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Characterization of wood plastic composites made from landfill-derived plastic and sawdust: Volatile compounds and olfactometric analysis

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ABSTRACT

Application of wood plastic composites (WPCs) obtained from recycled materials initially intended for landfill is usually limited by their composition, mainly focused on release of volatile organic compounds (VOCs) which could affect quality or human safety. The study of the VOCs released by a material is a requirement for new composite materials. Characterization and quantification of VOCs of several WPC produced with low density polyethylene (LDPE) and polyethylene/ethylene vinyl acetate (PE/EVA) films and sawdust were carried out, in each stage of production, by solid phase microextraction in headspace mode (HS-SPME) and gas chromatography–mass spectrometry (GC–MS). An odor profile was also obtained by HS-SPME and GC–MS coupled with olfactometry analysis. More than 140 compounds were observed in the raw materials and WPC samples. Some quantified compounds were considered WPC markers such as furfural, 2-methoxyphenol, N-methylphthalimide and 2,4-di-tert-butylphenol. Hexanoic acid, acetic acid, 2-methoxyphenol, acetylfuran, diacetyl, and aldehydes were the most important odorants. None of the VOCs were found to affect human safety for use of the WPC.

1. Introduction

Reusing waste materials destined for landfills is a challenge. The recycling of paper, plastic, glass, and metal is very established and widely applied. But the use of waste material blends composed of plastic and wood, known as WPC, is a current practice. According to Ashori (2008), WPC are produced by mixing plant fibers (wood and non-wood) and thermosets (epoxy and phenolic resins) or thermoplastics such as polyethylene (PE), polypropylene (PP) and polyninyl chloride (PVC). Additionally, additives such as colorants, coupling agents, stabilizers, blowing agents, reinforced agents, foaming agents, and lubricants could be applied to improve properties (Ndiaye et al., 2008; Schwarzinger et al., 2008; Fabiyi et al., 2009). The main applications of WPC are the automotive industry, construction and furniture, and industrial and consumer products. According to the study from Markarian (2008), the WPC market, including thermoplastics and thermosets, has been estimated globally at 900,000 metric tons, which 70% of this volume was consumed by North America, 20% by Europe, and 10% by Asia. In Europe, the market showed growth rates averaging 23% per year from 2003 to 2007 and predicted to continue at 26% per year through 2012.

Most publications on WPC are related to the physical, mechanical, and durability properties (Ashori and Nourbakhsh, 2009; Fabiyi and McDonald, 2010; Fabiyi et al., 2011, 2008; Shebani et al., 2009; Valente et al., 2011; Zhang et al., 2011), and some works described qualitative identification and semi-quantitative analysis of compounds from WPC products and subproducts, mainly derived from wood (Bhattacharya et al., 2009; Espert et al., 2005; Fabiyi et al., 2009, 2008; Schwarzinger et al., 2008). However, the application of recycled waste materials requires certain chemical requirements and safety certification in accordance to the intended use. Hence, information about the VOCs composition of WPC would be of great interest to industry and the consumer. In this regard, qualitative and quantitative analyses of 46 different recycled samples were carried out by HS-SMPE coupled to GC–MS. The SPME has been considered a fast and reliable tool to study the behavior of VOCs from acrylic adhesives used for food packaging multilayers manufactured with PE, PP, polyethylene terephthalate (PET), and couche and kraft paper (Canellas et al., 2010). SPME provides a very important concentration of the analytes on the microfiber containing the stationary phase and thus is recommended for trace analysis (Vera et al., 2011). Besides the composition of VOCs, the odor of the WPC is also important, as it could limit end use applications. Masking unpleasant odors with aroma is not always possible and successful and in any case the control of aroma should be one of the critical points in the final products. In this paper, the characterization of odor active

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compounds in one of the WPC prototypes under study was carried out by GC followed by simultaneous MS/olfactometry (GC–MS/O).

2. Materials and methods

2.1. Materials

LDPE and PE/EVA films and sawdust (from pallets), previously used in the agricultural and industrial sector in Spain, and destined for landfills were used. The films were washed using water, dried and cut in small pieces. The sawdust was screened through a mesh of 0.50 mm. The LDPE or PE/EVA films were extruded to produce pellets with barrel temperature set between 135 and 200 °C and screw speed of 50 rpm (Dr. Colin twin-screw extruder, Injection Laboratory Plastics Industry (TIIP) at the UNIZAR). The compounded WPC pellets (extrusion at 150–185 °C and screw speed of 25 rpm) were injection molded into test specimens at 180 °C (Mateu & Solé 55 t molding machine, TIIP). Finally, the prototypes were produced at industrial level. WPC were produced by compounding with plastic and different percentage of sawdust, maleic anhydride (MA; ⩾99%, Fluka, Madrid, Spain) and the masterbatch Recycloblend® 660 (RB) (Ciba Specialty Chemicals Inc., Basel, Switzerland). Odorizing agents, as liquid or powder vanilla (Fragrance Science and Argolide Quimica, respectively, both from Barcelona, Spain) were tested to mask the odor of the samples. Table 1 presents all 47 investigated samples. Fig. 1 shows examples of the WPC samples.

2.2. Characterization of VOCs

A previous study on the composition of VOCs in the raw materials using three SPME fibers: polydimethylsiloxane (PDMS, thickness of 100 μm), carboxen/polydimethylsiloxane (CAR/PDMS, 85 μm), and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm), all from Supelco (Bellefonte, PA, USA), indicated DVB/CAR/PDMS as the most efficient in the extraction of most compounds in this paper. Extraction was performed by using 0.75 g of each LDPE and PE/EVA films, and sawdust, independently, into a HS-vial of 20 mL with a PTFE septum. Three replicates were prepared for each material. The samples were conditioned for 10 min at 90 °C and the fiber was exposed to the HS at 90 °C for 10 min with agitation of 500 rpm. Blanks were run after each different sample as a control. A CTC Analytics CombiPAL autosampler from Agilent Technologies (Switzerland) was employed. The compounds were desorbed for 2 min on a HP 6890 gas chromatograph (GC) coupled to a HP 5973 quadrupole mass spectrometer detector (MS) (Agilent Technologies, Palo Alto, CA, USA). Injection at 250 °C in splitless mode was carried out. Separation was achieved using a HP-5 capillary column (30 m × 0.25 mm ID × 0.25 μm) and helium as carrier gas (1 mL/min). The temperature program was 50 °C to 300 °C at 10 °C/min and maintained for 5 min. The MS was operated in electron impact mode (70 eV) and the masses were scanned over of 55–400 m/z. VOCs were identified by retention time and mass spectra of pure analytical standards, and also by comparing the mass spectra of the samples with the reference spectra in the National Institute of Standards and Technology mass spectral database (NIST).

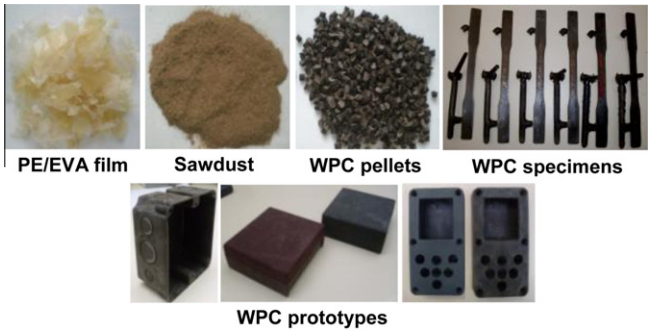

Fig. 1. Raw materials, WPC pellets (PE/EVA + 50% sawdust), WPC specimens (without sawdust and with 10–50% sawdust) and WPC final prototypes.

2.3. Quantification of VOCs

Stock solutions (5000 μg/g) were prepared using analytical standards (Sigma–Aldrich, Madrid, Spain; Merck, Darmstad,

Table 1
Description of the raw materials and the WPC materials produced.

No.	Material	Type	No.	Material	Type
1	Sawdust (S)	Powder	25	LDPE + 30%S + 5%MA	Pellets
2	Maleic anhydride (MA)	Flakes	26	LDPE + 10%S + 3%MA + 1%RB	Pellets
3	Recycloblend® 660 (RB)	Granules	27	LDPE + 30%S + 3%MA + 1%RB	Pellets
4	LDPE	Films	28	LDPE + 10%S	Specimens
5	PE/EVA	Films	29	LDPE + 20%S	Specimens
6	LDPE	Pellets	30	LDPE + 30%S	Specimens
7	PE/EVA	Pellets	31	LDPE + 40%S	Specimens
8	LDPE + 10%S	Pellets	32	LDPE + 50%S	Specimens
9	LDPE + 20%S	Pellets	33	LDPE + 10%S + 2%MA	Specimens
10	LDPE + 30%S	Pellets	34	LDPE + 10%S + 3%MA	Specimens
11	LDPE + 40%S	Pellets	35	LDPE + 10%S + 4%MA	Specimens
12	LDPE + 50%S	Pellets	36	LDPE + 10%S + 5%MA	Specimens
13	PE/EVA + 10%S	Pellets	37	LDPE + 30%S + 2%MA	Specimens
14	PE/EVA + 20%S	Pellets	38	LDPE + 30%S + 3%MA	Specimens
15	PE/EVA + 30%S	Pellets	39	LDPE + 30%S + 4%MA	Specimens
16	PE/EVA + 40%S	Pellets	40	LDPE + 30%S + 5%MA	Specimens
17	PE/EVA + 50%S	Pellets	41	LDPE + 20%S + 3%MA	Specimens
18	LDPE + 10%S + 2%MA	Pellets	42	LDPE + 40%S + 3%MA	Specimens
19	LDPE + 10%S + 3%MA	Pellets	43	LDPE + 10%S + 3%MA + 1%RB	Specimens
20	LDPE + 10%S + 4%MA	Pellets	44	LDPE + 30%S + 3%MA + 1%RB	Specimens
21	LDPE + 10%S + 5%MA	Pellets	45	LDPE + 10%S + 3%MA + 1%RB + 1%LV[a]	Specimens
22	LDPE + 30%S + 2%MA	Pellets	46	LDPE + 30%S + 3%MA + 1%RB + 1%PV[b]	Specimens
23	LDPE + 30%S + 3%MA	Pellets	47	Industrial: LDPE + 50%S + 5%MA	Final prototypes
24	LDPE + 30%S + 4%MA	Pellets			

[a] LV: liquid vanilla.
[b] PV: powder vanilla.

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