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Under glass weathering of hemp fibers reinforced polypropylene biocomposites: Impact of Volatile Organic Compounds emissions on indoor air quality

Célia Badji, Joana Beigbeder, Hélène Garay, Anne Bergeret, Jean-Charles Bénézet, Valérie Desauziers*

C2MA, Ecole des Mines d'Alès, 6 Avenue de Clavières, 30319, Alès Cedex, France

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ABSTRACT

Nowadays, natural fibers reinforced composite materials can be used in closed environments such as car cabins. It has hence become a necessity to study their emissions of Volatile Organic Compounds (VOCs) to check their impact on indoor air quality. The purpose of this work was first to study the emissions of VOCs from hemp fibers reinforced polypropylene (PP) biocomposites in comparison with neat PP. The influence of under windshield glass weathering on VOCs release was then investigated. The exposition lasted one year and the fiber loading influence on emissions was studied all along the weathering. The VOCs concentration at the material/air interface was determined using a passive sampling method involving an emission cell coupled with Solid Phase MicroExtraction (SPME). VOCs analysis was then carried out by gas chromatography coupled to mass spectrometry and flame ionization detections. One of the most significant results is the drastic increase of oxygenated compounds concentration during the exposition, especially for biocomposites. Among these oxidation by-products, formaldehyde, acetaldehyde, furfural and 2-furanmethanol, recognized as Cancerogen, Mutagen and toxic for Reproduction (CMR), were detected. A broad range of alkanes, specific of PP matrix degradation was also identified. Finally, measured concentrations of substances found in this work and listed in Vehicle Indoor Air Quality (VIAQ) standards were gathered in order to discuss the biocomposites emissions impact on indoor air quality.

1. Introduction

The development of natural fibers used as an alternative to glass fibers in the reinforcement of thermoplastic polymers has grown as the result of environmental concerns and the depletion of fossil resources. Indeed, their low density, good specific properties and low environmental impact make them attractive in fields like automobile and construction (decking). Moreover, the production of natural fibers composites could increase from 92,000 metric tons (MT) in 2012 to 370,000 MT in 2020 according to the incentives [1].

Concerning automotive sector, the use of biocomposite materials in vehicle interior parts is increasingly seen in replacement of glass fibers reinforced composites. They are mainly used in car binnacles like door panels and dashboards. Thermoplastics such as polypropylene (PP) and biopolyesters including polylactic acid (PLA) and polybutylene succinate (PBS) are mainly used as polymer matrices. However, the highlighting of the time spent in vehicles induces more investigations on the health impact of car interior pieces [2]. Indeed, transportation is the third environment that humans attend after houses and work places, where they are subjected to indoor air pollution. Moreover, the World Health Organization (WHO) has recognized interior air pollution of vehicles as a major threat to human health [3]. Several sources like traffic emissions, tobacco smoke or interior materials can result in a poor binnacle air quality. Recently, the "Sick Car Syndrome" has been highlighted as a result of the identification of toxic Volatile Organic Compounds (VOCs) emitted by binnacle pieces [4]. They are issued from the dashboard, door panels, seat coverings and flooring materials. They can cause eye, nose and throat irritations, allergic skin reactions, headaches and fatigue. Emitted VOCs can also be responsible for olfactory annoyance and could limit end use application [5,6].

Currently, some national regulations and standardizations have been implemented to improve vehicle indoor air quality (VIAQ). Korea government has been one of the first countries to manage VIAQ guideline. They have established the notification No. 2007-539 in 2007

* Corresponding author.
E-mail address: Valerie.Desauziers@mines-ales.fr (V. Desauziers).

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specifying limit concentration levels for 6 substances which are benzene, toluene, formaldehyde, xylene, ethylbenzene and styrene with limit levels ranging from 30 μg m^{-3} for benzene to 1600 μg m^{-3} for ethylbenzene [7,8]. After that, a study made by Korea Automobile Testing & Research Institute showed a significant concentration decrease in 5 years [9]. Car interior VOCs emissions are also coming under more scrutiny in China. Indeed, the standard GB/T 27630 implemented on 2012 is inspired from the recommendatory standard guideline for air quality assessment of passenger car issued on 2011 [10]. This applies the evaluation on binnacle air quality by proposing limit values for the previously mentioned 6 substances plus acetaldehyde and acrolein. Associations such as Japan Automobile Manufacturers Association (JAMA) and European Automobile Manufacturers Association (ACEA) recently made headway to improve VIAQ [11,12]. For instance, JAMA has drawn up the guideline "vehicle cabin VOC testing methods for passenger cars" for conducting the necessary VOC measurements. Nevertheless, the limit concentration levels are different between each country standard. Indeed, formaldehyde concentration limit ranges from 100 μg m^{-3} in Chinese and Japanese standards to 250 μg m^{-3} in Korean guideline. They only concern whole vehicle assessment whereas threshold values at the material scale are mostly imposed by automotive industries. In order to propose new vehicles complying with the VIAQ limit values, worldwide standards describing test methods for the determination of VOCs emissions from car trim components are already implemented. In Europe, ISO 12219 standards describe different protocols and scales for the determination of either VOCs concentrations in car indoor air or VOCs emission rate for materials [13–15].

Lots of studies dealt with pollutants emission in vehicles and the influence of different parameters on their concentrations. Most of the time, total VOCs (TVOCs) concentration is also measured, besides individual VOC levels, to evaluate indoor air quality [8,16–20]. In automotive and building industry, all VOCs whose retention times are between those of hexane and hexadecane under specific gas chromatographic conditions represent TVOCs [21]. It was shown that static conditions (parked, unventilated) favored higher TVOCs concentration in car cabins than specified driving conditions and ventilation. TVOCs level was decreased from 1980 μg m^{-3} in moderate-heat (almost 40 °C) and static conditions to 100 μg m^{-3} under 90-min driving conditions in a 1997 Ford vehicle [20]. Vehicle age also plays a role. Indeed, Chien compared measured levels in new cars for specified products with levels found in literature [18]. It was observed that they could be three orders of magnitude higher than those of older cars, but they decrease over time [22]. VOCs emission is strongly temperature dependent [22] but other parameters like relative humidity and interior trim compositions have also an influence. Indeed, leather pieces emit higher quantities than fabric pieces with a big influence on toluene VIAQ concentration which can increase by 39% [17,18]. The contribution of materials to the VIAQ is therefore very important. That is highlighted by a study only focused on VOCs emissions from materials [19]. Long-chain aliphatic hydrocarbons and aromatic compounds, like toluene and xylenes, were mostly identified and counted for 52% and 42% of TVOCs concentration respectively. Other chemical families like halocarbons, carbonyls and esters were also detected. This kind of study is not very widespread and to our knowledge, no work is published regarding emissions of VOCs emitted by car interior finished parts made of biocomposites.

Vegetal fibers used in biocomposites are known to be sensitive face to climatic conditions such as ultraviolet (UV) rays, high temperatures and humidity. Physico-chemical properties of natural fillers composites are thereby affected by water absorption and oxidation reactions leading to mechanical performance loss, chemical composition and visual aspect changes [23–30]. Some works described qualitative and semi-quantitative analysis of VOCs evolved from biocomposites. A study has been done on emissions of VOCs sampled by HeadSpace - Solid Phase MicroExtraction (HS-SPME) after a thermal ageing of cellulose and hemp fibers reinforced polypropylene (PP) composites [31]. Different VOCs chemical families were identified such as aliphatic hydrocarbons, carboxylic acids and alcohols but also compounds specific to natural fibers like 2-furanmethanol. K.W. Kim et al. worked on the reduction of TVOCs emission from pineapple and destarched cassava flour reinforced polylactic acid (PLA) and polybutylene succinate (PBS) biocomposites by the bake-out process [16]. The study investigated the influence of temperature and baking time on TVOCs emission factor. They noted a factor increase with temperature and a decrease with baking time. Otherwise, neat PLA and PBS presented lower emission factor than loaded ones. In the same line, H.S. Kim et al. worked on the reduction of odor and VOC emissions of vegetal flour filled reinforced PLA and PBS composites by incorporating porous inorganic fillers [32]. Volatile products emissions caused by high temperature manufacturing like tridecane from the matrix and furfural from bamboo flour were decreased. Olfactometric analyses carried out on natural fillers composites allowed to understand the high responsibility of oxygenated compounds issued from both the polymer and natural fillers to unpleasant odor [5]. However, no study deals with the VOCs emissions of biocomposites under real conditions of use since the impact of natural fiber composites ageing on VOCs emission is poorly documented. Indeed, standard measurement methods (e.g. emission chamber methods) are complex to implement and time consuming for the monitoring of the temporal evolution of VOCs emissions [33,34]. As an alternative, HS-SPME is the most widely used technique for sampling VOCs emitted by polymeric materials [5,31,35–37]. Its advantages are simplicity and time saving according to short extraction times. But this method involves material destruction by cutting it in small pieces for introduction in the headspace vial. Hence, this sampling procedure is not relevant to provide quantitative data related to surface emission. The sampling methodology used for this work and previously developed in our laboratory, is based on a home-made emission cell coupled with SPME [38,39]. This simple and non-destructive passive sampling method allows determining the VOCs concentration at the material/air interface which is related to the emission rate by the first Fick's law of diffusion under steady state conditions [39].

This study aims to assess the impact of VOCs emitted by hemp fibers reinforced PP on air quality and the influence of material ageing on theses emissions regarding hemp fibers rate and sampling temperature. A car interior environment was simulated by exposing laboratory-made materials under windshield glass for one year. Emitted VOCs were identified over the weathering and their concentrations at the material/air interface were determined. Results are discussed notably in terms of ageing impact, fiber contribution and health impact. For this latter, the European regulation classes of critical products according to their impact on human health and their concentrations were gathered as well as limit values already imposed, or at least advised, by VIAQ guidelines and national standards.

2. Materials and methods

2.1. Materials

Polypropylene grade H733-07 with a melt flow rate of 7.5 g/10 min (230 °C, 2.16 kg) was purchased from Braskem (Sao Paulo, Brazil) and used as polymer matrix. Hemp fibers with size included in the 2–6 mm range were provided by AgroChanvre (Barenton, France). Their retting lasted 38 days and their cellulose, hemicelluloses, lignin and lipophilic extractives rates of 82, 8, 5 and 3 wt% respectively were determined by successive chemical extractions based on TAPPI T264, ASTM D1104 standards. Two hemp fibers loading, 10 wt% (PP10) and 30 wt% (PP30), were tested (Table 1). Maleic anhydride grafted polypropylene (MA-g-PP) with a 1 wt% grafting rate, under the trademark Orevac CA100 and supplied by Arkema (France), was added at 3.1 wt% of PP as coupling agent.