

Towards understanding the health aspects of the processing of lignocellulosic fillers

Aleksander Hejna¹, Mariusz Marć²

¹Department of Polymer Technology, Gdańsk University of Technology, Gdańsk, Poland

²Department of Analytical Chemistry, Gdańsk University of Technology, Gdańsk, Poland

INTRODUCTION

The information related to the threats posed by particular chemicals are often included in datasheets. They are provided according to different systems or standards, such as 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]. 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.

EXPERIMENTAL

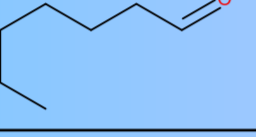

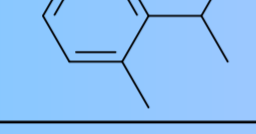



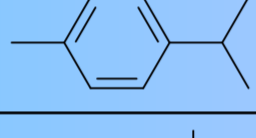

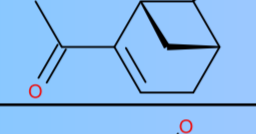











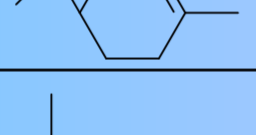

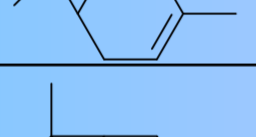

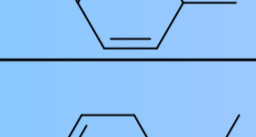

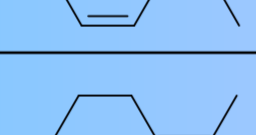

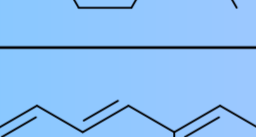





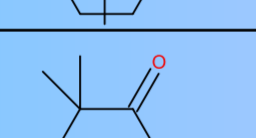

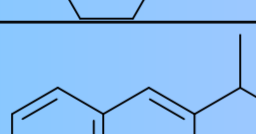


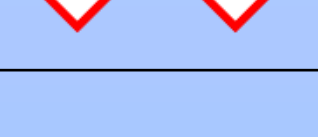
Three types of commercially available Arbocel[®] fillers (B400, CW630PU, and UFC100) were modified with varying content (1-15 wt%) of hexamethylene (HDI), isophorone (IPDI), methylene diphenyl (MDI), and toluene (TDI) diisocyanates, using GMF 106/2 Brabender batch mixer at room temperature.

BSG was thermo-mechanically treated using EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland), according to our patent application [6] at 60, 120, or 180 °C.

Emission studies were performed with the use of Radiello[®] passive samplers at the stage of analytes sampling from the gaseous phase. The identification of the main organic compounds in the air of enclosed space was performed with the use of TD-GC-MS system. Full procedure was described in details in our other work [7].

EMISSION OF VOCs FROM ISOCYANATE-MODIFIED CELLULOSE FIBERS

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
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
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

The assessment of VOCs emissions is crucial for the development of a truly environmentally-friendly processes. However, this factor is hardly investigated and described in the literature. In Table 1, there are summarized main compounds detected during modification of lignocellulose fillers, and BSG thermo-mechanical treatment, and their possible health threats. 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 or terpenoids – hydrocarbons and their derivatives containing additional functional groups. They are components of rosins, present in plants, mostly conifers, so they are often present in the lignocellulosic materials [8]. Terpenes and terpenoids should be considered as a potential health threat due to the irritating and possibly allergic impact on human body. They are described, e.g., with the following GHS statements:

- 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.

Except for health issues, terpenes and terpenoids may also pose an environmental threat. They are categorized, as:

- 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, expressed by the lethal concentration LC50 below 1 mg/L. For H411 and H412, values are lower than 10 and 100 mg/L. Moreover, the long-lasting effect indicate the bioconcentration factor higher than 500 [9].

The majority of terpenes and terpenoids show significant flammability [10]. They are rated as 2 or 3 by NFPA, indicating the flash point of 37.8-93.3 and 22.8-37.8 °C, respectively. 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 [11]. Therefore, serious precautions should be taken during the processing of lignocellulosic fillers since they can ignite at relatively low temperatures.

It is also very beneficial, considering the environmental friendliness of the diisocyanate modification, that no traces of diisocyanates were detected during process. Such an effect was related to the application of the ambient temperature and their low values of vapor pressure. Therefore, despite the common understanding of diisocyanates as very toxic, which is backed up by GHS standards (they 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). Despite rather low concentration, its presence among emitted VOCs is justified. It is applied as a plant growth regulator [12]. Regarding safety, it is hardly harmful to humans, but may pose a threat to the environment, mainly when generated in significant amounts, which could lead to its accumulation

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.

REFERENCES

- [1] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. [2] NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response. [3] Jorge, F.C. Mol. Cryst. Liq. Cryst. 2010, 522(1), 328–335. [4] Kalakul, S.; Malakul, P.; Siemanond, K.; et al. Clean. Prod. 2014, 71, 98–109. [5] Colman Lerner, J.E.; Sanchez, E.Y.; Sambeth, J.E.; et al. Atmos. Environ. 2012, 55, 440–447. [6] Hejna, A.; Formela, K. Polish patent application P.430449, 2019. [7] Hejna, A.; Marć, M.; Skórczewska, K.; et al. Eur. J. Wood Wood Prod. 2020, In Press. [8] Gaiolas, C.; Belgacem, M.N.; Silva, L.; et al. Colloid Interf. Sci. 2009, 330(2), 298–302. [9] Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Fourth revised edition. [10] Dev, S. Terpenoids. In Springer Series in Wood Science; Wimmer, R., Ed.; Springer: New York, USA, 1989; pp. 691–807. [11] Ormeño, E.; Céspedes, B.; Sánchez, I.A.; et al. Forest Ecol. Manag. 2009, 257(2), 471–482. [12] Brzozowski, R.; Skupiński, W.; Jamróz, M.H.; et al. J. Chromatogr. A 2002, 946(1-2), 221–227.

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