpose products (Montoneri et al., 2017; Arshadi et al., 2016) for use in the chemical industry, agriculture and animal husbandry. Particularly interesting are the papers reporting the performance of the BPs as biostimulants for the cultivation of tomato (Sortino et al., 2014) and maize (Rovero et al., 2015) plants, and as fillers for manufacturing solvent cast films (Franzoso et al., 2015 and 2016). Moreover, the post-harvest tomato and maize plants have been shown suitable feedstock for hot pressing manufacture of binderless fiberboards to be used for many different purposes in both the building construction and the home furnishing (Even et al., 2017). These findings are well in line with the EU zero waste strategy (Zerp Waste Europe, 2013). They prospect a desirable integration of both municipal and agriculture biowastes by recycling C repeatedly over the agriculture and urban environment. The success of this scenario depends on feedstock availability and processing costs, and on products performance. As widening the number of case studies offers more perspectives of success, the present work reports the manufacture and properties of composite plastic films obtained from a synthetic polymer from fossil feedstock and grinded post-harvest tomato (PHT) plants.

Tomato plants are grown worldwide for their edible fruits, with thousands of cultivars. In 2014, world production of tomatoes was 171 Mt, 31% in China, followed by India, the United States and Turkey as the major producers (FAOSTAT, 2017). Tomatoes accounted for 23% of the total fresh vegetable output of the European Union, more than half coming from Spain, Italy and Poland (De Cicco, 2016).

On the other hand, biobased plastics are key target materials of EU calls for research proposals (EU commission, 2017). Bioplastic packaging consumption has been estimated to be 125 kt in 2010 with an estimated market value of 454 M\$ (Roland-Holst et al., 2013). Yet, bioplastics represent currently only a small portion (under 1%) of the global market share of plastics (European bioplastics, 2016; Storz and Vorlop, 2013; Plastermat, 2013), which should be around 1-2 Mt/yr. Thus, bioplastics are a growing opportunity to recycle biowastes and market them in the form of plastic objects.

The above figures for both tomato plant production and bioplastics' market perspectives pose worthwhile scope for research effort aiming to valorize PHT plants for the production of new biobased plastic objects. One more reason for focusing research on biowastes for the production of biobased plastics is the fact that most biopolymers for manufacturing plastics are obtained from dedicated crops. However, the use of land to cultivate plants dedicated exclusively to the production of energy, materials or chemicals raises much socio-environmental and moral concern. Negative impacts on land, water, biodiversity, and food production and price arising from this practice are matter of dispute (Green facts, 2017; FAO 2018). On the contrary, the alternative use of biowastes as feedstock for the above scopes is unanimously welcome.

Some studies have already been performed on PHT plants as source of BPs (Franzoso et al., 2015b) for manufacturing through solvent casting composite mulch films to be used in agriculture. Generally, a plastic film must satisfy a number of requirements. It must be mechanically strong to withstand high shear stress and still recover its original shape. Moreover, it must be flexible, elastic,

easily processable and not expensive. No single polymer can satisfy all requirements for the many diversified uses of plastic films. Thus, composite films are made. The composite films made with BPs sourced from PHT contain a polyethylene commercial copolymer from fossil source, such as polyethylene-co-vinyl alcohol (EVOH) or polyethylene-co-acrylic acid (Franzoso et al 2016 and 2015, respectively), and 2-40 % BPs as fillers.

There are several reasons that do not allow fabricating plastic films made entirely from neat BPs. One is that BPs do not have melting and film forming properties. They are only soluble in water at pH values greater than 4. The evaporation of their water solutions results in the deposition of the solute in powder or fragile sheet form. Thus, neat BPs cannot be processed to obtain usable objects. Under these circumstances, the only possibility is compounding them with other polymeric materials to obtain processable blends. This has indeed been achieved exploiting the solubility properties of BPs and the above polyethylene copolymers in miscible hydrophilic solvents, reacting the BPs and the copolymer in solution, and casting the reaction product from the solvent.

Another reason for the manufacture of the above BPs-containing composites is that the BPs molecules keep some of the mechanical stiffness typical of the parent native lignin. Mechanical stiffness may enhance the capacity of the film to save its original shape when subjected to mechanical stress. However, it will also decrease the film flexibility and elasticity. Thus, in the BPs composites, the polyethylene copolymer is necessary to provide the required property of mechanical flexibility and processability. On the other hand, 2-10 % content of BPs filler enhances the film mechanical strength without compromising critically the desirable properties of the synthetic polymer. Moreover, the solubility properties of both the synthetic polyethylene copolymer and BPs in different miscible solvents allow the processability of their mixtures by solvent casting (Franzoso et al., 2015 and 2016).

So far, raw PHT plants have not been considered as potential fillers for the manufacture of composite plastic films using the solvent casting technique, due to their poor solubility properties and to the presence of the recalcitrant native lignin. However, most recently, Nisticò et al. (2016) have reported that EVOH-BPs blend films can be obtained also by single-screw melt extrusion. This work was carried out with some BPs obtained by hydrolysis of fermented municipal kitchen wastes. It evidenced some important facts. First, it must be considered that all BPs and their sourcing materials do not have melting properties (Franzoso et al., 2015 and 2016). They are stable up to 220 °C. They decompose at higher temperature without melting. Nevertheless, the possibility of processing by single-screw extrusion the EVOH-BPs mixes investigated by Nisticò et al. (2016) prospected that, by the same process, composites films might be obtained also from EVOH-PHT mixes. Second, for 2-10 wt % BPs content in the blend mix, no significant or critical deterioration was found for the mechanical properties of the blend compared to the neat EVOH film (Franzoso et al., 2015 and 2016; Nisticò et al., 2016). This implied that important cost and environmental benefits could be attained by manufacturing composites. They would stem from substituting part of the synthetic polymer with a low cost biomaterial derived from renewable source, while still maintaining the same mechanical properties of the neat synthetic polymer.

For the case study of the above BPs from fermented urban biowastes (Nisticò et al., 2016), cost benefits can be readily appreciated. Indeed, poly vinyl alcohol-co-ethylene is a special high cost polymer, with a market price (Alibaba.com, 2017) of about 6 €/kg. The BPs production cost is estimated 0.1-0.5 €/kg (Montoneri et al., 2011). It arises mainly from reagents and energy consumption by the hydrolysis of the sourcing biowaste. By comparison, the PHT plants are not processed chemically and do not require energy to drive a chemical reaction. Thus, even higher cost reduction and environmental benefits are potentially attainable by using the collected, not chemically processed PHT plants material as fillers to manufacture the EVOH composites.

In order to evaluate the feasibility of the above option, the present work reports not only the performance of the EVOH-PHT blend films, but also its comparison with the performance of the

previously reported EVOH-BPs blend films (Nisticò et al., 2016) that were obtained under the same conditions.

2. Methods

2.1. Starting materials, films preparation and chemical analyses.

Post-harvest tomato (PHT) plants (*Lycopersicon Esculentum* Cv. Naomi F1) and commercial EVOH pellets (Soarnol by Nippon Gohsei Europe GmbH) were available from previous work (Franzoso et al., 2015 and 2016). The PHT plant material was analyzed for its content of ash, elemental C and N, and C types and functional groups, according to previously reported methods (Franzoso et al., 2015 and 2016; Nisticò et al., 2016; Evon et al., 2017). The chemical compositions of both BPs and PHT were also analyzed on a macroscopic scale. This included contents for moisture, cellulose, hemicelluloses, lignin and water-soluble components. The moisture content was determined according to ISO 665:2000 (ISO, 2012). The cellulose, hemicelluloses and lignin contents were determined by the use of the acid detergent fiber-neutral detergent fiber (ADF-NDF) method of Van Soest and Wine (1967 and 1968). Similarly, the water-soluble components were estimated by measuring the mass loss of the test sample after 1 h in boiling water. All determinations were carried out in duplicates.

The PHT plant material was grinded in several steps and sieved to obtain a powder with particle size comprised between 125 and 63 μm . The EVOH commercial pellets were liquid nitrogen freeze-grinded using a Fritsch (Germany) PULVERISETTE 19 cutting mill. Prior to extrusion, the PHT and EVOH powders were dried overnight in an oven set at 50 °C to reduce the moisture content. The dried powders were then hand-mixed to yield EVOH-PHT mixtures containing 2, 5 and 10 % PHT. Composite sheet film production from the EVOH-PHT powders 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 calendar speed and 0.84 mm lip height at the level of the outlet die. The temperature profile used was as follows: 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. Temperature and pressure of the material at the outlet die were monitored continuously during the extrusion. The volumetric flow was not set, but estimated based on the selected screw speed.

2.2. Water vapor sorption measurements.

Dynamic vapor sorption (DVS) was performed with a DVS Advantage automated gravimetric vapor sorption (Surface Measurement Systems Ltd., London, UK) analyzer. The instrument measures the uptake of vapor gravimetrically using a Cahn D200 recording ultramicrobalance with a mass resolution of $\pm 0.1 \mu\text{g}$. Relative humidity (RH) around the sample was controlled by mixing saturated and dry carrier gas streams using mass flow controllers. Temperature was maintained constant ($25 \pm 0.1^\circ\text{C}$) by enclosing the entire system in a temperature-controlled incubator. Before analysis, the samples were stored in a desiccator. For each experiment, the sample was immediately placed into the DVS analyzer under a continuous stream of dry ($<0.1\%$ RH) air. A sample size between 15 and 25 mg was used. Prior to exposure to water vapor, the samples were dried at 0% RH to remove superficial water present and establish a dry baseline mass. Measurement were performed at 0%, 15%, 30%, 45%, 60%, 75% and 90% RH. At each RH value, the sample mass was allowed to reach equilibrium before increasing RH to the next value. Isotherm DVS values were calculated from the complete moisture sorption profile using the DVS Advanced Analysis Suite v3.6 software.

2.3. Differential scanning calorimetry (DSC) measurements.

The DSC measurements were performed using a Mettler Toledo (Switzerland) DSC1 calorimeter under nitrogen flow. About 15 mg sample was inserted inside hermetic aluminium sample pans. A first heating ramp at 10 °C/min from 0°C to 200°C was performed to erase sample thermal history. After 2 min at 200°C, the cooling ramp to 0°C at 10°C/min was started. The sample was then kept 2 min at 0°C. Afterwards, a second heating cycle, similar to the first one, was carried out. The glass transition (T_g), cold crystallization (T_c), and melting (T_m) temperatures were determined. The T_g value was taken as the midpoint of the DSC heating curve deflection from baseline. Enthalpy values were determined by integrating the area of the cold crystallization and melting peaks. The crystallinity degree (%X_c) for each blend was calculated according to the equation

$$\%X_c = 100 \Delta H_m / (w \Delta H_m^{\circ}) \quad (1)$$

where 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 (Franzoso et al., 2015b), and w is the EVOH mass fraction in the composite. The means of all the parameters were examined for significance by ANOVA using the software JMP version 9 (SAS Institute Inc., Cary, North Carolina, USA).

2.4. Tensile properties measurements.

Tensile tests were performed at room temperature with an Instron (USA) 4204 universal testing machine with cross-head maximum strength capacity of 500 N. A fixed cross-head rate of 5 mm/min was utilized in all cases, and results were taken as average of three tests (\pm standard deviation). Rectangular specimens (120 mm initial length) were used. Mean values of all parameters were examined for significance by ANOVA using the JMP version 9 (SAS Institute Inc., Cary, North Carolina, USA) software.

3. Results and discussion

3.1. PHT chemical nature and properties

Table 1 reports the chemical composition of the PHT used in the present work and of the BPs used in previous work (Nisticò et al., 2016) to manufacture the EVOH composites to be compared for performance. In essence, PHT is the powder obtained by grinding the collected post-harvest tomato plants. The BPs are the soluble hydrolysates of urban kitchen wastes, previously fermented under anaerobic conditions. The data shows that both PHT and BPs contain organic and mineral matter. The organic matter is characterized by several aliphatic and aromatic C types and functional groups. These represent the moieties of polysaccharide, protein, fat and lignin proximates, which are virtually present in the two materials (see next). The data shows that, compared to BPs, PHT contains more mineral matter. However, BPs organic matter contains more aliphatic C and less polysaccharides, as evidenced by the higher Af, and lower OR and OCO carbon contents, respectively. These different chemical features may be partly due to the different sourcing materials, i.e. the tomato plants for PHT and the urban kitchen wastes for BPs. However, the major factors are likely to be the anaerobic fermentation and chemical hydrolysis processes applied to the BPs sourcing biowastes. These were fermented under anaerobic conditions to yield biogas and digestate. The latter was then hydrolysed at pH 13 and 60 °C for 4 h (Sortino et al., 2014; Nisticò et al., 2016).

The PHT C types and functional groups in Table 1 represent the moieties of the native polysaccharide, protein, fat and lignin proximates. This chemical feature is consistent with the

lower water solubility of this material. For BPs, the C types and functional groups in Table 1 represent the memories of the native proximates that have survived the anaerobic fermentation and successive chemical hydrolysis processes of the sourcing biowastes. Fermentation leads to the mineralization of the native polysaccharide proximates. Native lignin, due to its recalcitrant nature, is more resistant. Native lignin is a highly cross-linked aromatic polymer, intimately bonded also to the other proximates. Fermentation changes this situation. Most native polysaccharide matter is converted to methane and carbon dioxide. The residual organic matter, containing the recalcitrant lignin, is recovered with the digestate. The successive chemical hydrolysis of the digestate leads to the formation of soluble lignin-like fragments (Franzoso et al., 2015; Sortino et al., 2014).

These facts were confirmed by the proximates chemical analysis of both BPs and PHT, conducted on a macroscopic scale (see Methods), with really different compositions. The data in Table 2 shows that on the one hand, water-soluble compounds represent 99% of BPs dry matter, confirming that BPs are indeed soluble biopolymers. Consequently, the contents of BPs in the cellulose, hemicelluloses and lignin proximates are all three negligible. On the other hand, water-solubles inside PHT represent only 22% of its dry matter, meaning that the majority of organic matter inside PHT is not soluble in water. In particular, the post-harvest tomato plant contained a significant amount of lignocellulosic fibers with cellulose, hemicelluloses and lignin representing 33%, 11% and 8%, respectively, of its dry matter.

The different chemical nature of PHT and BPs is reflected in the different water vapor sensitivity of the two materials. Fig. 1 shows that the water uptake by PHT increases up to 29 % upon increasing relative humidity to 90 %. By comparison, the water uptake by BPs was reported to increase up to 48 % upon increasing relative humidity to 90 % (Nisticò et al., 2016). This seems related to the higher content of hydrophilic carboxyl groups in BPs.

3.2. Blend film preparation, water vapor sensitivity and thermal properties

The composition and processing conditions of the PHT blend films produced in this work by single-screw extrusion were worked out to be similar to those previously reported for the manufacture of the EVOH-BPs blends (Nisticò et al., 2016). In essence, sheet film production was carried out at 165-195 °C. Previous thermogravimetric analysis of both BPs (Nisticò et al., 2016) and PHT (Evon et al., 2017) powder indicated that no significant thermal degradation of these materials occurs below 220°C. Table 3 and 4 report the blend sheet dimensional data and thermal characterization. Fig. 2 shows the aspect of the investigated films. Upon increasing the filler content up to 10 %, the film becomes increasingly dark colored (Fig. 2), and the film thickness (Table 3) tends to gradually increase. All films could be bent at a 180 ° angle or rolled over. However, they tended to become more and more rigid upon increasing the filler content. This was probably due to the high ash content. 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 outlet die) on the long term.

Water vapor sensitivity was also measured for the EVOH-PHT blend sheet films. Fig. 3 shows that with no more than 5% filler content (EPHT2 and EPHT5 blends), the water vapor sorption is roughly comparable to that of neat EVOH (E0 sample), with uptakes all situated between 0.6 and 1.0% at 90% relative humidity. On the contrary, the water vapor uptake was much more important at 10% filler content (6.5% at 90% relative humidity). Thus, the higher the PHT filler content in the blend, the higher is the water vapor sensitivity of the EVOH-PHT sheet film. The same phenomenon has been reported also for the EVOH-BPs blends (Nisticò et al., 2016). However, the water uptake of the BPs blends at 10% filler content was about 24 % relatively higher than that of the PHT blends at equal filler content. This confirms once again the higher hydrophilicity of BPs compared to PHT.

Table 4 reports the data obtained from the DSC scans of neat EVOH and the EVOH-PHT blends. No significant difference or trend of the reported data are observed by increasing the filler

content in the blend. By comparison, the values for melting (ΔH_m) and cold crystallization (ΔH_c) enthalpies of the BPs blends showed a trend to slightly decrease by 6-13 % upon increasing the filler content (Nisticò et al., 2016). The different thermal behaviors between PHT and BPs blends upon increasing the filler content may reveal better affinity for and interactions with the EVOH matrix by BPs, compared to PHT. As discussed in the above subsection, the BPs are more hydrophilic than PHT. Since the EVOH polymeric matrix is water sensitive, in principle, the higher is the filler water affinity, the better is its affinity to the EVOH matrix, and the better is the interaction between the filler and the polymeric matrix. In previous work (Nisticò et al., 2016; Franzoso et al., 2016), the changes in the values of the DSC parameters observed for the EVOH-BPs blends have been explained with chemical reaction and/or interactions occurring between EVOH and BPs, which cause a change of the EVOH polymer composition and/or the morphology upon increasing the BPs content. Consequently, the no trend or changes observed for the EVOH-PHT blends upon increasing the filler content are consistent with no significant interaction between EVOH and PHT.

3.3. Blend films' tensile properties

The data in Fig. 4 shows that the PHT blends reproduce the behavior of the BPs blends. In essence, the values of all indicators of mechanical performance tend to decrease significantly upon increasing the filler content. However, statistically, no significant difference is assessed upon comparing values from PHT and BPs films at equal filler content. Several factors may explain the lower performance of the blends, compared to the neat EVOH film. One may be the fillers' ash content. The second factor is likely to be the presence of native lignin and/or lignin-like matter inside PHT and BPs, respectively. Both factors will contribute to higher mechanical stiffness, and lower elasticity and flexibility of the blends, compared to the neat EVOH film. The main parameter affecting the blends mechanical properties appears to be the filler content. The different chemical compositions shown in Table 1 and 2, and the different hydrophilicity, water vapor sensitivity and potential chemical affinity of the two fillers (see 3.1 and 3.2 subsections) do not seem to result in significantly different tensile properties of the PHT blend films compared to the BPs blend films.

Notwithstanding the above fillers effects, to properly evaluate the impact of the data in Fig. 4 on the possible blends' uses, it should be taken in consideration that the blend films exhibit Young's modulus values in the range of the values published for many multipurpose polymers (The engineering tools, 2016) that are used for manufacturing a wide range of consumer products, and for most commercial plastic bags (Foreman et al., 2016). For examples, some typical commercial starch-based and low density polyethylene mulch films (Schettini et al., 2005) have Young's modulus of 247 MPa and 160 MPa, respectively. Moreover, for use in specific applications requiring higher strength, the PHT and BPs blends could be fabricated with higher thickness than the thickness values reported in Table 3. This would allow achieving the same strength and assure the same performance as higher modulus materials during service. In this context, taking in consideration the lower cost of the PHT materials, this approach might turn out successful.

3.4. Relevance of the results and perspectives

This work addresses the topic of renewable materials with properties suitable for applications, which is currently matter of great interest. In recent years, research on bio-based polymers has been intensified with the intent to find alternatives to synthetic polymers from fossil sources. Reasons for this are coping with depletion of fossil sources and growing environmental impact due to their exploitation. However, until now, 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

two € kg⁻¹ (Kanellos, 2009), current biopolymers are from about 2.0 to 7.0 times more expensive (Roland-Host et al., 2013). The latter ones are obtained from dedicated crops, such as starch, or from fermentation, such as polyhydroxylalkanoates. Most biopolymers are obtained from dedicated crops. The use of land to cultivate plants for energy or chemicals' production raises much socio-environmental and moral concern. Negative impacts on land, water and biodiversity, and food production count among the most discussed side effects of this practice (Green facts, 2017; FAO, 2008). Using corn as non-food feedstock may cause food price increase and thus can be controversial. So far, bio-wastes, as sources of biopolymers, have not been much investigated. Yet, their valorization for this scope can potentially overcome the socio-environmental and moral criticalities connected to the exploitation of dedicated crop for producing chemicals.

In this context, the exploitation of negative cost biowastes (Sheldon-Coulson, 2011), such as municipal food wastes or post-harvest tomato plants is a step forward for the achievement of the above objectives. Previous work has reported that the economic benefits deriving from the substitution of synthetic poly vinyl alcohol-co-ethylene with the BPs from fermented urban biowastes (see Introduction). These stem from the relatively low 0.1-0.5 € kg⁻¹ BPs production cost compared to the six € kg⁻¹ market price of poly vinyl alcohol-co-ethylene (Alibaba.com, 2017) case study (Franzoso et al., 2015a). The finding reported in the present work that similar mechanical performance may be obtained with the BPs and PHT blends prospects that even higher cost reduction and environmental benefits are potentially attainable by using the not chemically processed PHT plants material as fillers to manufacture composites with synthetic polymers.

As of 2007, it was estimated that worldwide production of bioplastics amounted to approximately 360,000 metric tons (890,000 metric tons by 2012) and was projected to reach 1.5 to 4.4 million metric tons by 2020 (Roland-Holst et al., 2017). Bioplastics are currently only in a small portion (under 1%) of global market share of plastics (Montoneri, 2017). Thus, the global plastics production is estimated 150 Mt yr⁻¹. Environmentally, the substitution of 1 kg fossil C with 1 kg renewable C is worth 3.43 kg lower CO₂ emission stemming from the lower fossil C consumption. Economically, the substitution of 1 kg traditional fossil resins with 1 kg BPs or PHT is worth more than one € lower production cost.

At the light of the above stakes and of the experimental results obtained in the present tomato case study, further investigation on the PHT and BPs materials is worthwhile. For example, the decrease in the tensile properties of the EVOH-PHT and EVOH-BPs blend films compared to the neat EVOH film suggests the lack of sufficient affinity between each of the two fillers and the thermoplastic synthetic polymer matrix. New formulations, which included other post-harvest plant materials, other synthetic polymers, and additives like coupling agents to improve the compatibility of the interface between the synthetic copolymer and the filler, might exhibit improved tensile properties. This is quite likely. Franzoso et al. (2015b) have investigated blend films made from polyethylene-co-acrylic acid (PEAA) and the BPs made by hydrolysis of PHT and of fermented food and gardening biowaste. They have shown that, compared with neat PEAA, the PEAA blend films containing 5 to 10% BPs exhibited 2 to 6 x higher Young's modulus, over 3 x higher stress at yield point and somewhat lower strain at break (55–280% vs. over 300%). The better relative performance of the PEAA-BPs blend films, compared to the EVOH-BPs blend films, may be due to the better affinity of the PEAA and BPs, both containing hydrophilic carboxyl groups.

The results of the present work and the previous work by Franzoso et al. (2015 and 2016) offer vast intriguing research scope. A wide range of biowaste materials and synthetic polymers is available. Thus, a wide range of formulations comprising synthetic polymers blended with biowaste-sourced materials may be obtained. It is obvious that each application has specific material property requirements. Rarely, one single material has all needed properties. Specific formulations are necessary for each intended applications. Certainly, the development of new biobased materials using post-harvest plants without chemical treatment widens the perspectives to

realize cost-effective value-added biobased products for more sustainable end-of-life phase (EU commission, 2017).

4. Conclusions

The present paper reports a case study showing, for the first time, that raw (i.e. not chemically pretreated) post-harvest tomato plants may be suitable as fillers to manufacture composite films by co-extrusion with synthetic polymers from fossil sources. This is a step forward for the manufacture of innovative plastic articles for consumers' use. There is plenty of worldwide tomato plant production to guarantee a cost effective supply of PHT material for the production of biobased plastics containing PHT as filler. There is also a growing market for biobased plastics. The fabrication of composite films made from synthetic polymers and PHT as fillers, or other post-harvest food plants, implies several cost and environmental benefits. The most desirable ones are (i) lowering the production cost of plastic materials, and (ii) reducing the consumption of synthetic polymers from fossil sources, the depletion of fossil sources, and the associated environmental impact. Moreover, the combined use of raw post-harvest plants and chemically processed urban biowastes for the production of soluble multipurpose biopolymers prospects benefits also for the management of biowastes through the realization of a desirable C cycle integrating the urban and rural environment.

Acknowledgment

This work was carried out within the framework of the COST-European Cooperation in Science and Technology EUBis Action TD1203, specifically through the COST-STSM-TD1203- 26977.

References

- [Alibaba.com, 2017. EVOH - SOARNOL SG-654-NG, http://www.alibaba.com/product-detail/EVOH-SOARNOL-SG-654-NG_169861914.html](http://www.alibaba.com/product-detail/EVOH-SOARNOL-SG-654-NG_169861914.html) (Accessed April, 2017).
- Arshadi, M. Attard, T. M., Bogel-Lukasik, R., Brncic, M., da Costa Lopes, A. M., Finell, M., Geladi, P., Gerschenson, L. N., Gogus, F., Herrero, M., Hunt, A. J., Ibáñez, E., Kamm, B., Mateos-Aparicio, I., Matias, A., Mavroudis, N. E., Montoneri, E., Morais, A. R. C., Nilsson, C., Papaioannou, E. H., Richel, A., Rupérez, P., Skrbic, B., Solarov, M. B., Švarc-Gajić, J., Waldron, K., Yuste, F., 2016. Pre-treatment and extraction techniques for recovery of added value compounds from wastes throughout the agri-food chain. *Green Chemistry* 18, 6160 – 6204.
- De Ciccio, A., 2016. Eurostat, The fruit and vegetable sector in the EU - a statistical overview, [http://ec.europa.eu/eurostat/statisticsexplained/index.php/The fruit and vegetable sector in the EU - a statistical overview](http://ec.europa.eu/eurostat/statisticsexplained/index.php/The_fruit_and_vegetable_sector_in_the_EU_-_a_statistical_overview), (Accessed April 2017).
- EU commission, BBI 2017 call, <https://www.bbi-europe.eu/participate/calls-proposals-2017> (Accessed April 2017).
- European Bioplastics, 2016. Bioplastics facts and figures, http://www.google.it/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0ahUKEwiyMt7lrq7LAhXCBRQKHSBsBMMQFggnMAE&url=http%3A%2F%2Fwww.muoviteollisuus.fi%2Fdocument.php%2F1%2F156%2FEuropean_bioplastics_-_facts_and_figures%2Fb4313531b6f32c56e3b4a4d3d5fdd15c&usq=AFQjCNGRZsjgqlXbzlwgl2n_uTKZx51RfA&sig2=d_G6fqLgWyJL82H-GWbVsw, (Accessed April 2017),
- Evon, P., Labonne, L., Nisticò, R., Montoneri, E., Vaca-Garcia, C., Negre, M., 2017. Thermopressed binderless fiberboards from post-harvest tomato and maize plants. *Trends in Green Chemistry* 3, 1-7, doi: 10.21767/2471-9889.100014.

- FAO, 2008. The state of food and agriculture, Part I: biofuels: prospects, risks and opportunities, <http://www.fao.org/docrep/011/i0100e/i0100e00.htm> (Accessed April 2017).
- FAOSTAT, 2017. Crops, Tomatoes, <http://www.fao.org/faostat/en/#data/QC/visualize> (Accessed April 2017).
- Foreman, J., Gill, P. S., Sauerbrunn, S. R., 2016. Tensile Modulus of Plastic Films, <http://www.tainstruments.com/pdf/literature/TA038.pdf> (Accessed April 2017).
- Franzoso, F., Tabasso, S., Antonioli, D., Montoneri, E., Persico, P., Laus, M., Mendichi, R., Negre, M., 2015a. Films made from poly (vinyl alcohol-co-ethylene) and soluble biopolymers isolated from municipal biowaste. *J. Appl. Polym. Sci.* 132 (4), 1301, doi: 10.1002/app.41359.
- Franzoso, F., Causone, D., Tabasso, S., Antonioli, D., Montoneri, E., Persico, P., Laus, M., Mendichi, R., Negre, M., 2015b. Films made from polyethylene-co-acrylic acid and soluble biopolymers sourced from agricultural and municipal biowaste. *J. Appl. Polym. Sci.* 132 (18), start page 5803, doi: 10.1002/app.41909.
- Franzoso, F., Vaca-Garcia, C., Rouilly, A., Evon, P., Montoneri, E., Persico, P., Mendichi, R., Nisticò, R., Francavilla, M., 2016. Extruded versus solvent cast blends of poly(vinyl alcohol-co-ethylene) and biopolymers isolated from municipal biowaste. *J. Appl. Polym. Sci.* 133 (9), 2110, doi: 10.1002/Aapp.43009.
- Green Facts, 2017. Liquid Biofuels for Transport Prospects, risks and opportunities, <http://www.greenfacts.org/en/biofuels/1-3/4-environmental-impacts.htm> (Accessed April 2017).
- ISO, 2000. ISO 665:2000. Oilseeds determination of moisture and volatile matter content, <https://www.iso.org/standard/31099.html> (Accessed April, 2017).
- Kanellos, M., 2009. Bioplastics Close in Price to Regular Plastic and Trader Joe's Coconut Packages, <https://www.google.it/#q=83.%09Kanellos+M%2C+Bioplastics+Close+in+Price+to+Regular+Plastic+and+Trader+Joe%E2%80%99s+Coconut+Packages>, (accessed March 7, 2016).
- Montoneri, E., Mainero, D., Boffa, V., Perrone, D. G., Montoneri, C., 2011. Biochemenergy: a project to turn a urban wastes treatment plant into biorefinery for the production of energy, chemicals and consumer's products with friendly environmental impact. *Int. J. Global Environmental Issues* 11, 170-196.
- Montoneri, E., 2017. Municipal Waste Treatment, Technological Scale up and Commercial Exploitation: The Case of Bio-waste Lignin to Soluble Lignin-like Polymers, In: *Waste Reduction and Valorization*, Chapter 8, , Springer, doi:10.1007/978-3-319-50088-1.
- Nisticò, R., Evon, P., Labonne, L., Vaca-Medina, G., Montoneri, E., Francavilla, M., Vaca-Garcia, C., Magnacca, G., Franzoso, F., Negre, M., 2016. Extruded poly(ethylene-co-vinyl alcohol) composite films containing biopolymers isolated from municipal biowaste, *Chemistry Select* 1, 2354-2365, doi: 10.1002/slct.201600335.
- Plastermat, 2013. Bioplastics to grow to 7% of total plastics market by 2020, <http://www.plastemart.com/Plastic-Technical-Article.asp?LiteratureID=1903&Paper=bioplastics-to-grow-to-7-per-cent-total-plastics-market-by-2020>, (Accessed April 2017).
- Roland-Holst, D., Triolo, R., Heft-Neal, S., Bayrami, B., 2013. Bioplastics in California, <http://www.calrecycle.ca.gov/publications/Documents/1469%5C20131469.pdf> (Accessed April 2017).
- Rovero, A., Vitali, M., Rosso, D., Montoneri, E., Chitarra, W., Tabasso, S., Ginepro, M., Lovisolo, C., 2015. Sustainable maize production urban biowaste products. *International Journal of Agronomy and Agricultural Research* 6, 75-91.
- Sheldon-Coulson, G.A., 2011. Production of Levulinic Acid in Urban Biorefineries, Master of Science Thesis in Technology and Policy. Massachusetts Institute of Technology, <https://dspace.mit.edu/bitstream/handle/1721.1/68450/769021899-MIT.pdf?sequence=2>, (accessed March 7, 2016).

- Sortino, O., Montoneri, E., Patanè, C., Rosato, R., Tabasso, S., Ginepro, M., 2014. Benefits for agriculture and the environment from urban waste. *Sci. Total Environ.* 487C, 443-451.
- Storz, H., Vorlop, K. D., 2013. Bio-based plastics: status, challenges and trends. *Appl Agric Forestry Res* 4, 321-332.
- Schettini, E., Vox, G., Malinconico, M., Immirzi, B., Santagata, G., 2005. Physical properties of innovative biodegradable spray coating for soil mulching in greenhouse cultivation. *Acta Hort. ISHS* 691, 725–732, *Proc. IC on Greensys*, G. van Straten Ed., http://wwwlib.teiep.gr/images/stories/acta/Acta%20691/691_89.pdf (Accessed April 2017).
- The engineering toolbox, 2016. Modulus of Elasticity or Young's Modulus – and Tensile Modulus for Common Materials, http://www.engineeringtoolbox.com/young-modulus-d_417.html (Accessed April 2017).
- Van Soest, P.J., Wine, R.H., 1967. Use of detergents in the analysis of fibrous feeds. Part iv. Determination of plant cell-wall constituents. *J. Assoc. Off. Agric. Chem.* 50, 50-55.
- Van Soest, P.J., Wine, R.H., 1968. Determination of lignin and cellulose in acid-detergent fiber with permanganate. *J. Assoc. Off. Agric. Chem.* 51, 780-785.
- Zero Waste Europe, 2013, <http://www.zerowasteurope.eu/wp-content/uploads/2013/04/ZW-Hierarchy.pdf> (Accessed April 2017)

Table 1

Ash, total C and N, water soluble matter, and C distribution over different C types and functional groups^a for BPs and PHT, as weight % relative to total dry matter.

	Ash		Total C		Total N		Water soluble matter	
BPs	15.4		45.1		7.9		99	
PHT	20.2		36.4		3.5		22	
	Al	OMe + NR	OR	OCO	Ph	PhOY	COX	CO
BPs	19.6	4.46	6.31	1.53	4.33	1.44	7.17	0.27
PHT	5.20	2.62	18.1	4.22	2.51	1.24	2.29	0.22

^aAliphatic (Al), methoxy (OMe), ammine (NR), alkoxy (RO), anomeric (OCO), aromatic (Ph), phenoxy and phenol (PhOY, Y = Ph, R, H), amide and carboxylic acid (COX, X = N or H), ketone (C=O) C.

Table 2

Moisture and native proximates' content in BPs and PHT (see Methods).

	Moisture (%)	Cellulose (%) dry matter)	Hemicelluloses (% dry matter)	Lignin (% dry matter)	Water-soluble components (% dry matter)
BPs	5.0±0.4	Negligible	Negligible	Negligible	99.0±0.0
PHT	4.5±0.1	33.1±0.2	10.5±0.0	7.8±0.1	22.0±0.2

Table 3

Blend sheet films^a dimensional data, and recorded pressure and temperature at the outlet die of the extruded material during single-screw extrusion.

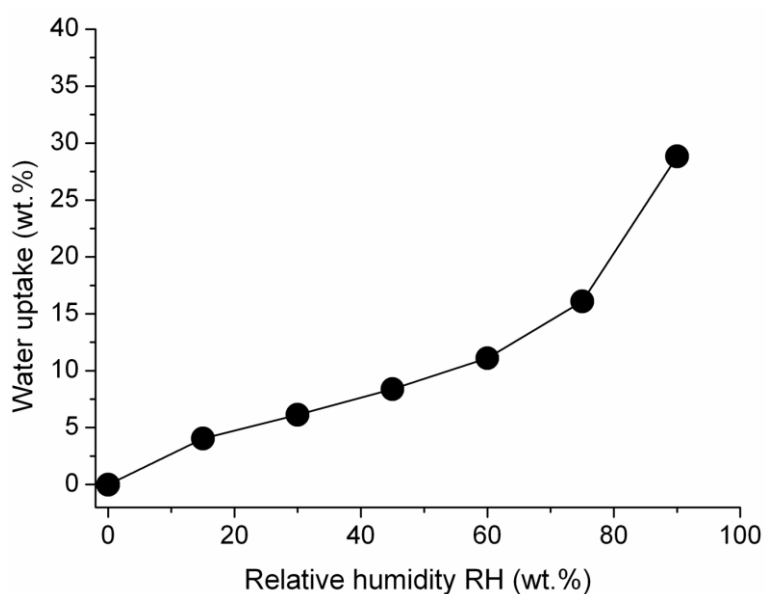
Sample	Length (m)	Width (cm)	Thickness (μm)	Weight (kg)	Pressure (bar)	Temperature (°C)
E0	9.1	2.9	130±44	0.040	104±1	198±1
EBP2	8.4	3.2	223±25	0.066	116±1	202±1
EBP5	8.5	3.5	250±17	0.082	128±6	203±1
EBP10	8.3	4.5	450±35	0.078	116±3	203±1
EPHT2	8.8	3.3	305 ± 21	0.072	114±4	209±2
EPHT5	8.8	3.5	306 ± 27	0.070	114±1	209±1
EPHT10	8.3	3.0	345 ± 21	0.040	84±2	206±2

^aNeat EVOH (E0), EVOH containing 2, 5, 10% BPs (EBP2, EBP5 and EBP10, respectively), EVOH containing 2, 5, 10 % post-harvest tomato plant material (EPHT2, EPHT5 and EPHT10, respectively). Data for BPs blends obtained in previous work (Nisticò et al., 2016)

Table 4Blend sheet films: DSC and crystallinity analysis.^a

Sample	T _g (°C)	T _c (°C)	T _m (°C)	ΔH _c (J/g)	ΔH _m (J/g)	%X _c (%)
E0	46.7±0.0	145.3±0.8	170.8±1.1	58.5±0.4	62.6±0.0	37
EPHT2	49.1±7.5	146.7±4.4	170.7±3.5	58.9±3.8	65.2±3.3	39
EPHT5	43.8±4.2	144.5±2.6	169.7±2.8	57.4±0.2	58.9±0.6	37
EPHT10	45.3±0.4	143.5±1.3	171.6±0.7	56.0±3.5	62.7±0.7	41

^aSample legends as in Table 3. DSC parameters legends in Methods section. Values are means of two measurements ± standard deviation. Means in each column show not significant difference (P≤0.05 Tukey tests).

**Fig. 1.** Water sensitivity evaluation of PHT using the DVS technique.**Fig. 2.** Blend sheet films at different filler contents. Legends as in Table 3

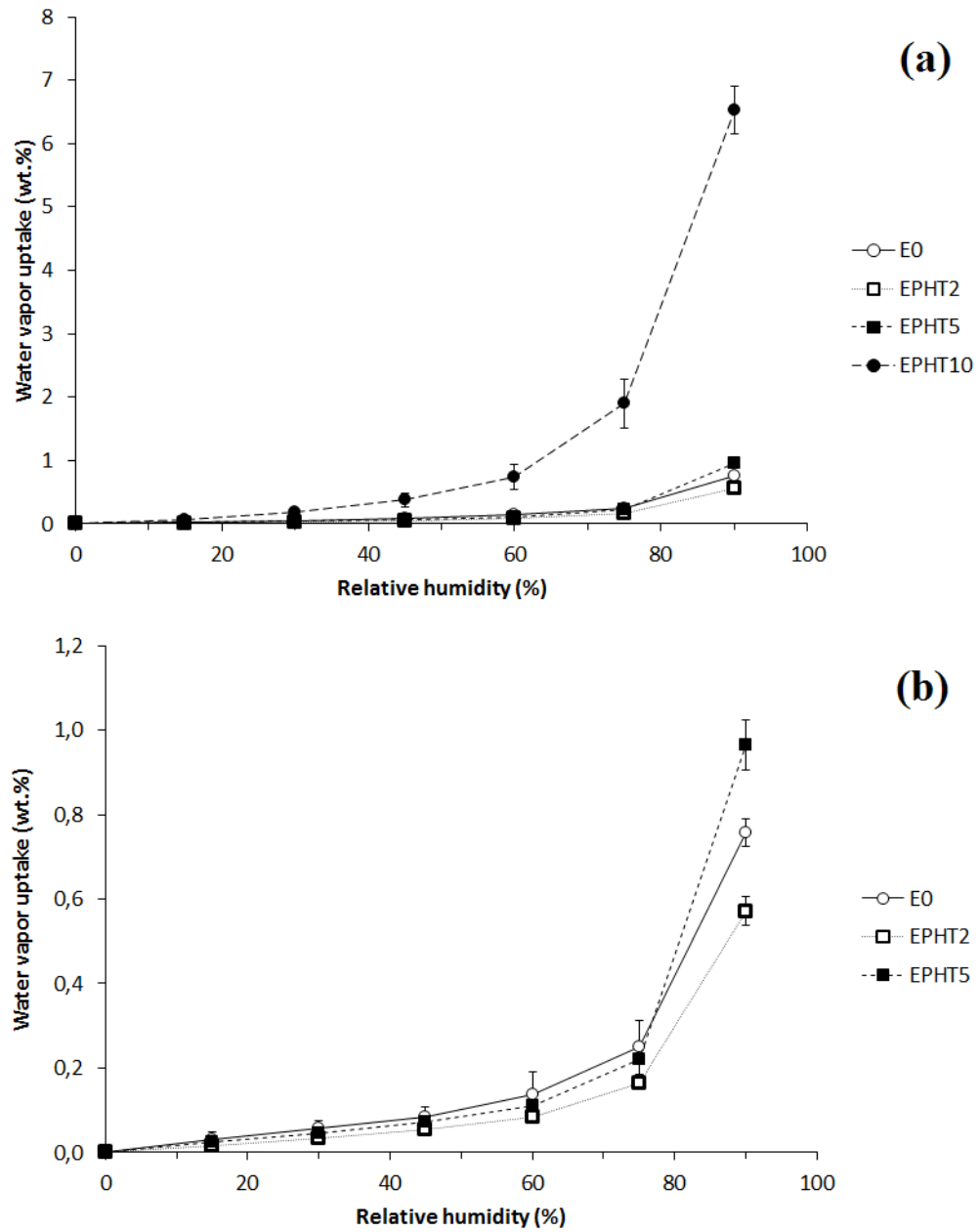


Fig. 3. Water vapor sensitivity evaluation by DVS analysis for neat EVOH and EVOH-PHT blend sheet films (sample legends as in Table 3): (a) all films (with error bars for EPHT10 film only), (b) magnification for E0, EPHT2 and EPHT5 films with error bars.

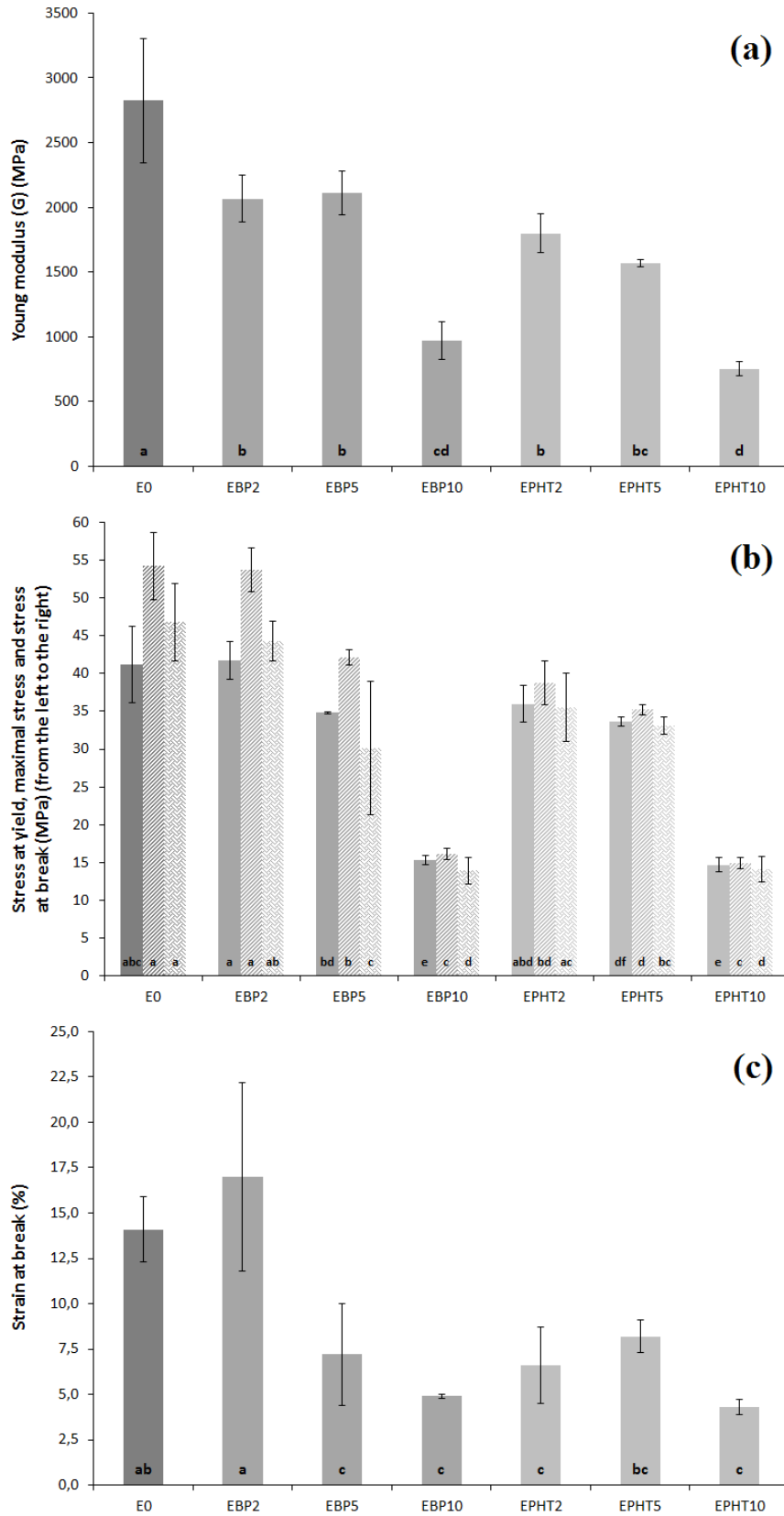


Fig. 4. Film tensile properties: (a) Young modulus (G), (b) stress at yield, maximal stress and stress at break, (c) strain at break. Sample legends as in Table 3. Values are means of triplicate measurements. For each analyte, means with different letters are significantly different ($P \leq 0.05$ Tukey tests). Data for BPs blends obtained in previous work (Nisticò et al., 2016).