Available online at www.sciencedirect.com

ScienceDirect

Procedia Materials Science 8 (2015) 778 – 785

Procedia Materials Science

www.elsevier.com/locate/procedia

International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Comparative Study of Agroindustrial Wastes for their use in Polymer Matrix Composites

Cintia S. Navas[a]*, María M. Reboredo[b] , Dolly L.Granados[a]

[a]*Chemical Engineering Institute, Faculty of Engineering, National University of San Juan , 1109 Libertador San Martin Avenue (West), San Juan 5400, Argentina.*

[b]*Institute of Materials Science and Technology (INTEMA), National University of Mar del Plata (UNMdP), Av. Juan B. Justo 4302 Mar del Plata, Buenos Aires , (B7608FDQ), Argentina.*

Abstract

Natural fibers are composed mainly of cellulose, hemicellulose and lignin, with the composition varying according to the type of plant and geographic region. Their low density, easy processing, low cost, abundance and biodegradability make them ideal for use as organic filler in polymer matrices. The final properties and, therefore, the potential applications of the obtained composite materials, depend on the composition of the fiber, the interfacial adhesion with the matrix, the size of the particle and the aggregate weight percent. In this paper we revise the suitability of wastes from olive and wine industries through a comparative study of the resulting particles for subsequent use in polymer matrix composites. The residues used are olive wet husk, olive pits and grape stalks. The particles, dried and ground, were characterized by proximate analysis, acid-base groups, X-ray diffraction, thermal tests and scanning electron microscopy. The olive wet husk showed a wider particle size distribution, the olive pits showed a more narrow distribution and better stability against thermal degradation and the grape stalks exhibited the greater amount of surface groups and a more fibrous structure. The first characteristic favors the compatibility with polar polymer matrices, while the second would grant best composite mechanical properties.

Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013

Keywords: Agro-industrial wastes; Olive wet husk; Olive Pits; Grape stalks; Characterization.

* Corresponding author. Tel.: +54-0264-4211700-453-35; fax: +54-0264-4200-289.
E-mail address: cnavas@unsj.edu.ar

Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013
doi:10.1016/j.mspro.2015.04.135

1. Introduction

The need to replace petroleum products, increased environmental, social and economic awareness, and sustainability concepts, have stimulated the search for green materials compatible with the environment. Globally, the abundance and availability of natural and agro-industrial waste is responsible for a new interest in sustainable technology research Kalia et al. (2011). This is reflected in the strong growth experienced in recent years by the global market of natural fiber composites, above 11% a year Celluwood 2008.

In our country, agriculture is one of the main economic activities. The industrialization of agricultural products produced thousands of tons of waste, taking a special interest the vegetable materials, due to their many potential uses, including the production of composite materials in structural applications Matos et al. (2010). This is the case of waste from olive industry which also has the characteristic of being highly polluting and difficult to treat for disposal Caputo et al. (2003), Suna Erses Yay et al. (2012), Inan et. al. (2004). Among these, the so-called "olive wet husk", mixture of liquids and dissolved solids with a large organic load, is one of the most difficult to treat, dispose or add value. Internationally emerging treatment alternatives exist but they need to be improved and completed Paraskeva and Diamadopoulos (2006). Regarding the wine industry, generates among other wastes, stalks of grapes, which is the cluster woody structure Deiana et al. (2009).

The addition of dry solids such as organic fillers in polymer matrices could offer potential advantages in sustainability by using raw materials from renewable resources. It offers the possibility of developing suitable materials according to the destination or use, reducing costs and improving the mechanical properties. Moreover, the lignocellulosic materials have additional advantages such as its low density, do not require complex equipment to process, not cause abrasion during processing and are abundant Tserki et al. (2005).

To use and design materials for industrial applications is imperative to determine the material properties that will affect their performance Baillie (2004). The mechanical, thermal and electrical properties, and therefore, the final application of the composite materials obtained, depend on the morphology and composition of the particles Kim and Netravali (2013), Perinovic et al. (2010), Bishaya et al (2011).

This paper aims to identify particle characteristics (composition, surface topology, thermal stability, etc.) that explain different features when they are incorporated in the polymer matrices. The residues used are olive wet husk, olive pits and grape stalk.

2. Materials and methods

2.1. Preparation of the material

Selected wastes from the agroindustrial activity of the Cuyo region, Argentina, were used. Olive wet husk and olive pits from the manufacture of olive oil, were supplied by Solfrut from San Juan and Nucete from Mendoza, respectively. The stalks of grapes, vinification process waste, were supplied by Bodegas Callia. The samples were identified as GS (grape stalk), OP (olive pits) and OWH (olive wet husk), Fig. 1.

The olive pits and the grape stalks were at first air dried for 48 hours and then dried in an oven DALVO, DHRI model, at 100 °C for 24 hours. The olive wet husk was dried at 60 ° C for 5 days, because the drying at 100 °C form a dark layer that may involve degradation of the material.

Fig. 1. (a) Olive wet husk; (b) Olive pit; (c) Grape stalks.

All the dried materials were grounded with a coffee grinder RECCO, MOCO2 model at 1850 rpm for 20 min and were sized classified using a set of sieves which range is between #4 and #100 (equivalent to 4.75 and 0.150 mm, respectively, according to standard ASTME 11:81).

2.2. *Physicochemical characterization*

The moisture content of the waste as received from the industry was determined. The dried samples of the materials were characterized by proximate analysis and acid and basic groups content. The proximate analysis included the determination of moisture content (ASTM D 2867-95), ash (ASTM D 2866-94) and volatile matter (ASTM E - 872-82).

Boehm titration method was used for determination of surface chemical groups. This method consists of a series of volumetric analysis where solid samples are contacted with different solutions, including NaOH, Na_2CO_3, $NaHCO_3$ and HCl, to selectively neutralize acid and basic groups Boehm (1994). Basic sites are neutralized with HCl solution (0.05 N). Carboxyl groups are determined with NaHCO3; the difference between groups evaluated with Na_2CO_3 and $NaHCO_3$ is attributed to lactone groups, and the difference of those evaluated with NaOH and Na_2CO_3, to phenolic groups.

2.3. Particle size distribution

Milled dry materials were classified by sizes using sieves with a set of ranges between #4 and #100, quantifying the mass fraction retained on each sieve. The particle size distribution analysis was performed by the Weibull probability distribution, suitable for particles obtained by crushing and grinding Basu et al. (2009), Krifa (2009).

2.4. Thermal analysis

Thermogravimetric analysis of the materials was performed on a Shimadzu TGA-50, by heating the samples in a temperature range of 25-900 °C under a nitrogen gas flow of 20 ml/min and a heating rate of 10 °C/min. The weight of the samples was approximately 8 mg.

2.5. X-ray diffraction

X-ray diffraction was performed using a X'PERT PRO diffractometer equipped with CuKα radiation and step size of 0.02°/min, from 10° to 80° 2θ, at room temperature, using a voltage of 40 KV and a current of 30 mA.

2.6. Scanning electron microscopy

Scanning electron microscopy allows the observation of materials surfaces and provides images of the topography of them. A microscope JEOL 6460LV was used. The samples were covered with a thin gold layer (300 Å) by using argon plasma.

3. Results and discussion

3.1. Physico-chemical characterization of materials

The results of the proximate analysis of the dried samples are shown in Table 2. The olive wet husk also presents the highest moisture content of the three samples. It is also observed that the grape stalk has less volatile content and higher proportion of fixed carbon.

Table 1. Moisture content.

Material	Moisture (%)
OWH	71.59
OP	5.23
GS	14.87

Table 2. Proximate analysis.

Material	Moisture (%)	Ashes (%)	Volatiles (%)	Fixed Carbon (%)
OWH	10.47	2.73	86.15	0.65
OP	5.35	4.76	87.78	2.11
GS	7.32	9.16	71.91	11.61

Table 3 shows the surface groups, lactones, carboxyls, phenols and basics groups determined by the method of Boehm. It is evident that the grape stalk has the highest proportion in acid groups (carboxyl and lactones) and total basic groups, while the olive pit has the lowest proportion. Thus, considering the amount of surface groups of these materials, we have the sequence GS> OWH> OP, positioning the grape stalk as the most suitable for its use as a filler in polar polymer matrices.

Table 3. Presence of acid and basic groups in the materials.

Material	Groups (meq/g)			
	Carboxyl	Lactones	Phenols	Basics
OWH	1.179	1.018	2.694	3.691
OP	1.265	0.510	0.000	3.227
GS	2.605	2.189	3.959	4.281

3.2. Particle size distribution

Fig. 2 shows the particle size distribution after sieving. It can be said that the distribution of the olive wet husk is positively asymmetric while the olive pit and the grape stalk curves present a quite symmetrical shape similar to a normal distribution. The large amplitude in olive wet husk distribution indicates the presence of particles of different sizes, which would be associated with a better grade of packing, upon integration with the polymer matrix Seyni et al. (2009), Fu et al. (2008).

Weibull parameters are shown in Table 4. The parameter K is the shape parameter and is a measure of the dispersion of particle sizes while λ is the scale parameter, and represents the average particle size. The lower value of λ correspond to the grape stalk and it reflects that it is the easiest to grind.

Table 4. Weibull parameters of the samples.

Model parameters	Material		
	OWH	OP	GS
K	2.185	3.927	3.359
λ	2.496	0.467	0.378

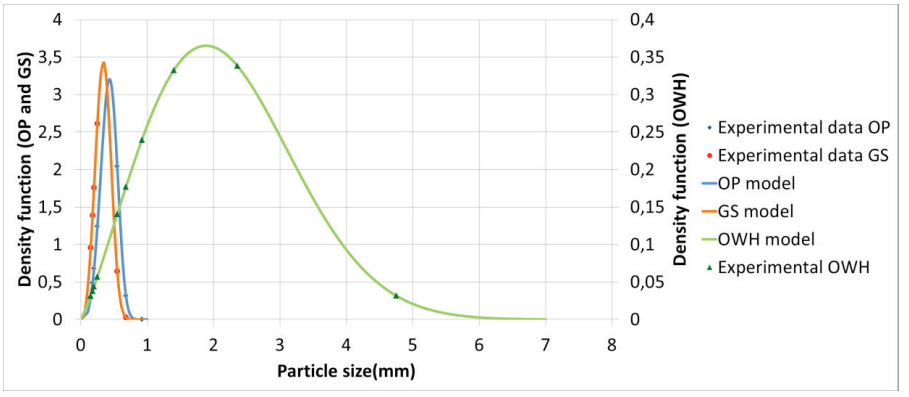

Fig. 2. Particle size distribution.

3.3. Thermogravimetric analysis

The thermal stability of lignocellulosic materials used as filler or reinforcement in polymer matrix composites is of paramount importance. The manufacturing of composites requires the mixing of fibers/fillers and matrix at high temperatures, above the melting point (thermoplastics) or reaction temperature (thermosetting) of the polymeric matrices. A prolonged exposure of the natural fillers at such high temperatures raises question about the potential degradation of the fillers. Hence, it is imperative that one should determine the degradation profile of lignocellulosic materials prior to use in composites applications Tserki et al. (2005).

The curves derived from the mass loss as a function of temperature, DTGA, are shown in Fig. 3. These curves illustrate that the thermal degradation occurs as a multistep process for all the materials tested, which is expected given their composition. There are five peaks of thermal decomposition, whose values were assigned according to the Manals-Cutiño et al. (2011) and Krause Sammartino et al. (2010). The first is related to moisture loss. The second represents the loss of extractables, such as terpenes, tannins, fatty acids, oils and resins. Above 250 °C carbohydrate (pectin, hemicellulose and cellulose) and lignin are decomposed. The third degradation peak is attributed to the loss of hemicellulose. Cellulose, the fourth peak, is the most thermally resistant of the carbohydrate group, decomposing at temperatures above 350 °C. Finally, in the fifth stage, take place the decomposition of the lignin between 350 and 500 °C, and the carbonaceous residue, from 400 °C, produced by pyrolysis of carbohydrates. As a consequence of the complexity of the process of decomposition of the lignin (tridimensional polymer), and the thermal degradation of carbonaceous residue, appears a shoulder in the DTGA thermogram of lignocellulosic materials in the temperature range of 362-694 °C.

The degradation temperature range, the temperature corresponding to the maximum rate of degradation and the corresponding weight loss that occurs in each stage, are summarized in Table 5.

Table 5. Thermogravimetric analysis of the samples.

Sample		OWH			OP			GS	
Components	Temp. Range	Tmáx (°C)	Weight loss %	Temp. Range	Tmáx (°C)	Weight loss %	Temp. Range	Tmáx (°C)	Weight loss %
Moisture	24 - 114	54	6.21	24 - 117	37	4.39	24 - 128	57	5.47
Extractables	114 - 254	239	10.58	117- 250	229	4.33	128 - 227	200	7.81
Hemicellulose	254 - 333	301	23.53	250 - 311	-	16.36	227 - 280	266	17.71
Cellulose	333 - 448	378	20.73	311 - 370	340	28.56	380 - 384	310	21.89
Lignin	448 - 546	-	10.93	370 - 450	384	12.87	384 - 694	-	25.89

These tests show that the olive pit is the most stable material, starting its degradation about 30 °C above the grape stalk and about 10 °C just after the olive wet husk. The final mass obtained for the olive wet husk, olive pits and grape stalks was 16, 18 and 12 %, respectively, indicating that the grape stalks decompose more.

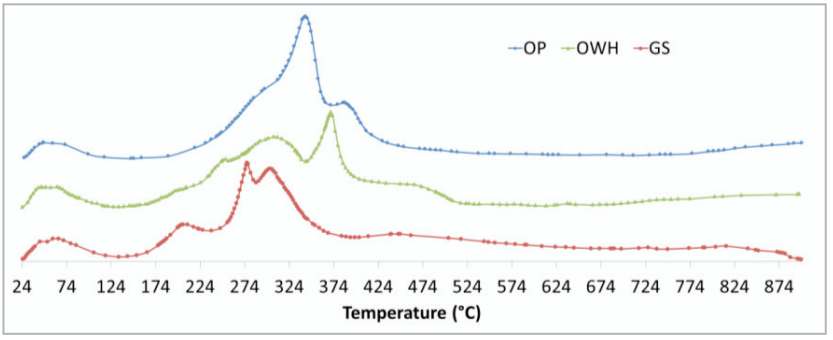

Fig. 3. DTGA samples of OWH, GS and OP.

The grape stalk has a distinct decomposition process in comparison to OP and OWH. This may be related to the higher presence of surface groups.

About the hemicelluloses content, which is obtained by the difference of weights, olive wet husk has the greater proportion, being sequentially increasing materials GS <OP <OWH. Regarding the presence of cellulose, olive pit has the greater proportion, being sequentially increasing materials SG <OWH <OP.

3.4. X-ray diffraction

Fig. 4 shows the X-Ray diffraction patterns of the materials. It can be seen that all of them have a peak at 22.6 ° (2 θ) characteristic of crystalline cellulose type I (corresponds to the 002 plane) and, for OP and GS, a second peak at 34.5 ° (2 θ), corresponding to the 023 or 004 planes. Cellulose molecules are oriented at random and have the tendency to form hydrogen bridge links, inter-and intramolecular. The packing density of the cellulose is highly crystalline and may contain up to 80% of crystalline regions. The remaining fraction has a lower packing density and it is known as amorphous cellulose. Most plants consist of 45 or 50 % of cellulose (dry basis), but this value can vary from as high as 90% in cotton to values of 30% from fiber of stems Bledzki et al. (2002). According to the area under the peaks corresponding to crystalline cellulose, the highest content corresponds to the olive pit, while the grape stalk has the lowest value (coincidentally with its stem structure). This tendency agrees with that found by thermogravimetric analysis.

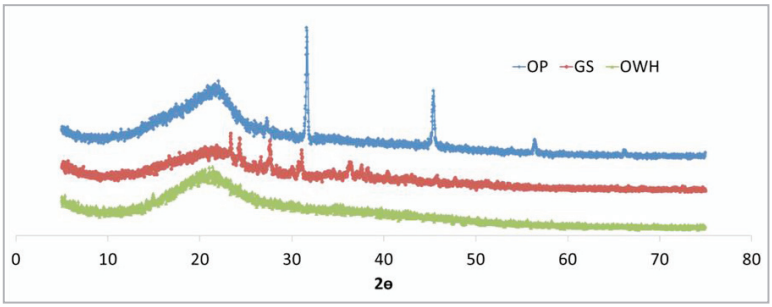

Fig. 4. XR diffractrograms of samples.

3.5. Differential scanning microscopy

Fig. 5 shows scanning electron micrographs of the structures of the three materials. The micrographs show that the three materials are covered with an unevenly distributed layer, whose composition is probably waxes Tserki et al. (2005).

It is interesting to observe that the grape stalk morphology is very different from that of olive wet husk and olive pits. This is due to its particular woody structure. The micrographs a and b allow to see that both, the olive wet husk and olive pit, present particles with similar morphologies (globular). Besides, a larger agglomeration of particles can be seen in the case of the olive pit. Moreover, the grape stalk shows elongated particles with an aspect ratio (length/diameter) considerably greater than 1 (microfibers). Knowledge of the length and width, including dimensions, defects and structure, is important to compare the different types of natural fibers. The length/width ratio gives an indication of the potential strength properties of fiber-filled composites Bledzki et al. (2002).

The micrographs d, e and f show more clearly the difference in the particle surface: stratified for olive wet husk and olive pit, and rough surfaces for the grape stalk.

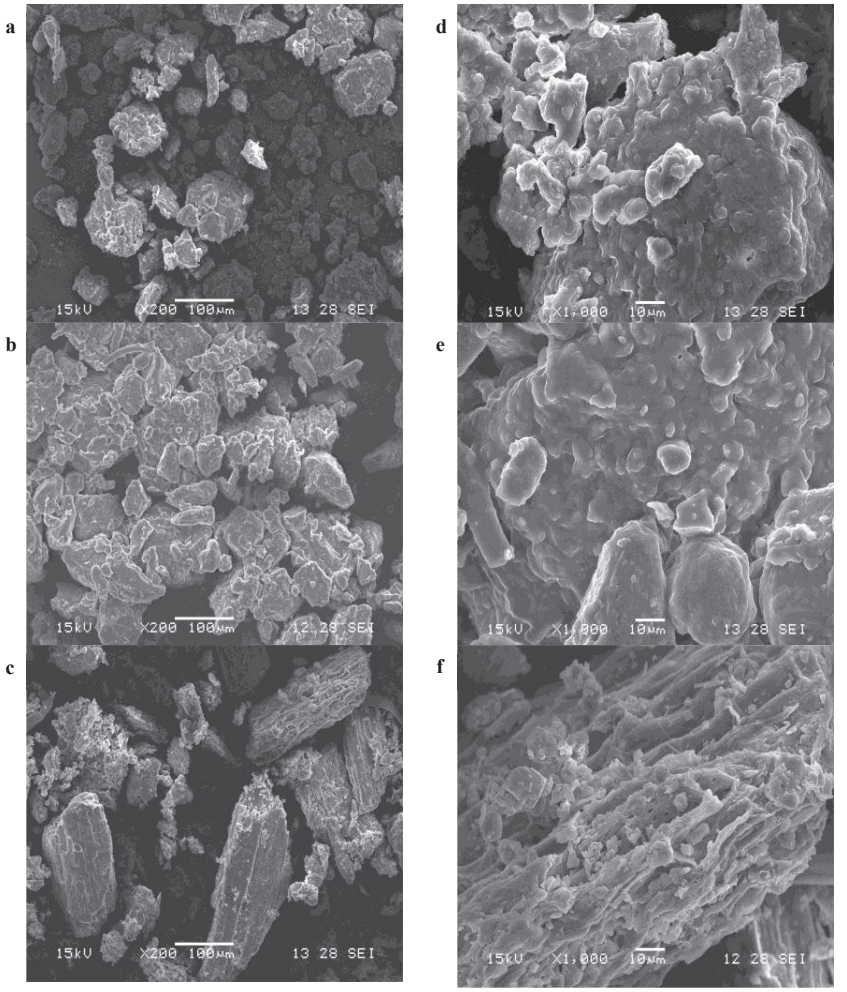

Fig. 5. The SEM images of (a) OWH, (b) OP and (c) GS, with a magnification of 200x, on the left. On the right, the same sequence with a magnification of 1000x.

4. Conclusions

The three materials studied are highly hygroscopic. Olive wet husk has a high moisture content, about 70%, which implies an additional cost to condition it for use as a filler. This can be minimized increasing the time of exposure to the sun. Also has a broader distribution of particle sizes, which implies a sieve classification process more complex, however it could be an advantage at the time of incorporation into polymers because they achieve a more efficient packing and distribution of particles in the matrix. By contrast, the olive pits fracture on a narrow size distribution and are more stable against thermal degradation. However, their high oil content makes it difficult to grind, as the material tends to form a paste. Grape stalk presents the highest amount of surface groups and a fibrous structure. The first feature enhances their adhesion with polar polymeric matrices, while the second would provide better mechanical properties to the final composite. Regarding to thermal degradation processes of the three materials, although there are some differences, the temperature limit of use is very similar for all, restricting its use to thermoset polymers that cure at relatively low temperatures or low temperature thermoplastic polymers (polyethylene and optionally polypropylene). These observations must be considered when evaluating the final properties of the resulting composites using a polymeric resin with different proportions of the three agro-industrial wastes. By incorporating these plant particles into polymer matrices the influence of particle type, composition,

physicochemical and morphological characteristics in the final properties of the composite can be evaluated. Later works are planned to evaluate the characteristics of the resulting composite using the three wastes studied and associated with the characteristics evaluated in this work.

Acknowledgements

The authors would like to thank the National Research Council of Argentina (CONICET) for the financial support (Research Fellowship to Cintia S. Navas). Special thanks to Prof. Diana Fasce, Prof. Mirna Mosiewicki and Prof. Pablo Botta from the Institute of Materials Science and Technology (INTEMA).

References

Baillie, C., 2004. Green composites: Polymer composites and the environment. Woodhead Publishing.

Basu, B., Tiwari, D., Kundu, D., Prasad, R., 2009. Is Weibull distribution the most appropriate statistical strength distribution for brittle materials? . Ceramics International 35, 237–246.

Bishaya, I., Abd-El-Messiehb, S., Mansour, S., 2011. Electrical, mechanical and thermal properties of polyvinyl chloride composites filled with aluminum powder. Materials & Design 32, 1, 62–68.

Bledzki, A., Sperber, V. and Faruk, O., 2002. Natural and Wood Fibre Reinforcement in Polymers. Rapra Review Reports, Report 152, ISSN: 0889-3144, 13, 8, pp.12.

Boehm, H.P., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 32, 759-769.

Caputo, A., Scacchia, F. and Pelagagge, P., 2003. Disposal of by-products in olive oil industry: waste-to-energy solutions. Applied Thermal Engineering 23, 2, 197–214.

Deiana, A., Sardella, M., Silva, H., Amaya, A. and Tancredi, N., 2009. Use of grape stalk, a waste of the viticulture industry, to obtain activated carbon. Journal of Hazardous Materials 172, 1, 13–19.

Fu, S., Feng, X., Lauke, B., Mai, Y., 2008. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites. Composites Part B 39, 933–961.

Inan, H., Dimoglo, A., Şimşek, H. and Karpuzcu, M., 2004. Olive oil mill wastewater treatment by means of electro-coagulation. Separation and Purification Technology 36, 1, 23–31.

Kalia, S., Kaith, B. S. and Kaur, Inderjeet (eds.), 2011. Cellulose Fibers: Bio-and Nano-Polymer Composites. Springer-Verlag Berlin Heidelberg.

Kim, J. and Netravali, A., 2013. Fabrication of advanced “green” composites using potassium hydroxide (KOH) treated liquid crystalline (LC) cellulose fibers. Journal of Materials Science 48, 11, 3950-3957.

Krause Sammartino, L. E, Aranguren, M. I., Reboredo, M. M., 2010. Chemical and Mechanical characterization of two South-American plant fibers for polymer reinforcement: Caranday Palm and Phormium. Applied Polymer Science 115, 2236-2245.

Krifa, M., 2009. A mixed Weibull model for size reduction of particulate and fibrous materials. Powder Technology 194, 233–238.

Manals-Cutiño, E., Penedo-Medina, M., Giralt-Ortega, G., 2011. Análisis termogravimétrico y térmico diferencial de diferentes biomasas vegetales. Tecnología Química 31, 2, 36-43.

Matos, M., Barreiro, M. and Gandini, A., 2010. Olive stone as a renewable source of biopolyols. Industrial Crops and Products 32, 7-12.

Natural fiber composites market: Technical progress report, CIP-EIP-Eco-Innovation-2008: Pilot and market replication projects, Celluwood 2008.

Paraskeva, P. and Diamadopoulos, E., 2006. Technologies for olive mill wastewater (OMW) treatment: a review. Journal Chemical Technology Biotechnology, 81, 1475–1485.

Perinovic, S., Andricic, B. and Erceg, M., 2010. Thermal properties of poly(l-lactide)/olive stone flour composites. Thermochimica Acta 510, 97–102.

Seyni, A., Le Bolay, N., Molina-Boisseau, S., 2009. On the interest of using degradable fillers in co-ground composite materials. Powder Technology 190, 176–184.

Suna Erses Yay, A., Volkan Oral, H., Turgut Onay, T. and Orhan Yenigün, T., 2012. A study on olive oil mill wastewater management in Turkey: A questionnaire and experimental approach. Resources.Conservation and Recycling 60, 64–71.

Tserki, V., Matzinos, P., Kokkou, S., Panayiotou, C., 2005. Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part I. Surface chemical modification and characterization of waste flour. Composites Part A 36, 965–974.

Tserki, V., Matzinos, P., Kokkou, S., Panayiotou, C., 2005. Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part I. Surface chemical modification and characterization of waste flour. Composites: Part A 36, 965–974.