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This is the accepted version of:

L. Sartore, F. Bignotti, S. Pandini, A. D'Amore, L. Di Landro
Green Composites and Blends from Leather Industry Waste
Polymer Composites, Vol. 37, N. 12, 2016, p. 3416-3422
doi:10.1002/pc.23541

The final publication is available at <https://doi.org/10.1002/pc.23541>

Access to the published version may require subscription.

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Green Composites and Blends from Leather Industry Waste

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Abstract page**Green Composites and Blends from Leather Industry Waste**

Blends based on protein hydrolysate (PH), derived from waste products of the leather industry, and poly(ethylene-co-vinyl acetate) (EVA), were obtained by reactive blending and their physico-chemical properties as well as their mechanical and rheological behavior were evaluated. The effect of vinyl acetate content and of a transesterification agent added to increase interaction between polymer and bio-based components were investigated. Novel biodegradable polymeric materials for spray mulching coatings were also obtained from hydrolyzed proteins and end-functionalized poly(ethylene glycol) (PEG), which was used as crosslinking agent. These products, almost entirely obtained from renewable sources, represent a new type of biodegradable material which looks promising for several applications, for instance in packaging or in agriculture as transplanting or mulching films with additional fertilizing action of PH.

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Abbreviation:

PH	protein hydrolysate;
EVA	poly(ethylene-co-vinyl acetate);
PEG	poly(ethylene glycol);
PE	polyethylene;
VA	vinyl acetate;
TA	transesterification agents;
CB	carbon black;
WS	cellulose microfibers;
SP	wood cellulose microfibers;
DMTA	Torsional dynamic-mechanical tests;
SEM	Scanning electron microscopy;
E	Young's modulus;
σ_b	Tensile strength;
ϵ_b	Elongation at break.

Abstract

Blends based on protein hydrolysate (PH), derived from waste products of the leather industry, and poly(ethylene-co-vinyl acetate) (EVA), were obtained by reactive blending and their physico-chemical properties as well as their mechanical and rheological behavior were evaluated. The effect of vinyl acetate content and of a transesterification agent added to increase interaction between polymer and bio-based components were investigated. Novel biodegradable polymeric materials for spray mulching coatings were also obtained from hydrolyzed proteins and end-functionalized poly(ethylene glycol) (PEG), which was used as crosslinking agent. These products, almost entirely obtained from renewable sources, represent a new type of biodegradable material which looks promising for several applications, for instance in packaging or in agriculture as transplanting or mulching films with additional fertilizing action of PH.

Keywords: poly(ethylene-co-vinyl acetate); protein hydrolysate; biocomposites; poly(ethylene glycol); mulching film.

1. Introduction

The increasing use of traditional, non-biodegradable plastics has raised environmental awareness of the need to develop a new generation of environmentally friendly materials. Particularly relevant are those made with raw products obtained both from renewable sources and from by-products of different productive activities. Environmentally degradable polymers and their blends with natural reinforcements are important for modern technology since they can be usually considered as ecologically safe materials. In this respect, all polymeric materials that undergo complete or partial degradation after their service life become preferable.

One of the ways to reach this goal consists in the development of new polymeric materials such as blends and composites, characterized by the presence of bio-based components [1]. A synthetic polymer is often needed in these materials to impart the required physical or mechanical properties to the blends. Blending bio-based components with non-biodegradable commodity polymers can reduce the total amount of plastic wastes, although it may not be considered as a definitive solution to the environmental problem caused by their disposal. Many

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5 of the candidate biodegradable polymers, moreover, have some limitations in their mechanical
6 properties or processability or costs.
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9 Among bio-based polymers, proteins have shown to be versatile materials that combine many
10 valuable characteristics for technical applications, such as good reactivity and processability,
11 both in solution and in the melt [2]. An important industrial source of proteins is for example the
12 leather production. Hydrolyzed proteins derived from collagen are composed of a mixture of
13 oligopeptides originating from enzymatic or chemical hydrolysis of solid wastes generated
14 downstream of leather chrome tanning stage (leather shavings). Thus, PH is easily available at
15 low cost and is readily biodegradable [3]. In this paper, PH was used to develop new biobased
16 materials that could find a number of interesting applications in different industrial sectors, for
17 example as materials for packaging or products for agriculture ranging from flexible mulching
18 films to rigid containers for plants and systems for controlled release of fertilizers [4-6].
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21 One of the prospective possibilities of adding value to PH is its use as additive for some
22 synthetic polymers aimed at improving and possibly “directing” their biodegradation properties.
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26 Polymer blending is one of the easiest and most cost efficient ways to produce new materials
27 with desired properties and characteristics. However, a great number of polymers are
28 thermodynamically immiscible in blends because of their low entropy of mixing. Therefore,
29 many researchers express considerable interest in compatibilization and, particularly, in reactive
30 compatibilization of immiscible polymers [7-9]. Reactive compatibilization is used to overcome
31 agglomeration problems and the usually weak adhesion between immiscible phases by creating
32 chemical bonds across the interface [10-13].
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36 The polyester family has the possibility to induce chemical reactions mainly through
37 transesterification. Concerning the exchange reaction in polyesters, researches usually deal with
38 polymer blends in which ester bonds are in the chain backbone. On the contrary, there are few
39 investigations related to polymers like EVA whose reactive groups are located in the side chains.
40 EVA is a modification of polyethylene (PE) with vinyl acetate as co-monomer; the introduction
41 of vinyl acetate groups in the main chain increases mechanical flexibility and reduces the
42 crystallinity compared to plain PE [14]. It has many characteristics of thermoplastic elastomers,
43 which can be tailored by changing the vinyl acetate content. EVA addition to biodegradable
44 polymers in blends may provide improved mechanical properties, better ozone resistance, good
45 weather resistance and relatively lower material cost. Although EVA is considered a non-
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5 biodegradable polymer, it can experience biodegradation under particular conditions, especially
6 when a high percentage of vinyl acetate is present in the copolymer [4, 15].
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10 In this research, blends based on EVA with different vinyl acetate and PH contents were
11 produced by reactive blending in a Brabender mixer and their physico-chemical properties and
12 mechanical and rheological behavior were investigated. These blends represent a new type of
13 flexible materials with promising performances for the substitution of traditional polymers in a
14 number of industrial and agricultural applications. Besides, the stiffness and hardness of these
15 blends can be tuned in accordance with the requirements entailed by the expected applications.
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19 In addition, the development and characterization of novel biodegradable materials obtained
20 from PH and poly(ethylene glycol) (PEG), used as crosslinking agent, are described. Different
21 end-functionalized PEGs as well as natural fillers and additives in different proportions were
22 investigated to obtain water suspensions capable of consistent film formation. In this form, the
23 material can be suitable for low pressure spraying techniques, which make it a valid alternative to
24 polyethylene films for soil mulching in terms of application procedures and biocompatibility.
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30 **2. Experimental**

31 **2.1 Materials**

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33 Ethylene-vinyl acetate random copolymers with vinyl acetate (VA) contents of 38-41 % (EVA
34 40), 27-29 % (EVA 28) and 17-19 % (EVA 18) were received from Arkema, Legnago Italy
35 (EVATANE[®]).
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40 Tetrabutylammonium tetraphenylborate was purchased from Sigma Aldrich Co (Milan, Italy)
41 and used as transesterification agent (TA).
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43 Poly(ethylene glycol) diglycidyl ether (molecular weight = 526 Da) was supplied by Sigma-
44 Aldrich and used as received.
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46 Carbon black (CB) was supplied by Degussa-Hüls (Düsseldorf, Germany) with an average
47 primary particle size of 23 nm.
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49 Cellulose microfibers (WS) extracted from cotton, with a fiber length of 300-500 μm , were
50 supplied by West System, Bay City, Michigan, USA; wood-cellulose microfibers (SP), with a
51 fiber length of 200-300 μm , were supplied by Gurit (Zürich, Switzerland). WS and SP were used
52 as raw materials.
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5 Protein hydrolysate was a slightly yellow product, chromium-free, obtained from Sicit
6 Chemitech S.p.A (Vicenza, Italy) as a waste product of chemical hydrolysis in the leather
7 production process.
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10 11 12 **2.2 Sample preparation**

13 **PH-EVA blends**

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15 PH-EVA blends with different compositions were prepared by melt reaction of PH and EVA
16 in the presence of TA in a Brabender mixer. All materials were dried at 50 °C in vacuum for 12
17 hrs before blending. Torque-time curves were recorded to get information on the compounding
18 effectiveness and shear stability of the blends. Compounding was performed at 150 °C and 50
19 rpm for about 5 min. All the blend samples were then compression molded by hot pressing at 150
20 °C to make sheets with 1 or 2 mm thickness, from which the specimens for mechanical
21 measurements were obtained. Blends compositions and mechanical properties are reported in
22 Table 1.
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28 **PH-PEG biocomposites**

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30 Biodegradable polymeric materials were prepared starting from protein-based aqueous
31 solution, obtained by dissolving the proper amount of bifunctional PEG in a 25% (w/v) solution
32 of PH. The desired amount of natural fillers and water, up to a final 18 wt % concentration, were
33 added under stirring at 50°C. In order to obtain black mulching films, CB was added too. The
34 suspension was kept under stirring for a few minutes at 50°C and after the addition of the proper
35 amount of crosslinking agent, the liquid mulching material was sprayed onto the soil surface.
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40 Cast films were also prepared by slow evaporation of the water suspension at room
41 temperature. The dry formulations were hot pressed at 50°C to realize 2 mm thick sheets, from
42 which specimens for tensile tests were prepared. Table 2 reports composition and mechanical
43 properties of different formulations of PH-PEG and natural fibers filled blends.
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48 **2.3 Mechanical and morphological analysis**

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50 Tensile tests were performed by an Instron Model 3366 Universal Testing Machine. Elastic
51 modulus, strength and elongation at break were determined on 2 mm thick and 10 mm wide bars,
52 with a gauge length of 80 mm; crosshead speed was 2 mm/min. Tensile tests were performed at
53 room temperature after specimen conditioning at 55 °C for 2 hrs under vacuum.
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5 Torsional dynamic-mechanical tests (DMTA) were performed on 2 mm thick specimens by a
6 Rheometrics RDAII rheometer. Temperature sweep tests (-100 °C/+100 °C) at 1 Hz frequency
7 were carried out. Curves of complex viscosity vs. frequency at 150 °C were also determined.
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10 Morphological analysis of blends after cryogenic fracture was done by SEM (Cambridge S
11 260) in order to estimate phase distribution. Specimens were observed after gold metallization.
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14 15 **3. Results and Discussion**

16 17 **3.1 PH-EVA blends properties**

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19 The compatibility of PH and EVA was studied by reactive blending in a Brabender mixer;
20 PH-EVA blends were prepared with different composition and starting from EVA with different
21 vinyl acetate content. The recording of torque vs. time during blend production allowed to follow
22 the viscosity evolution during mixing and to reach blends stability at the end of mixing. It was
23 observed that after an initial reduction of torque, the viscosity of blends increased to a fairly
24 stable situation after about two minutes. The presence of a transesterification agent reduced the
25 time to reach stability thus improving processability. After blending, the resulting material
26 appeared visually homogeneous suggesting a good dispersion. Mechanical properties are
27 markedly modified by addition of PH, as shown in Table 1 and in Figure 1. The addition of PH
28 promotes for all the materials a regular stiffening effect which is particularly strong in the case of
29 PH50-EVA18. It is interesting to notice that for the blends with higher VA contents (40, 28) a
30 highly ductile behavior was observed, with elongations at break above 900% for PH amounts up
31 to 35%, and at about 600% for the highest PH content. In the case of PH-EVA18 a less ductile
32 behavior was found and the addition of PH induced a more remarkable reduction of the
33 elongation at break. This trend may be a consequence of less favorable chemical interactions of
34 the blend components, due to the low VA content in EVA18.
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47 Measurements of complex viscosity vs. frequency of PH-EVA 40 blends (Fig. 2) show that
48 melt viscosity increases with increasing the PH content. Moreover, the presence of TA leads to a
49 somewhat higher viscosity compared to the corresponding blend with no TA; this may suggest an
50 effective compatibilizing action of TA, i.e. increasing transesterification reaction, leading to
51 modification of interactions of PH with EVA although a definite relationship between viscosity
52 and compatibilization is not clear [9, 11].
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5 The hydrolytic degradation was assessed by immersing specimens in distilled water at room
6 temperature and evaluating the weight loss over a period of about three months (Fig. 3). From the
7 beginning of the experiment, the blend without TA shows a constant weight loss of about 50 %,
8 which corresponds to its PH content. By contrast the corresponding blend prepared in the
9 presence of TA shows a slower release of material increasing gradually with time. The same
10 behavior is displayed also by the other blends of Figure 3. Interestingly, the measurements after
11 2000 hrs show in the blends with TA a weight loss greater than expected on the basis of their
12 composition and still increasing, probably due to increased chemical interactions between the
13 two phases.
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20 Figure 4 shows SEM micrographs of PH-EVA 40 with 50% PH (Fig. 4A), and its blend with
21 TA (Fig. 4B); a dispersion of particles was observed. Chemical investigations showed that the
22 continuous phase is rich in PH while the particles are made of EVA. Interestingly, the rubbery
23 EVA particles, with diameters ranging from 10 to 15 μm , are fairly homogeneously distributed in
24 the PH matrix, possibly leading to toughening effects. Fracture surfaces always show eventual
25 detachment of particles; however, less defined interfaces between particles and matrix appear
26 when TA is present, indicating good interaction at the filler-matrix interface.
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32 33 34 **3.2 PH-PEG derivatives for film coating**

35 A second investigation was carried out to assess the possibility to develop a biodegradable
36 polymeric material capable of consistent film formation when directly applied to soil by spray.
37 PH and PEG were chosen as starting materials to prepare this innovative biodegradable sprayable
38 coating; to modulate their physico-chemical and mechanical properties, grafting and crosslinking
39 of different formulations were developed. PEG is a water soluble polymer largely used in protein
40 modification; the derivatization of enzymes and peptides with PEG is a technology that has been
41 remarkably developed to obtain biomaterials having valuable properties for use both in the
42 biomedical field and as novel biocatalysts, due to the presence of polyethylene glycol chains
43 bound to the surface [16].
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50 PH-PEG derivatives were prepared in water solutions following a synthetic procedure which
51 involves the reaction between protein hydrolysate or gelatine amino-groups with the functional
52 end groups of PEG. In order to maintain a number of reactive end groups able to produce
53 crosslinking, an excess of bifunctional PEG (diglycidyl PEG or diacrylate PEG) over protein
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5 amino-groups was employed. PH-PEG derivatives were produced with various quantitative and
6 qualitative compositions differing for PEG type and PEG molecular weight. These are key
7 parameters for optimum products utilization, in particular by spray deposition, as well as to
8 modulate the durability and the degradation rate of the coatings. PH-PEG derivatives containing
9 20% PEG showed a modification of PH amino-groups, evaluated by colorimetric assays [17], of
10 about 40% and 20% when diglycidyl PEG or diacrylate PEG was used, respectively.
11 Furthermore, only the diglycidyl PEG derivatives showed extensive gel formation and finally
12 solidified, thus confirming their higher reactivity towards PH functional groups. For this reason
13 diacrylate PEG derivatives were not further investigated.
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15 Besides, because of the limited features of biodegradable matrices in several applications, a
16 way to improve their thermo-mechanical properties and to decrease their water sensitivity, thus
17 preserving biodegradability, was investigated by using natural fibers as biodegradable fillers. In
18 fact, the properties and costs of biodegradable polymers can be modified and improved not only
19 by blending, crosslinking and grafting, but also through the addition of fillers from renewable
20 resources, such as wood cellulose fibers, to obtain biocomposite materials. Table 2 reports the
21 composition of the more representative formulations based on PH-PEG and different natural
22 fibers, obtained by means of diglycidyl-PEG derivatives. In order to ensure good mechanical
23 properties and to enhance the environmental life time of proteinaceous derivatives, increasing
24 amounts of fibers (from 10% to 50%) were added, while the matrix of biocomposites was always
25 constituted of PH and PEG in a ratio of 9:1. Finally, in order to obtain insoluble materials with
26 good mechanical properties, improved water resistance and controlled degradation rate in soil, a
27 crosslinking agent (ethylene diamine) able to react with possibly unreacted diglycidyl-PEG was
28 added.
29

30 Table 2 also summarizes the mechanical properties of the various samples. The addition of
31 natural fibers to PH-PEG hardened the resulting biocomposites, while CB darkened the coating
32 color preventing possible photo-oxidation. PH-PEG films containing up to 30% different
33 cellulose fibers maintained a ductile behavior, whereas severe embrittlement was observed for
34 contents of 50%. The 30% cellulose fibers content seems to be the most interesting composition
35 as far as mechanical properties are concerned. An increase of Young's modulus and stress at
36 break was observed when both 30% SP or WS fibers were added to the PH-PEG matrices.
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5 In order to investigate the phase morphology of the biocomposites, as well as to understand
6 the degradation behavior of mulching films, morphological analyses were carried out on
7 cryogenic film fracture surfaces by using scanning electron microscopy. To this purpose, a
8 concentrated water dispersion of sample PH-PEG-SP30 was sprayed onto a glass surface.
9 Crosslinking and water evaporation took place simultaneously originating a regular continuous
10 coating having an average thickness of 0.6-0.8 mm. As reported in Figure 5A and 5B, where the
11 product is sprayed onto a glass surface and then detached, the film obtained by low-pressure
12 spray technique is flawless, flexible and resistant to tearing.

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18 The morphological analysis performed on the biocomposite obtained by spray (Fig. 6A)
19 clearly shows a regular distribution of lignocellulosic microfibrils within the polymeric matrix
20 and the absence of any stratification of the fibers. The morphological analysis performed on the
21 same sample directly sprayed onto the soil and exposed for six months (Fig. 6B) shows a
22 different pattern for the two film sides. The side exposed to the light (right side of Fig. 6B) does
23 not differ significantly from the original one, with no evident indication of degradation, while the
24 surface facing the soil (left side of Fig. 6B) consists almost exclusively of fibers, thus indicating
25 that degradation starts from the polymeric component of the material. The biodegradation
26 process occurs more rapidly at the side where a direct contact between the film and
27 microorganism happens, and the remaining fibers can act as a barrier modulating the
28 environmental duration of the blend. The tensile tests performed on this aged film (last line of
29 Table 2) showed very good retention of mechanical properties, confirming that the introduction
30 of cellulose microfibrils can be used as a further tool to tune the mechanical performance and to
31 enhance the material lifetime.

32 33 34 35 36 37 38 39 40 41 42 43 44 **Conclusions**

45 Reactive blending of different amounts of PH-based biodegradable materials and EVA can
46 lead to flexible or rigid materials, which may be processed to obtain stretchy films or stiff plastic
47 components suitable for a number of applications. The addition of a transesterification agent
48 increases PH-EVA interactions with positive effects on dispersion and mechanical properties.

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New polymeric protein-based biocomposites to be used as water dispersions to generate *in situ*
biobased films and coatings by low-pressure spray were also developed. The biodegradable
coatings, which are almost completely manufactured from renewable-based raw materials,

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5 showed good mechanical performance; the introduction of cellulose microfibrils can be used as a
6 further tool to tune the mechanical properties and the environmental durability of the product.
7 This combination of properties makes the new biocomposites an ecologically friendly alternative
8 to synthetic petro-chemical polymers for several applications, in particular for soil mulching.
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13 **Acknowledgments**

14 The authors thank Sicit Group (Italy) for supporting this research.

15
16 The contribution of Gloria Spagnoli, Isabella Peroni and Maria Rosaria Pagano in the
17 experimental testing is gratefully acknowledged.
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REFERENCES

1. A. K. Mohanty, M. Misra, L. T. Drzal, *Natural Fibers, Biopolymers and Biocomposites*, CRC Press, Taylor and Francis, Boca Raton FL, (2005).
2. L. Sartore, M. Penco, A. Sassi, M.C. Candido, New Biodegradable Polymeric Derivatives, International Patent n° PCT/IB2007/055167, (2007).
3. E. Chiellini, P. Cinelli, A. Corti, E.R. Kenawy, *Polym. Degrad. Stab.* **73** 549-555 (2001).
4. D. L. Kaplan, J. M. Mayer, D. Ball, J. McCassie, A. L. Allen, P. Stenhouse, *Biodegradable Polymers and Packaging*, C. Ching, D. L. Kaplan, E. L. Thomas, Eds. Technomic, Lancaster, PA, USA, (1993).
5. L. Sartore, G. Vox E. Schettini, *J. Polym. Environ.* **21**, 718-725 (2013).
6. E. Schettini, L. Sartore, M. Barbaglio, G. Vox, *Acta Horticulturae (ISHS)* **952**, 359-366 (2012).
7. A.I. Isayev, *Encyclopedia of Polymer Blends*, Wiley-VCH, Weinheim, Germany, (2011).
8. L. Sartore, M. Penco, S. Della Sciucca, R. Mendichi, L. Di Landro, S. D'Antone, *J. Appl. Polym. Sci.* **100**, 4654-4660 (2006).
9. F. Severini, M. Pegoraro, L. Di Landro, *Angew. Makromol. Chem.*, **190**, 177-186 (1991).
10. S. Bruce Brown, , *Polymer Blends Handbook*, Ed. L. A. Utracki, Kluwer Academic Publishers, Dordrecht 339-415 (2003).
11. M.M. Coleman, J. Graf, P.C. Painter, *Specific Interaction and the Miscibility of Polymer Blends*, Technomic, Lancaster, (1991).
12. I. Aravind, S. Thomas, *Reactive compatibilization of polymer blends* Society of Plastics Engineers (SPE), Plastics Research Online 10.1002/spepro.003188, (2010).
13. M. Penco, L. Sartore, S. Della Sciucca, L. Di Landro, A. D'Amore, *Macromol. Symp.*, **247**, 252-259 (2007).
14. X.M. Shi, J. Zhang, J. Jin, S.J. Chen, *eXPRESS Polym. Lett.* **2**, 623-629 (2008).
15. C. Abrusci, J.L. Pablos, I. Marin, E. Espi, T. Corrales, F. Catalina, *J. Appl. Polym. Sci.*, **126**, 1664-1675 (2012).
16. L. Sartore, P. Caliceti, O. Schiavon, F. M. Veronese, *Appl. Biochem. Biotech.* **27(1)**, 45-54 (1991).

17. A.F.S.A. Habeeb, *Anal. Biochem.* **14 (3)** 328-336 (1966).

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Caption to Figures

Figure 1. Elastic modulus of different PH-EVA blends as a function of the PH content. EVA with 40%, 28% and 18% vinyl acetate content was used.

Figure 2. Complex viscosity curves at 150°C of EVA and PH-EVA40 blends with different PH contents (a) and with or without TA (b).

Figure 3. Weight loss of different PH-EVA blends in distilled water.

Figure 4. SEM micrographs of PH50-EVA40 blend (a), and the same blend with the transesterification agent (b).

Figure 5. Film formation on glass surface: after crosslinking and water evaporation, the PH-PEG-SP30 film with (a) and without carbon black (b), is easily detached.

Figure 6. Scanning electron microscopy image of a mulching film section (PH-PEG-SP30) obtained after cryogenic fracture (a) and of the same sample after six month's exposition to soil and sunlight (b).

Table 1. PH-EVA blends properties

Sample	Composition		Tensile Properties		
	PH(wt%)	EVA(wt%)	E ^a (MPa)	σ_b^b (MPa)	ϵ_b^c (%)
EVA40	-	100	2±0,4	>4	>900
PH20-EVA40	19.8	80.2	8±1	>4.4	>900
PH35-EVA40	36.5	63.5	11±2	>4.4	>900
PH50-EVA40	50.4	49.6	35±10	3.4±0.4	600±20
EVA28	-	100	13±1	>5.2	>900
PH20-EVA28	20.2	79.8	40±10	>5.2	>900
PH35-EVA28	35.0	65.0	75±15	>5.5	>900
PH50-EVA28	49.9	50.1	146±15	5±0.4	620±20
EVA18	-	100	13±1	4.9±0.4	700±5
PH20-EVA18	20.1	79.9	23±5	4.1±0.4	238±15
PH35-EVA18	34.6	65.4	56±4	3.3±0.4	118±10
PH50-EVA18	49.6	50.4	256±30	2.8±0.4	36±3

^a E = Young's modulus; ^b σ_b = tensile strength; ^c ϵ_b = elongation at break.

Table 2. Composition and mechanical properties of PH-PEG biocomposites

Sample	Composition					Tensile properties		
	PH (%)	PEG ^a (%)	CB (%)	Fibers (%)	Et-NH ₂ ^d (%)	E ^e (MPa) (±70)	σ _b ^f (MPa) (±3)	ε _b ^g (%) (±1)
PH-PEG	89.9	9.6	-	-	0.5	1450	32	10
PH-PEG-CB 2,5	86.9	10.1	2.5	-	0.5	880	16	38
PH-PEG-SP 10	78.2	8.7	2.5	10.0 ^b	0.5	998	11	41
PH-PEG-SP 30	60.6	6.7	2.5	29.9 ^b	0.3	3540	45	5
PH-PEG-SP 50	42.6	4.7	2.5	50.0 ^b	0.2	1816	28	4
PH-PEG-WS 10	78.2	8.7	2.5	10.1 ^c	0.5	1226	20	8
PH-PEG-WS 30	60.4	6.7	2.5	30.1 ^c	0.3	2125	26	3
PH-PEG-WS 50	42.8	4.7	2.5	49.8 ^c	0.2	256	2	2
PH-PEG-SP 30*	-	-	-	-	-	1030	7	1

^a PEG was poly(ethylene glycol) diglycidyl ether (molecular weight = 526 Da); ^b SP microfibers were added; ^c WS microfibers were added; ^d Et-NH₂ was ethylene diamine; ^e E = Young's modulus; ^f σ_b = tensile strength; ^g ε_b = elongation at break; *Tensile test done after permanence of PH-PEG-SP 30 on soil for six months.

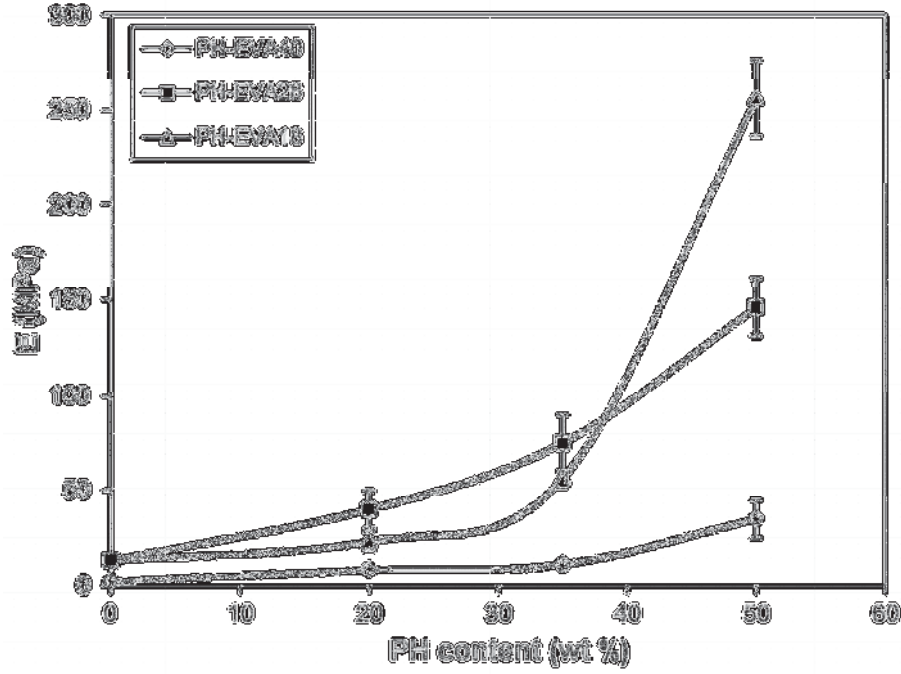


Figure 1. Elastic modulus of different PH-EVA blends as a function of the PH content. EVA with 40%, 28% and 18% vinyl acetate content was used.
361x270mm (300 x 300 DPI)

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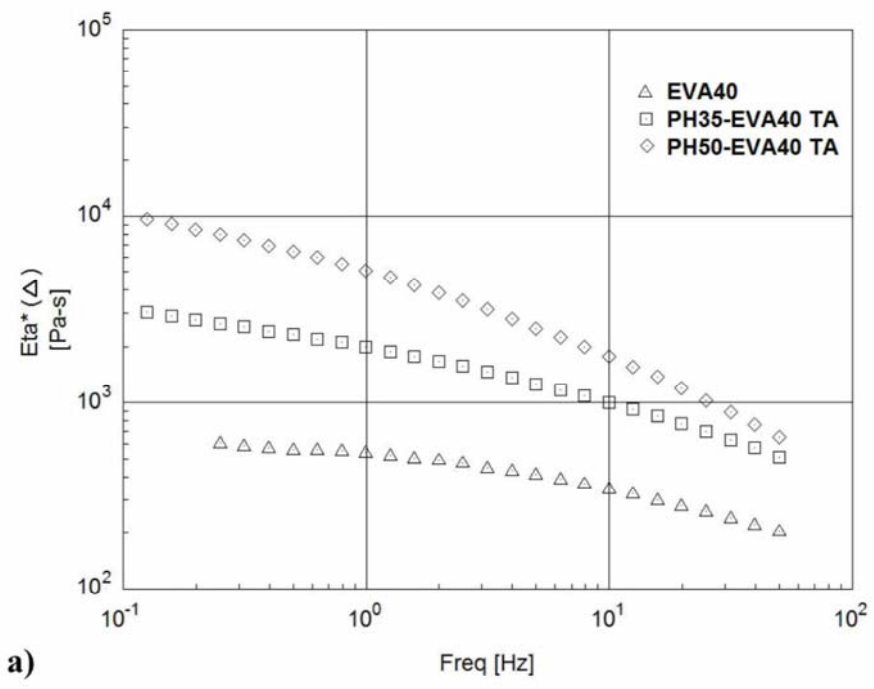


Figure 2. Complex viscosity curves at 150°C of EVA and PH-EVA40 blends with different PH contents (a) and with or without TA (b).
361x270mm (300 x 300 DPI)

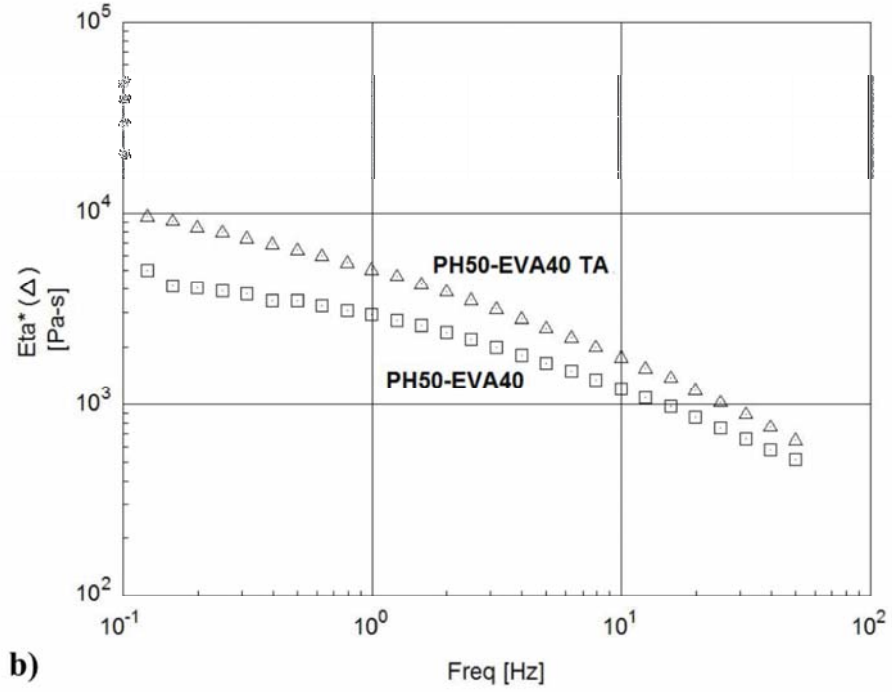


Figure 2. Complex viscosity curves at 150°C of EVA and PH-EVA40 blends with different PH contents (a) and with or without TA (b).
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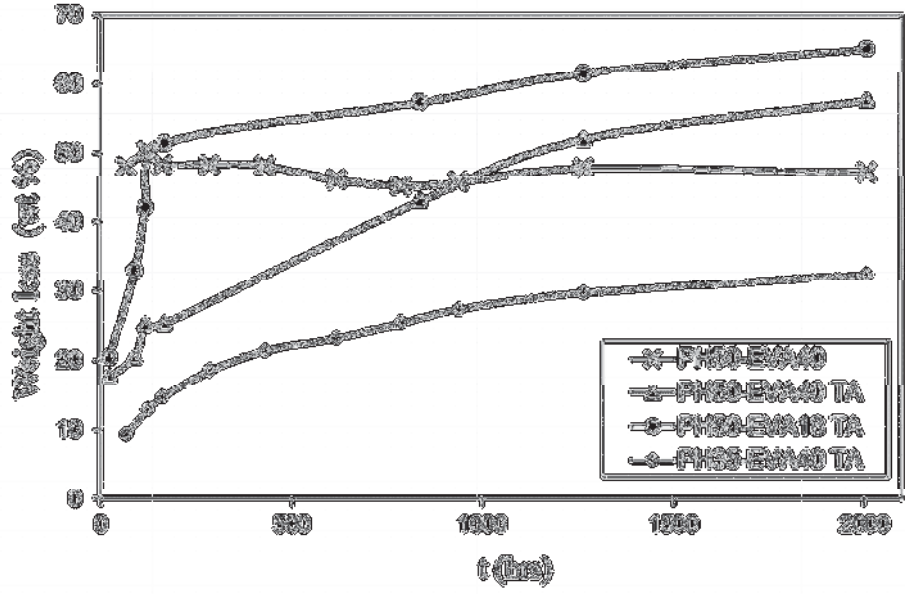


Figure 3. Weight loss of different PH-EVA blends in distilled water.
361x270mm (300 x 300 DPI)

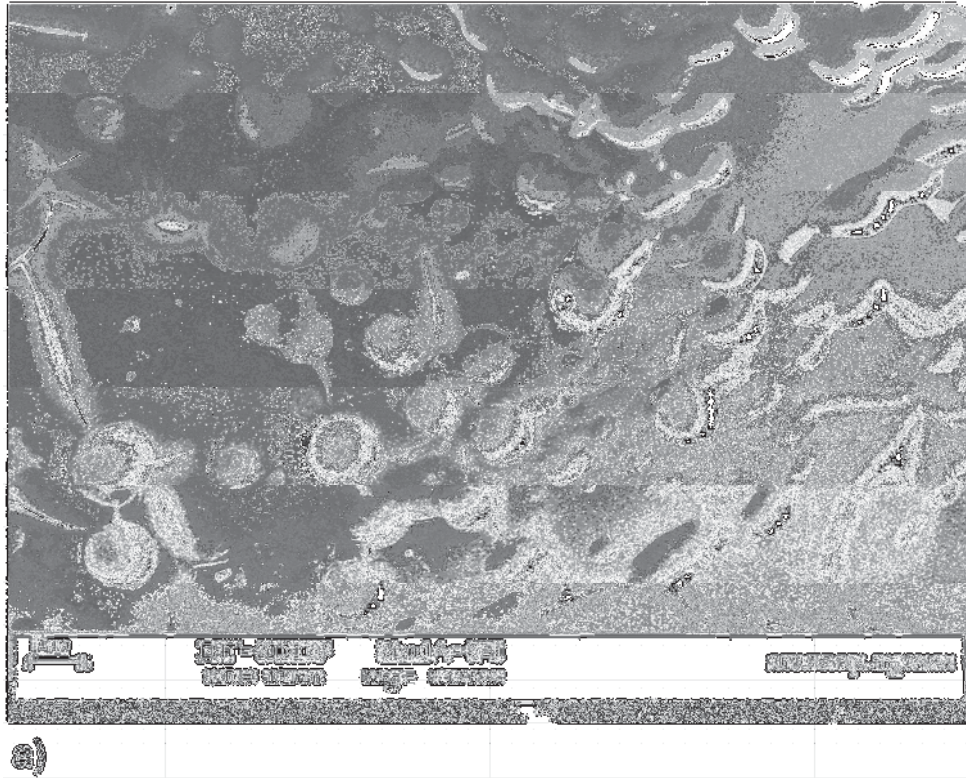


Figure 4. SEM micrographs of PH50-EVA40 blend (a), and the same blend with the transesterification agent (b).
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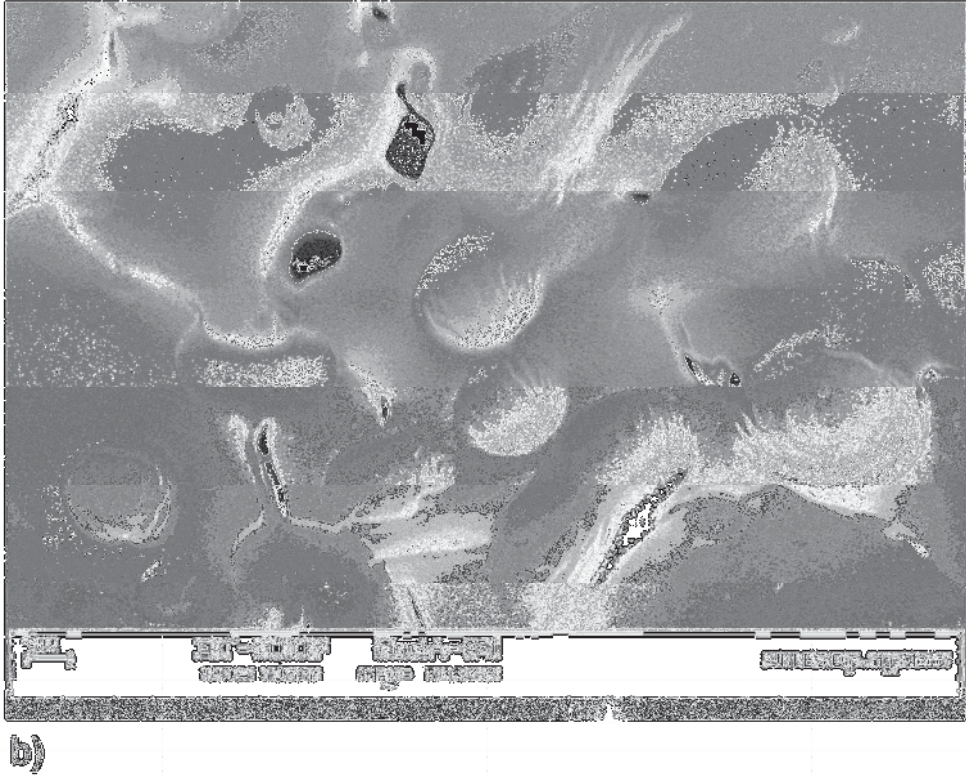


Figure 4. SEM micrographs of PH50-EVA40 blend (a), and the same blend with the transesterification agent (b).
373x299mm (300 x 300 DPI)

view



Figure 5. Film formation on glass surface: after crosslinking and water evaporation, the PH-PEG-SP30 film with (a) and without carbon black (b), is easily detached.
422x299mm (300 x 300 DPI)

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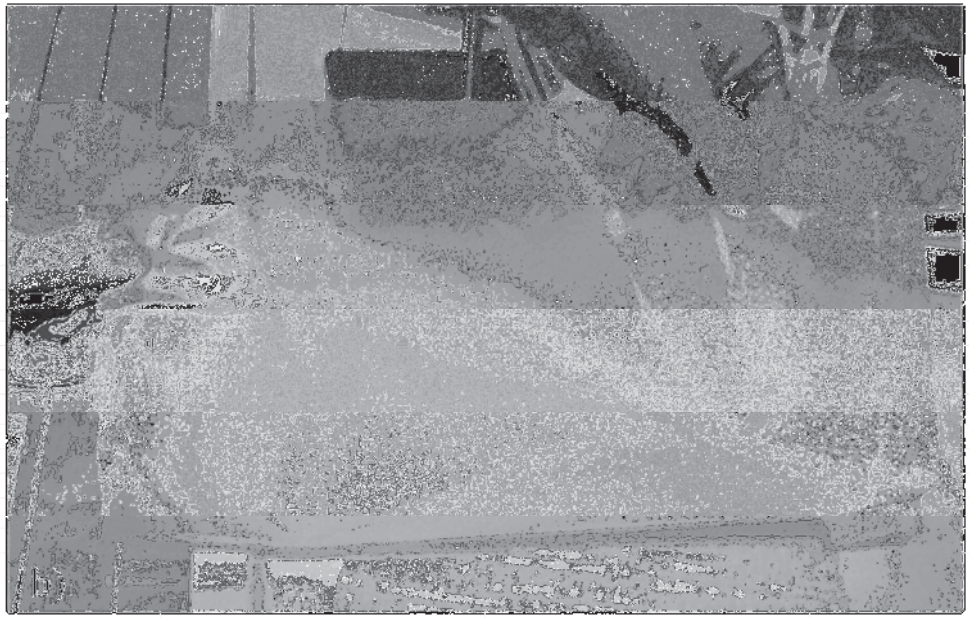


Figure 5. Film formation on glass surface: after crosslinking and water evaporation, the PH-PEG-SP30 film with (a) and without carbon black (b), is easily detached.
468x299mm (300 x 300 DPI)

Review

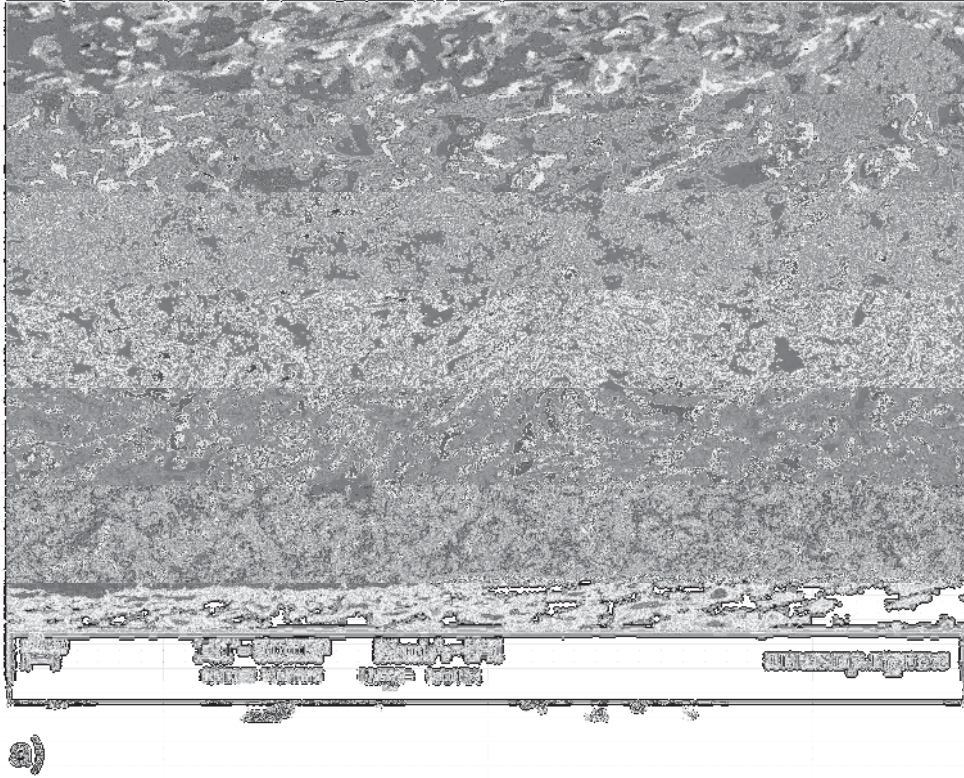
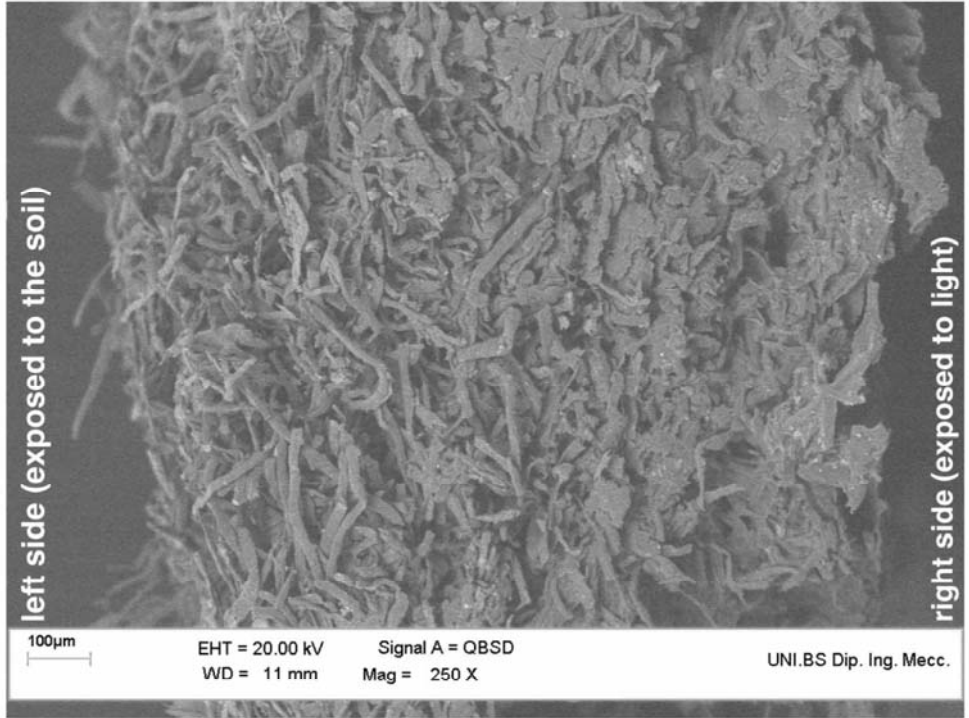


Figure 6. Scanning electron microscopy image of a mulching film section (PH-PEG-SP30) obtained after cryogenic fracture (a) and of the same sample after six month's exposition to soil and sunlight (b).
373x299mm (300 x 300 DPI)

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Figure 6. Scanning electron microscopy image of a mulching film section (PH-PEG-SP30) obtained after cryogenic fracture (a) and of the same sample after six month's exposition to soil and sunlight (b).
375x299mm (300 x 300 DPI)

view