

Towards Understanding the Health Aspects of the Processing of Lignocellulosic Fillers [†]

Aleksander Hejna ^{1,*} and Mariusz Marc ²

¹ Department of Polymer Technology, Gdańsk University of Technology, Narutowicza 11/12 80-233 Gdańsk, Poland; aleksander.hejna@pg.gda.pl

² Department of Analytical Chemistry, Gdańsk University of Technology, Narutowicza 11/12 80-233 Gdańsk, Poland; mariusz.marc@pg.edu.pl

* Correspondence: aleksander.hejna@pg.gda.pl; Tel.: +48-58-347-2234

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Abstract: Health and safety issues should be addressed during the development and investigation of the industrial processes. In order to develop a sustainable process and fully evaluate its benefits and drawbacks for its optimization, it is crucial to determine its impact on the surrounding environment. This study aimed to assess the emission of volatile organic compounds during the modification of lignocellulosic fillers with passive dosimetry. Two types of processes were investigated: diisocyanate treatment of commercial lignocellulosic fillers in a batch mixer and thermo-mechanical treatment of brewers' spent grain using a twin-screw extruder. The presence of multiple terpenes and terpenoids was detected during the processing of fillers. The main compounds detected during modification were camphene, 3-carene, limonene, α -pinene, and cymenes. These compounds can show the irritating and allergic character, according to the Globally Harmonized System of Classification and Labelling of Chemicals, as well as NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response. Some of them are also characterized by relatively low values of flash point, even below 40 °C. Therefore, their emissions during the modification of cellulose materials should be carefully monitored, and proper precautions need to be taken.

Keywords: Lignocellulosic fillers; volatile organic compounds; emissions; brewers' spent grain; modification;

1. Introduction

There are multiple systems, standards, and indicators which are defining the health and environmental threats posed by particular chemicals. Among the most popular, which are often included in safety datasheets, should be mentioned Globally Harmonized System of Classification and Labelling of Chemicals (GHS) and NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response [1,2].

Globally Harmonized System of Classification and Labelling of Chemicals is an internationally agreed standard, which specifies the criteria for assessment and evaluation of hazards, as well as for the preparation of harmonized safety datasheets providing essential information about chemicals. It describes chemicals with a combination of hazard statements and pictograms indicating the physical, health, and environmental properties of materials and threats they may pose to the environment.

NFPA 704 system is commonly known as "safety square" or "fire diamond" and is applied to enable possibly quick and efficient identification of the risks related to the use of a particular compound and selection of the proper handling procedure. This system was developed by National Fire Protection Association from the United States to assess chemicals' flammability, health, and instability of chemicals on a scale from 0 (minimal hazard) to 4 (severe hazard). Moreover, in exceptional cases, it also provides information about special hazards related to the material.

As mentioned above, the information related to the threats posed by particular chemicals are often included in datasheets. Nevertheless, except for their intentional use in well-defined and designed chemical reactions, different chemical compounds may also be generated in various more complex (in terms of chemistry) processes, e.g., related to the processing of waste or bio-based materials, which could be applied as fillers for wood polymer composites [3]. Therefore, in order to develop a sustainable process and fully evaluate its benefits and drawbacks for its optimization, it is crucial to determine its impact on the surrounding environment [4]. One of the possibilities is the emission of volatile organic compounds (VOCs), which is a crucial aspect of occupational safety and health [5]. In the presented work, we introduced the passive dosimetry to aimed to assess the emission of VOCs during the modification of lignocellulosic fillers. Two types of processes were investigated: diisocyanate treatment of commercial lignocellulosic fillers in a batch mixer and thermo-mechanical treatment of brewers' spent grain (BSG) using a twin-screw extruder.

2. Experimental

2.1. Materials

Three types of commercially available Arbocel® fillers from JRS J. Rettenmaier & Söhne GmbH (Germany) were used in the presented study: B400, CW630PU, and UFC100. They were characterized by an average particle length of 900, 40, and 8 µm, respectively. Fillers B400 and UFC100 contained over 99.5% of cellulose, while the CW630PU filler was wood flour.

Their modifications were performed with four different isocyanates: hexamethylene (HDI), isophorone (IPDI), methylene diphenyl (MDI), and toluene (TDI), which were acquired from Sigma Aldrich (Poland). The purity of HDI, IPDI, and MDI was 98%, 99%, and 98%, respectively. For TDI, the mixture of 2,4-TDI and 2,6-TDI in the 80/20 ratio was used.

Brewers' spent grain used in the presented study was obtained from Energetyka Złoczew sp. z o.o. (Poland). It was already dried by the supplier. Brewers' spent grain was applied as a representative for waste lignocellulosic material, which after proper treatment, could be introduced into wood polymer composites. It is composed of cellulose, hemicellulose, and lignin, with moderate amounts of proteins and lipids, which may provide additional features to resulting composites [6].

2.2. Modification of lignocellulosic fillers with diisocyanates

Fillers were modified using GMF 106/2 Brabender batch mixer at room temperature (21.1-23.1 °C) and rotor speed of 100 rpm. The fillers were mixed with a calculated amount of diisocyanate, 1.0, 2.5, 5.0, 10.0, or 15.0 wt%, respectively, to the mass of filler. Mixing was performed for 5 minutes, and then samples were put in zipper storage bags.

Room temperature was applied to reduce the possible emissions of diisocyanates, which at 20-25 °C show low vapor pressure (7.0, 0.04, 0.0007, and 4.0 Pa, respectively for HDI, IPDI, MDI, and TDI). At higher temperatures, their volatility is significantly increasing. When the temperature is elevated to 50 °C, the vapor pressure of TDI, IPDI, and MDI is increased 11.9, 22.5, and 33.5 times.

2.3. Extrusion grinding of BSG

BSG was thermo-mechanically treated using EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland), according to our patent application [7]. The used extruder has an L/d

ratio of 40. Parameters of the process were: throughput – 3 kg/h; screw speed – 225 rpm; barrel temperature – 60, 120, or 180 °C. Then, BSG was left in order to cool down at room temperature.

2.4. Assessment of VOCs emissions

Assessment of volatile organic compounds emissions during the processing of lignocellulosic fillers was carried out employing the Radiello® diffusive passive samplers (Fondazione Salvatore Maugeri, Padova, Italy) at the stage of analyte sampling from the gaseous phase. The mentioned passive sampler was equipped with a yellow diffusive membrane and the cylindrical container filled with sorption medium Carbograph 4 dedicated for VOCs sampling. Detailed information about the characteristics and working parameters of the Radiello® passive sampler was in detail listed elsewhere [8,9]. In brief, the analytical procedure aimed at the qualitative determination of VOCs present in the gaseous phase on the studied workplace included the following steps: (i) each time two independent Radiello® passive samplers were placed in the studied workplace, at a distance of more than 1 m; (ii) the exposure time in the studied indoor environment was set up for 4 hours; (iii) sampling devices were placed close to the studied workplace and in the close neighborhood to the materials preparation area; (iv) the temperature was monitored during whole working period and was in the range from 21.1 up to 23.1 °C; (v) after the analytes sampling period, the containers with a sorption medium were removed from the diffusive membrane and placed inside the glass tubes closed with polyethylene nut; (vi) containers with sorption medium were stored at 4 °C no longer than 12 hours after sampling.

The identification of the main VOCs that occurs in the gaseous phase of the studied indoor environment was performed with the use of thermal desorption technique (Unity v.2, Markes International Ltd., Pontyclun, UK), connected with gas chromatography (Agilent Technologies 6890) combined with a mass spectrometer (5873 Network Mass Selective Detector, Agilent Technologies). The cylindrical containers filled with sorption medium were liberated at the temperature of 290 °C by 15 min. During this process, the analytes were transported to the microtrap. Then, the analytes were liberated from the microtrap heating up to 300 °C and maintained by 5 min and transported by the helium flow rate (1.5 mL·min⁻¹) to the GC capillary column (Agilent 122-5563, J&W DB-5MS, 60 m × 0.25 mm × 1 µm). The GC oven temperature program was as follows: 50 °C for 1 min, then raised at a rate of 10 °C·min⁻¹ up to 280 °C and maintained for 10 min. The temperature of the TD-GC transfer line was set to 150 °C, and the temperature of the GC-MS transfer line was 280 °C. The employed mass spectrometer was working in a SCAN mode. Detailed information about the principals and characteristic of the thermal desorption technique were presented elsewhere [10,11]. In order to eliminate signals associated with other processes occurring in the laboratory hall and select only signals related to the performed modification, as well as to ensure the reliability of obtained results, the "background" was also analyzed.

3. Results

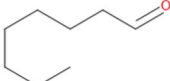

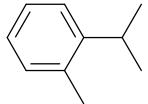

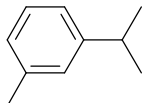

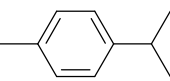

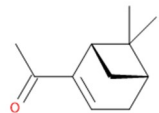

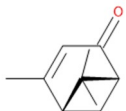

As mentioned above, the assessment of VOCs emissions is very important for the development of a truly environmentally-friendly industrial process. Nevertheless, this factor is hardly investigated and described in the literature regarding lignocellulosic fillers processing. In Table 1, there are summarized main compounds detected during diisocyanate modification of fillers and brewers' spent grain thermo-mechanical treatment, together with the properties characterizing their possible health impacts. Moreover, for all detected compounds, there are presented codes and pictograms, according to NFPA 704 and GHS standards [1,2].

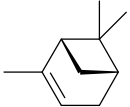

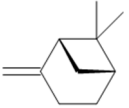

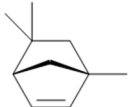

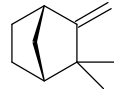

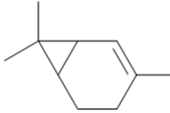

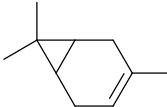

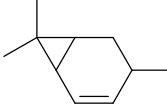

The majority of detected compounds can be classified as terpenes and terpenoids. They are hydrocarbons and their derivatives containing additional functional groups. Terpenes and terpenoids are components of rosins, present in different plants, mostly conifers. Therefore they are often present in the lignocellulosic materials, such as wood flour or BSG [12]. Terpenes and terpenoids should be considered as a potential health threat due to the irritating and possibly allergic

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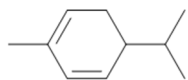

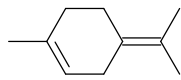

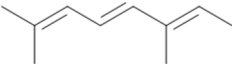

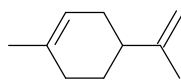

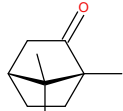

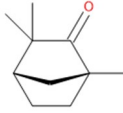

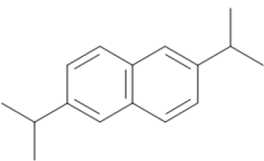

impact on human skin and eyes. They are described, e.g., with the following health statements according to GHS standards: H304 – May be fatal if swallowed and enters airways; H315 – Causes skin irritation; H319 – Causes serious eye irritation; H335 – May cause respiratory irritation; H371 – May cause damage to organs; H372 – Causes damage to organs through prolonged or repeated exposure.

Table 1. Volatile organic compounds detected during the processing of lignocellulosic materials.

Compound	Formula	Chemical structure	Boiling point, °C	Vapor pressure, Pa	Flash point, °C	NFPA 704 codes			GHS pictograms	Lignocellulosic filler modification	Extrusion grinding of BSG
						F	H	I			
Octanal	C ₈ H ₁₆ O		171	266	51	2	0	0		Yes	No
<i>o</i> -Cymene	C ₁₀ H ₁₄		178	200	50	2	1	0		Yes	Yes
<i>m</i> -Cymene	C ₁₀ H ₁₄		175	200	47	2	1	0		Yes	Yes
<i>p</i> -Cymene	C ₁₀ H ₁₄		177	200	47	2	1	0		Yes	Yes
Myrtenal	C ₁₀ H ₁₄ O		220	19	78	2	1	0		Yes	No
Verbenone	C ₁₀ H ₁₄ O		227	10	85	2	2	0		Yes	No

Compound	Formula	Chemical structure	Boiling point, °C	Vapor pressure, Pa	Flash point, °C	NFPA 704 codes			GHS pictograms	Lignocellulosic filler modification	Extrusion grinding of BSG
						F	H	I			
α -Pinene	C ₁₀ H ₁₆		156	633	33	3	1	0		Yes	Yes
β -pinene	C ₁₀ H ₁₆		166	391	36	3	1	0		Yes	No
β -fenchene	C ₁₀ H ₁₆		157	526	25	2	3	1		Yes	No
Camphene	C ₁₀ H ₁₆		160	333	34	3	2	1		Yes	Yes
2-Carene	C ₁₀ H ₁₆		168	496	38	2	2	0		Yes	No
3-Carene	C ₁₀ H ₁₆		170	496	46	2	2	0		Yes	Yes
4-Carene	C ₁₀ H ₁₆		168	555	38	2	2	0		Yes	No



Compound	Formula	Chemical structure	Boiling point, °C	Vapor pressure, Pa	Flash point, °C	NFPA 704 codes			GHS pictograms	Lignocellulosic filler modification	Extrusion grinding of BSG
						F	H	I			
α -Phellandrene	C ₁₀ H ₁₆		174	187	46	2	1	0		Yes	No
Terpinene	C ₁₀ H ₁₆		186	99	37	3	2	2		Yes	Yes
Alloocimene	C ₁₀ H ₁₆		189	109	69	2	1	0		Yes	No
Limonene	C ₁₀ H ₁₆		176	190	50	2	3	0		Yes	Yes
Camphor	C ₁₀ H ₁₆ O		209	27	54	2	2	0		Yes	Yes
Fenchone	C ₁₀ H ₁₆ O		194	109	60	0	3	0		Yes	No
2,6-Diisopropylnaphthalene	C ₁₆ H ₂₆		279	0.07	140	1	0	0		No	Yes



Moreover, except for health issues, terpenes and terpenoids may pose an environmental threat. Therefore they are categorized, e.g., according to the following statements: H400 – Very toxic to aquatic life; H410 – Very toxic to aquatic life with long-lasting effects; H411 – Toxic to aquatic life with long-lasting effects; H412 – Harmful to aquatic life with long-lasting effects.

Statements H400 and H410 are related to the high toxicity towards aquatic life, expressed by the lethal concentration LC₅₀ lower than 1 mg/L. For H411 and H412, its values are lower than 10 and 100 mg/L, respectively. Moreover, statements pointing to the long-lasting effect indicate the bioconcentration factor higher than 500 [13].

The majority of terpenes and terpenoids are characterized by significant flammability [14]. They are rated as 2 or 3 by NFPA, indicating the flash point in the range of 37.8-93.3 and 22.8-37.8 °C, respectively. Moreover, compounds with a flash point below 60 °C are marked as flammable, according to GHS. Flammability of terpenes and terpenoids is a commonly known issue because their high content in particular species of wood increases fire threat [15]. Therefore, serious precautions have to be taken during the processing of lignocellulosic fillers since they can ignite at relatively low temperatures.

It is also very interesting and actually very beneficial, considering the environmental friendliness of the diisocyanate modification process, that no traces of applied diisocyanates were detected during modification. Such an effect was related to the application of the ambient temperature, together with their low values of vapor pressure. Therefore, despite the common understanding of diisocyanates as very toxic, which is backed up by GHS standards (diisocyanates are categorized as irritating, allergic, harmful, or even fatal), their proper application for modification of lignocellulosic materials should be considered as relatively safe.

Regarding thermo-mechanical processing of BSG, the only compound that was not detected during the treatment of cellulose and wood flour was 2,6-diisopropylnaphthalene (DIPN). Although it was detected in relatively small amounts, its presence among emitted VOCs is justified. This compound is often applied as a plant growth regulator by farmers [16]. Therefore, it was not detected during the modification of cellulose and wood flour originated mostly from conifer trees. Regarding the safety of DIPN, it is not particularly harmful to humans but may pose a threat to the environment, mainly when generated in significant amounts, which could lead to its accumulation.

5. Conclusions

The presented paper aimed to investigate the emissions of volatile organic compounds during the processing of lignocellulosic fillers, which could be potentially applied in the manufacturing of wood polymer composites. Two types of the processes were analyzed: chemical modification of commercially available cellulosic fillers and thermo-mechanical modification of waste material – brewers' spent grain. The majority of detected compounds can be classified as terpenes and terpenoids, among which the main were camphene, 3-carene, limonene, α -pinene, and cymenes. Their presence was related to the chemical structure and origin of investigated materials. Moreover, the information related to the health and environmental threats posed by detected chemicals were provided. Future works would be aimed to complement the presented research by the quantitative analysis of particular volatile organic compounds emissions and compare them with their thresholds.

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Author Contributions: A.H. and M.M. conceived and designed the experiments; A.H. and M.M. performed the experiments; A.H. and M.M. analyzed the data; A.H. and M.M. contributed reagents/materials/analysis tools; A.H. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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