

Extrusion and injection moulding induced degradation of date palm fibre - polypropylene composites

Sandra Domenek^{a*}, Françoise Berzin^d, Violette Ducruet^a, Cédric Plessis^a, Hom Dhakal^c,
Emmanuel Richaud^b Johnny Beaugrand^{d,e}

^aUniversité Paris-Saclay, INRAE, AgroParisTech, UMR SayFood, 91300, Massy, France

^bPIMM, ENSAM - CNRS - CNAM, 151 Boulevard de l'Hôpital, F-75013 Paris Cedex, France

^cAdvanced Materials and Manufacturing (AMM) Research Group, University of Portsmouth, School of Mechanical and Design Engineering, Anglesea Road, Anglesea Building, PO1 3DJ, UK.

^dUniversité de Reims Champagne Ardenne, INRAE, FARE, UMR A 614, 51097 Reims, France

^eINRAE, UR1268 Biopolymères Interactions Assemblages, 44 316 Nantes, France

***Corresponding author:** Sandra Domenek, Université Paris-Saclay, INRAE, AgroParisTech, UMR SayFood, 1 avenue des Olympiades, F-91300 Massy, France

Email: sandra.domenek@agroparistech.fr

ABSTRACT

The use of date palm fibres, which are an abundant by-product of agriculture, as natural reinforcement in polypropylene (PP) was studied. Because odour emissions are one of the major challenges for natural fibre-based composites, the emission of Volatile Organic Compounds (VOC) generated at different processing steps was analysed online. The severest degradation on the date palm fibre morphology was observed at the injection moulding step, but even when degradation occurred date palm fibres were an effective reinforcement of PP and increased the Young's modulus significantly. Generation of odorous compounds caused by thermal degradation of date palm fibres such as furfural alcohol or methyl furfural was astonishingly low during the twin-screw extrusion and granulation process. In coherence with the evolution of the fibre morphology, the most critical processing step was the injection process. In conclusion, date palm fibres are a promising natural fibre for the production of natural fibre-based composites. Adapted twin-screw extrusion conditions allow for minimizing VOC emissions, but particular attention needs to be given to the optimization of the injection process.

Keywords: polypropylene, twin screw extrusion, injection moulding, VOC, thermal degradation

Introduction

Natural fibre-based polymer composites, are of interest in industrial applications such as interior parts in the automobile and building sectors. The main advantages of the natural fibres are their low density but sufficient stiffness compared to inorganic fibres, high specific strength and modulus, high flexibility, non-abrasive nature, good thermal and acoustic insulation properties. They are furthermore biobased, which is an advantage as societies are seeking for increasing the part of renewable resources in the manufacturing industry, and relatively inexpensive [1-3]. Natural fibres can be derived from biomass wastes, such as leaves or stems, which brings further advantage to the economic and ecological balance of biocomposites in that they constitute a market opportunity of underexploited by-products of the agriculture and food industry. With that respect, date palm fibres are an abundant source, which receives growing interest [4-12]. Date palms (*Phoenix dactylifera L.*) are the third most abundant palm species after coconut and oil palms and largely cultivated in North Africa and the Middle East [12]. The production of dates leaves behind huge amounts of by-products, such as dry leaves and sheaths, which are usually burned in the fields.

Date palm fibres have lower density (0.92 g/cm^3) compared to other bast fibres (hemp density 1.14 g/cm^3 , e.g.) [11]. Date palm fibre-based composites were developed using polycaprolactone (PCL) [8, 10] and polypropylene (PP) [5, 9, 11, 12].

PP is a largely used polymer in the composites industry with numerous applications in buildings and vehicles. Odour of natural fibre-based composites can be problematic for their use in interior parts. PP undergoes degradation during processing, which leads to the generation of volatile organic compounds (VOCs). Interestingly, biocomposites using biodegradable polymers, such as polylactide develop less odour [3]. In particular, oxidative degradation yields aldehydes and ketones, some of them have a characteristic smell [13, 14]. The use of antioxidants for the protection of PP during processing is therefore widely employed and nowadays biobased antioxidants are developed [15, 16]. The thermal degradation of natural fibres in plastics processing conditions leads to the so called empyreuma odour, *i.e.* a specific smell and taste coming from decomposition products of animal or vegetable substances burnt in close vessels [17]. Natural fibres are lignocellulosic biomass. In particular, date palm fibres are composed of 46 wt% cellulose, 18 wt% hemicellulose, 20 wt% lignin, and 11 wt% ashes [10]. Although cellulose is quite thermally resistant, the thermal decomposition temperatures of hemicelluloses and lignin fall generally in the range of the processing temperatures [18, 19].

At low temperature, the presence of lignocellulosic fibres has low impact on the PP degradation, but at higher temperature, it can interfere [17]. The odour emission can be attenuated by the use of scavengers and by optimising the thermal processing of composites [19].

This study aims to investigate the performance of date palm fibres as a natural reinforcement for polymers, the impact of processing conditions on the overall mechanical properties of the composites, and the specific impact of the processing steps on the degradation of fibres and PP. PP grafted with maleic anhydride was used as a fibre/matrix compatibilizer. This technique, which was already proposed in the early 2000 [20, 21], is now widely used in biocomposites [22]. In particular, the emission of VOCs at different moments during the processing was probed directly in the headspace of the extruder, the extruded strands and the injected specimens using head space solid phase microextraction (HS-SPME) coupled to gas chromatography and mass spectrometry (GC-MS) on the date palm fibre/PP composites. HS-SPME is a widely used solvent free extraction technique with low detection threshold for the qualitative analysis of volatile substances in many different fields, including polymer processing and analysis [14, 17, 23-26]. To gain new insights, composites were produced by twin-screw extrusion and injection moulding, the two most used manufacturing processes. PP grafted with maleic anhydride (PP-g-MA) was added in small amount (2.5 wt%), because it is a well-known compatibilizer in natural fibre-based composites [7, 27, 28]. The twin-screw extrusion parameters were modelled and characterised by numerical simulation. The impact of the processing on composites was extensively studied analysing the morphology of date palm fibres, mechanical properties of the composites, and degradation of the PP-based matrix. The creation of VOCs at different processing steps was further analysed and correlated to the processing parameters.

Materials and Methods

Materials

Polypropylene PPH 5060 (PP) purchased from Total Petrochemicals is a homopolymer with a melt flow index of 6 g/10 min (230°C, 2.16 kg), a melting temperature of 164°C and a molar mass of 320,000 g/mol. Polypropylene grafted with maleic anhydride (PP-g-MA) was added in order to improve the interfacial adhesion between the fibres and the PP matrix. Solvents and Solid Phase MicroExtraction (SPME) fibres were purchased from Sigma Aldrich (France).

Plant fibre material

Date palm fibres (*Phoenix dactylifera* L.) were obtained from a farm in Al-Ahsa (Saudi Arabia), as decametric bundles. Prior to twin-screw extrusion, the palm bundles were chopped into a master batch with an average length of 1 ± 0.7 cm with a plant shredder equipped with a 2 mm square sieve (Retsch, Haan Germany). The chopped fibre bundles were then stored at 20°C and 50% relative humidity (RH) in a climatic chamber before use.

Composite manufacturing

The composites were prepared using chopped date palm fibre mixed at 20 wt% with a PP/PP-g-MA matrix in a laboratory-scale twin-screw co-rotating extruder (ZSE 27 MAXX, Leistritz, Germany), according to the protocol of [10]. Extruder main characteristics are as follows: centreline distance 22.7 mm, screw diameter 28.3 mm, length/diameter ratio 36. The screw profile is shown in Figure 1. PP and PP-g-MA were fed as solid pellets in barrel element 1, while the fibres were introduced in barrel 4. The profile is constituted of screw conveying elements, a left-handed element and a block of kneading discs. The left-handed element was used for the melting of the matrix, while the block of kneading discs helped to disperse the fibres. The barrel temperature was set at 160°C for all experiments. Two values of screw speed (100 and 300 rpm) and feed rate (0.4 and 0.8 kg·h⁻¹ for date palm fibres, 1.6 and 3.2 kg·h⁻¹ for PP + PP-g-MA) have been tested. For each condition, two experiments were performed: matrix only (PP + PP-g-MA) and matrix with 20 wt% fibres. The sample nomenclature remembers the processing conditions, it is explained in Table 1.

Table 1. Sample nomenclature containing the information of composition and twin-screw extrusion conditions

Sample name	Composition	Total flow rate (kg·h ⁻¹)	Screw speed (rpm)
PP-1.6-100	PP + 2.5 wt% PP-g-MA	1.6	100
PP-1.6-300	PP + 2.5 wt% PP-g-MA	1.6	300
PP-3.2-100	PP + 2.5 wt% PP-g-MA	3.2	100
PP-DF-2-100	PP + 2.5 wt% PP-g-MA + 20 wt% date palm fibre	2	100
PP-DF-2-300	PP + 2.5 wt% PP-g-MA + 20 wt% date palm fibre	2	300
PP-DF-4-100	P + 2.5 wt% PP-g-MA + 20 wt% date palm fibre	4	100

The flow simulation software Ludovic[®], dedicated to twin-screw extrusion [29-32], was used to estimate some parameters of the compounding process. Specifically, Ludovic[®] was used to

calculate both the local temperature along the extruder and the residence time, according to the parametric study.

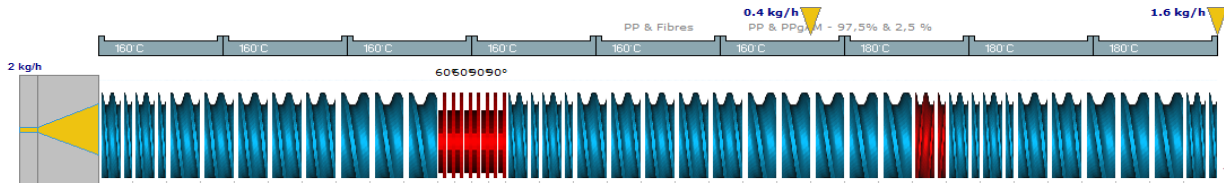


Figure 1. Screw profile of the twin-screw extruder

After extrusion, the composite strands were cooled down at room temperature, conditioned under controlled atmosphere (20°C, 65% RH), pelletized (approximately 15 mm in length). Standard dumbbell specimens were injected using a bench scale DSM Xplore (Geleen, The Netherlands), according to the procedure of [33]. The injection temperature was 190°C and that of the mould 40°C with a cycle time of 5 min. The injection pressure was set to $1.5 \cdot 10^3$ kN·m⁻². The injection-moulded specimens (NF EN ISO 527 – 2 A) were 75 mm long and 2 mm thick. At least eight specimens were tested for each condition.

Date palm fibre extraction from both the extrudates and the injected composites

To analyse the fibre content and to evaluate if any changes were induced during the compounding process, extruded strands with a length of 2 cm were collected every 10 cm according to the protocol described by Beaugrand & Berzin [34]. The fiber content of each piece was analyzed. For the injected samples, fractured tensile test samples (after injection and testing) were collected and pooled from at least 10 composite pieces. The PP/PPgMA matrix was extracted by o-xylene (Sigma Aldrich) under reflux for 60 hours using a ‘Soxhlet’ device.

Analysis of fibre morphology

The dimensions and morphologies of the extracted fibres were then obtained by image analysis via the morphometric description method of [35] using a 2D high resolution image scanner (Epson V850 pro). The fibres were scattered on the scanner glass with taking care to keep them individualized. The images were acquired in 8-bit greyscale at a resolution of 4800 dpi, representing theoretically 5.29 µm per pixel. A sample photo and further information is given in the supporting information S3. The dimensions were obtained for each individual particle and averaged. Therefore the (L_w/D_w) represents the average of all individual shape factors. The L_w and D_w values are also averages of the individual dimensions.

Rheological and mechanical testing

The rheological behaviour of the PP/PP-g-MA matrix and the composite with 20 wt.% palm fibre was measured on a parallel-plate rheometer (Ares, TA Instruments) in small-amplitude oscillatory shear at 180°C. Strain sweeps were carried out to determine the linear domain and frequency sweeps were then performed in the linear domain between 0.1 and 100 rad.s⁻¹. For mechanical testing, specimens were stored in controlled environment (23°C / 50 % relative humidity (RH), ISO 291:2008) for 3 days. Tensile tests in longitudinal direction were performed on the neat matrix and composites using a Testwell universal tester (Saint Ouen, France) located in the same room with controlled environment (23°C, 50 % RH), with a crosshead speed of 1 mm.min⁻¹. The load was measured with a nominal length of 10 mm and with a 2 kN sensor, the tests were carried out with an axial extensometer (Axial extensometer 3542, Epsilon tech, Jackson, USA). A minimal of 8 specimens of each type were tested. Mean values are given with the standard deviation.

Size exclusion chromatography

Size-exclusion chromatography (SEC) was performed thanks to a high temperature gel permeation chromatograph (PL-GPC 220® Agilent Technologies). The samples were cut into pieces and dissolved with 1,2,4-trichlorobenzene (Chromasolv, Sigma–Aldrich®) at a concentration of 1 mg mL⁻¹. The eluent contained 0.03 wt% of 2,6-di-tert-butyl-4-methylphenol (BHT, Fluka) to stabilize the polymer against oxidative degradation. The solutions were stirred during 15 min at 150°C and filtered before injection. The separation was carried out on a sequence of a guard column and two columns PLGel Olexis®. Peaks were detected with a refractive index detector (Agilent, France). The temperature was set at 135°C, and the flow rate was 1 mg mL⁻¹. The calibration curve was established with the help of 4 Polystyrene Shodex® narrow standards of respective molecular weights of 1.47·10⁶, 2.57·10⁵, 4.65·10⁴ and 7.21·10³ g mol⁻¹. Molar mass values were then estimated from the universal calibration method [36] using the Mark-Houwink constants $k_{PS} = 0.000161$, $\alpha_{PS} = 0.677$, $k_{PP} = 0.000834$. and $\alpha_{PP} = 0.8$ in trichlorobenzene at 135°C.

Analysis of VOC in the headspace of the extruder and in the composites

HS-SPME analysis of VOC of date palm fibres

Date palm fibre samples of approximately 0.5 g were sealed in 20 mL glass vials closed with silicon/PTFE septa. The sample vials were incubated at different temperatures (70, 180, 200°C) for 25 min using a 75 µm Carboxen/Polydimethylsiloxane (CAR-PDMS) and a Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB-CAR-PDMS) fibre. The higher temperatures simulate extrusion and injection conditions, respectively. Three replicates were prepared for each condition. Desorption time of the SPME fibres was 5 min inside the injector (250 °C). After injection, the SPME fibres were cleaned at 270 °C for 10 min. For the analysis of the date palm fibres, the temperature program was as follows: initial isotherm at 30 °C for 5 min, then temperature ramp at 5 °C/min up to 230 °C, and a final isotherm at 230 °C for 5 min. The injector was set at 250 °C for 3 min split-less, then an inlet split of 30 mL/min was applied.

On-line sampling of VOC during the extrusion process

For the headspace sampling during twin-screw extrusion, the second opening of the extruder for material introduction downstream of the date palm fibre introduction was used (section 7 from the right side following extrusion flow, Figure 1). Two types of SPME fibres were put in the headspace for 5 min and then immediately sealed in 20 mL glass vials with silicon/PTFE septa. The fibre absorbents were CAR-PDMS and DVB-CAR-PDMS. The vials were stored at -20°C in a freezer until analysis. Two samplings were realized for each condition.

On-line sampling of composites

Samples of approximately 1 g were taken directly from the extrudate strand after the die and immediately sealed in 20 mL glass vials. Furthermore, approximately 1 g of pellets were sampled immediately after the pelletizer. The dumbbell samples after injection were sampled in Sovirel glass bottles with Teflon seals. They were cut into pieces and approximately 1 g of small pieces was sealed in 20 mL glass vials for HS-SPME analysis. All samples were stored inside sealed glass vials at -20°C in the freezer until analysis. Two replicates were prepared.

HS-SPME analysis of VOC of composites and extruder headspace

The SPME fibres containing the VOCs of the extruder headspace were mounted in the MPS2 GERSTEL autosampler and desorbed directly in the injector port (250°C, 5 min). The VOCs in the composites (strands, pellets, injected samples) were extracted using CAR-PDMS and DVB-CAR-PDMS fibres by incubation at 70°C for 15 min. Desorption time was 5 min inside

the injector (250°C). After injection, the SPME fibre was cleaned at 270°C for 10 min. Two analyses were carried out per sample.

GC-MS analysis of composites and extruder headspace

For the analysis of VOC, an Agilent Technologies 6890 gas chromatograph (GC) coupled with a mass spectrometer (5975 INERT), and Flame Ionization Detector (FID), and an autosampler (MPS2 GERSTEL), which allowed automated HeadSpace – Solid Phase MicroExtraction (HS-SPME) injections, were used. The chromatographic column was an Agilent J&W Scientific DB5-MS capillary column (30 m length x 0.32 mm inner diameter x 0.5 µm film thickness). The carrier gas was He at 1.3 mL/min.

The temperature program of the GC-FID-MS was the following: initial isotherm at 30°C for 5 min, then temperature ramp at 8°C.min⁻¹ up to 260°C, and a final isotherm at 260°C for 11 min. The injector was set at 250°C for 3 min split-less, then an inlet split of 50 mL.min⁻¹ was applied. The FID detector was set at 250°C with an air flow rate of 450 mL.min⁻¹ and a H₂ flow rate of 40 mL.min⁻¹. The parameters of mass spectrometer used for identification of VOCs were: electron impact ionization; electron energy, 70 eV; ion source, 230°C; electron multiplier voltage, 1470 eV; transfer line, 270°C; scanning, between 29 and 500 amu. The data were recorded by MSD ChemStation software and the identification of the constituents was achieved using mass spectral matches with Wiley7 NIST 05 mass spectra database.

Although the sample mass was constant for all analyses (approximately 1 g) and the small differences in mass normalized, the intensity of the chromatograms is also probably influenced by the area/volume ratio of the samples. Therefore, the pellets had a higher surface area compared to extrudates or injected samples at the same mass. For semi-quantification purposes, the single peak areas were normalized as a percentage of the total area of the chromatogram. The percentages were translated to an arbitrary intensity value from 1 to 5, where level 1 corresponds to less than 1% of the total chromatogram, level 2 to 1-5 %, level 3 to 5-15 %, level 4 to 15-30 %, and level 5 to more than 30 %.

Results and discussion

Simulation of extrusion conditions

In the aim to have a clear picture of the local temperature and residence time at different shear conditions to which the PP/PP-g-MA/date palm fibres were subjected, a simulation using the

Ludovic[®] software was carried out. The simulated graphs are shown in the supporting information S2. For that purpose, the rheological behaviour of the matrix and of the composite were measured. The corresponding complex viscosity curve of the PP-based matrix (supporting information S1) shows a classical Carreau-Yasuda behaviour [37], with a Newtonian plateau at 1300 Pa·s. The viscosity is much higher for the composite (10000 Pa·s at 10⁻¹ rad.s⁻¹) and follows a power-law behaviour, as often observed with natural fibre composites [30] or nanocomposites [38]. The Table 2 shows the simulation results of the different conditions. The viscosity increase of the material due to the presence of the fibres induced an increase of the final temperature as compared to the matrix. Those materials experienced supplementary time-temperature constraints which can further increase chemical degradation phenomena. The data provided by Ludovic[®] has been validated through many experimental measurements. For example, Carneiro et al. [39] showed that not only the final temperature but also the temperature profile along the screws predicted by the software were in very good agreement with reality. The simulated temperatures are high enough so that oxidative degradation of PP generating volatile molecules can occur within the residence time [40, 41].

Table 2. Simulation results of final temperature and residence time of the materials in the twin-screw extrusion process.

Sample	Screw speed (rpm)	Flow rate (kg/h)	Final temperature (°C)	Residence time (s)	Max. temperature* (°C)
PP-1.6-100	100	1.6	167	234	175
PP-1.6-300	300	1.6	202	204	215
PP-3.2-100	100	3.2	167	137	174
PP-DF-2-100	100	2	174	216	185
PP-DF-2-300	300	2	214	185	228
PP-DF-4-100	100	4	174	128	185

*The barrel temperature was constant at 160 °C. *Maximum temperature after date palm fibre introduction.*

Morphological and mechanical characteristics of date palm fibre/PP/PP-g-MA composites

Table 3. Morphological analysis of palm fibres after extrusion and injection

	Flow rate (kg/h)	Screw speed (rpm)	Sample type	L_w (μm)	D_w (μm)	(L_w/D_w) (-)
PP-DF-2-100	2	100	E	2909 (\pm 504)	377 (\pm 29)	7.2
			IS	1799 (\pm 195)	346 (\pm 23)	5.0
PP-DF-2-300	2	300	E	1830 (\pm 173)	271 (\pm 22)	4.2
			IS	1492 (\pm 153)	280 (\pm 28)	4.1
PP-DF-4-100	4	100	E	3194 (\pm 342)	314 (\pm 29)	5.6
			IS	1810 (\pm 201)	334 (\pm 27)	5.4

E = Extrudate strand; IS = Injected Specimens; L_w = fibre length, D_w = fibre diameter

The twin-screw processing conditions were chosen following former experiences [10] in order to preserve the morphology of date palm fibres in the composites. The morphometric characteristics of the date palm fibres extracted from both the extrudate composites and from the injected sample specimens tensile-tested are reported in Table 3. The impact of the process on the decrease in length, diameter, and morphology has been well documented [21], including the case of palm fibre [30, 34]. Consistent measurements with the state of the art were obtained in this study. First, the twin-screw extrusion decreased the length of the fibre elements. The effect was more important when the shear rate (proportional to screw speed) and the residence time were high [30]. Table 3 shows that the palm fibre elements were longer at 100 rpm compared to 300 rpm, and also longer with feed rate of 4 kg compared to 2 kg. The reduction in diameter is very moderate, at the exception of the 300 rpm condition. The injection clearly degraded the natural fibre length by a half. The final aspect ratios of the date palm fibre were all in the same order of magnitude and quite small.

The tensile properties of the samples obtained under different twin-screw extrusion conditions are reported in Table 4. As expected, the tensile results show that there is a clear influence of date palm fibre addition on the tensile strength, elastic modulus and strain at break. The reinforcement by the palm fibre is weak in term of tensile strength. The tensile modulus increased importantly, whereas tensile strain drastically decreased when compared to the neat polymer matrix. A similar trend was reported with the same palm fibre when compounded with

polycaprolactone [10] or PP [12] and attributed to low matrix/fibre adhesion. The improvement in tensile strength was obtained whatever the flow rate or screw speed used. The fact that the tensile reinforcement effects were almost similar for all processing conditions with date palm fibres is probably due to the identical mass fraction added, the mild of the twin-screw extrusion conditions on the date palm fibre dimensions [27], and the fact that the major degradation was observed during injection. As a conclusion, mild twin-screw processing conditions at screw speeds below 300 rpm allowed for the preservation of the fibre dimensions. The main optimisation work needs apparently to be carried out at the moment of injection moulding, involving high shear and temperature.

Table 4. Tensile mechanical properties of PP and PP/PP-g-MA/date fibre composites

	TS at break (MPa)	E (MPa)	ε (%)
PP/PP-g-MA blank	31 (± 1)	1048 (± 157)	68 (± 25)
PP-DF-2-100	33 (± 1)	1622 (± 181)	10 (± 2)
PP-DF-2-300	33 (± 2)	1639 (± 275)	9 (± 1)
PP-DF-4-100	34 (± 2)	1682 (± 165)	10 (± 1)

TS = tensile stress; E = Tensile modulus; ε = tensile strain at break

Induced degradation of the PP-based matrix

Table 5. Macromolecular chain length degradation of PP-based matrix during processing

		\bar{M}_n (Da)	\bar{M}_w (Da)	\bar{D}
PP/PP-g-MA blank	injection	23,900 ($\pm 5,900$)	216,600 ($\pm 22,700$)	9
PP-1.6-100	injection	31,600	281,200	9
PP-1.6-300	pellet	27,100 ($\pm 2,000$)	235,900 ($\pm 25,300$)	9
PP-3.2-100	pellet	18,500 ($\pm 1,600$)	199,300 ($\pm 37,300$)	11
PP-DF-2-100	pellet	29,600	237,400	8
	injection	27,600 ($\pm 16,800$)	257,600 ($\pm 51,900$)	9
PP-DF-2-300	pellet	22,900 ($\pm 4,600$)	204,100 ($\pm 21,000$)	9
	injection	24,500 ($\pm 21,300$)	235,300 ($\pm 57,100$)	10
PP-DF-4-100	pellet	17,700 ($\pm 8,200$)	237,400 ($\pm 57,900$)	13
	injection	27,000 ($\pm 15,500$)	239,100 ($\pm 53,900$)	9

The measurements of extrudates and pellets were pooled. For traceability, all measured datapoints are reported in the supporting information S4.

The impact of the processing conditions and the presence of the date palm fibres on the degradation of the PP-based matrix was tested by SEC, because the decrease in the macromolecular chain length is an important tracer of degradation. The data presented in Table 5 shows that the processing degraded non surprisingly the PP chains as compared to the data sheet of the PP pellets ($\bar{M}_w = 320,000$). This is caused by oxidative degradation of PP during processing [41, 42]. In the aim to determine the effect of the inclusion of the date palm fibres in PP on degradation, the data were compared to the values of neat PP granules, injected without further processing (first entry in Table 5). The addition of the date palm fibres had surprisingly very little impact on the PP chain length. The heterogeneity of the obtained data increased, and no statistically significant impact of the presence of date palm fibres in PP in addition to the processing on the macromolecular chain length was observed. We conclude that, from an applicative point of view, this is an encouraging result showing that date palm fibres could be a reinforcing adjuvant of PP without causing supplementary loss in molecular mass during processing.

Generation of VOCs during the extrusion process

Analysis of VOCs due to thermal degradation of palm fibres

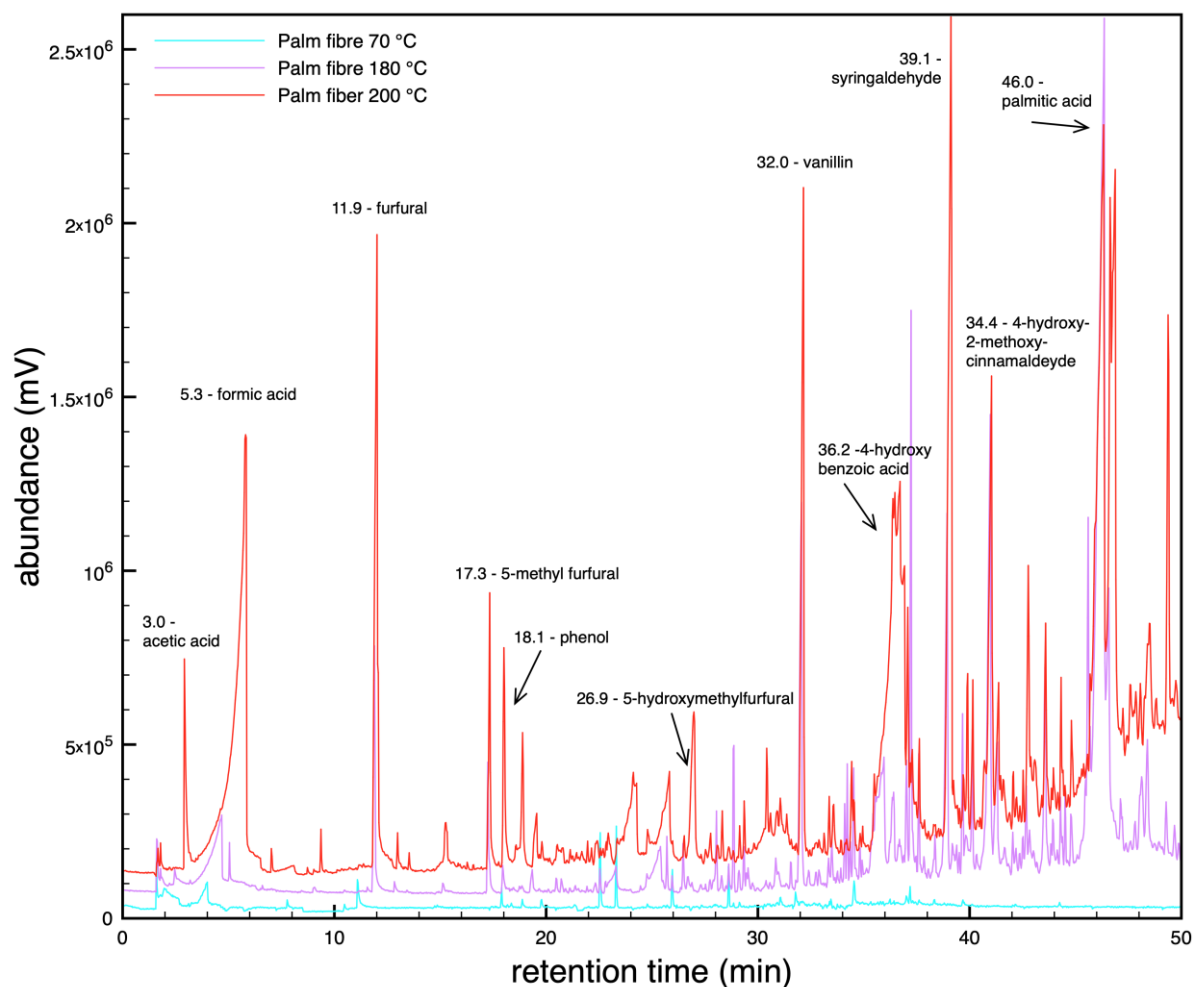


Figure 2. Volatile Organic Compounds of date palm fibres with the CAR/PDMS SPME fibre at different incubation temperatures. The most intense peaks of the heat-treated date palm fibres are attributed. Complete tentatively attribution and semi-quantification of peaks is given in the supporting information S5-Table S5.1.

The profile of the volatile organic compounds generated by the palm fibres was analysed after thermal treatment in the aim to identify pertinent odour markers of the date palm fibres. For analysis, the choice of the SPME fibre coating is an important factor in the aim to obtain an overview over the present VOCs. For example, [43] showed that CAR/PDMS coating extracted more efficiently compounds with low Kovats index ($KI < 980$) and DVB/CAR/PDMS those with higher KI. In that aim, the VOC profiles of date palm fibres, which were incubated at 70 and 180°C were extracted with a CAR/PDMS and a DVB/CAR/PDMS SPME fibre. The qualitative analysis of the chromatograms showed only few differences in extraction between both fibre types. The data are given in the supporting information S5 – Table S5.1. The DVB/CAR/PDMS fibre extracted more molecules at longer retention time and higher amounts

of the less volatile compounds. This behaviour was coherent with the use properties of the triple fibre, which targets molecules with higher KI. The identification of those compounds shows that they were mainly alkanes of different length scales. Those molecules were present in low amounts and did not contribute to the odour profile of the date palm fibres. Therefore, in the following the SPME extraction was carried out with the CAR/PDMS fibre, which extracted preferentially the short retention time VOCs relevant for the particular aroma signature of the heat-treated palm fibres.

Figure 2 shows the superposition of the chromatograms obtained after the extraction of the palm fibres at 70, 180 and 200°C by the CAR/PDMS fibre. At an extraction temperature of 70°C, only a few number of VOCs were detected and at low quantity. The compounds were short organic acids (formic acid, acetic acids), aldehydes (hexanal, octanal, nonanal, decanal, benzaldehyde), triacetine and isobutyric acid. Formic acid and acetic acid are markers of the degradation of lignocellulosic biomass [18, 44] but also markers of the degradation of PP [40]. Aldehydes, such as hexanal, nonanal, are degradation products of fatty acids, but can also be found in the aroma composition of dates with which the date palm leaves are in contact during harvesting [45]. At the higher temperatures 180 and 200°C, the aldehydes were also extracted, but a number of new compounds were generated (Figure 2). Date palm fibres are composed at average of approximately 46 % cellulose, 18 % hemicellulose, 20 % lignin [11]. Glucose-derived molecules, such as furfural, 5-methylfurfural, or 5-hydroxymethylfurfural, can be obtained by thermal dehydration [18, 46]. Hemicelluloses are more complex polymers composed of C5-sugars, mostly xylose, but also arabinose, galactose, mannose. The thermal degradation of xylose yields mainly furfural [44, 47], while galactose yields preferentially 5-hydroxymethyl-2-furaldehyde [44]. Lignins are branched aromatic polymers, biosynthesized from the monomeric units, syringyl, guaiacyl, and p-hydroxyphenyl alcohol. Aromatic molecules, such as syringaldehyde and 4-hydroxy-2-methoxycinnamaldehyde, originate thus most probably from the lignin fraction (approx. 20% in mass) of the date palm fibres. Furthermore, lignocellulosic biomass contains a monomeric fraction, which includes molecules such as vanillin [48]. 4-Hydroxybenzoic acid is a widely used antioxidant, its presence could be ascribed to contamination of the palm fibres during their usage and recycling process. Those different molecules yield an olfactive profile typical for the aroma of heat-treated natural fibres.

Generation of VOC during the extrusion process

VOCs during extrusion of PP/PP-g-MA

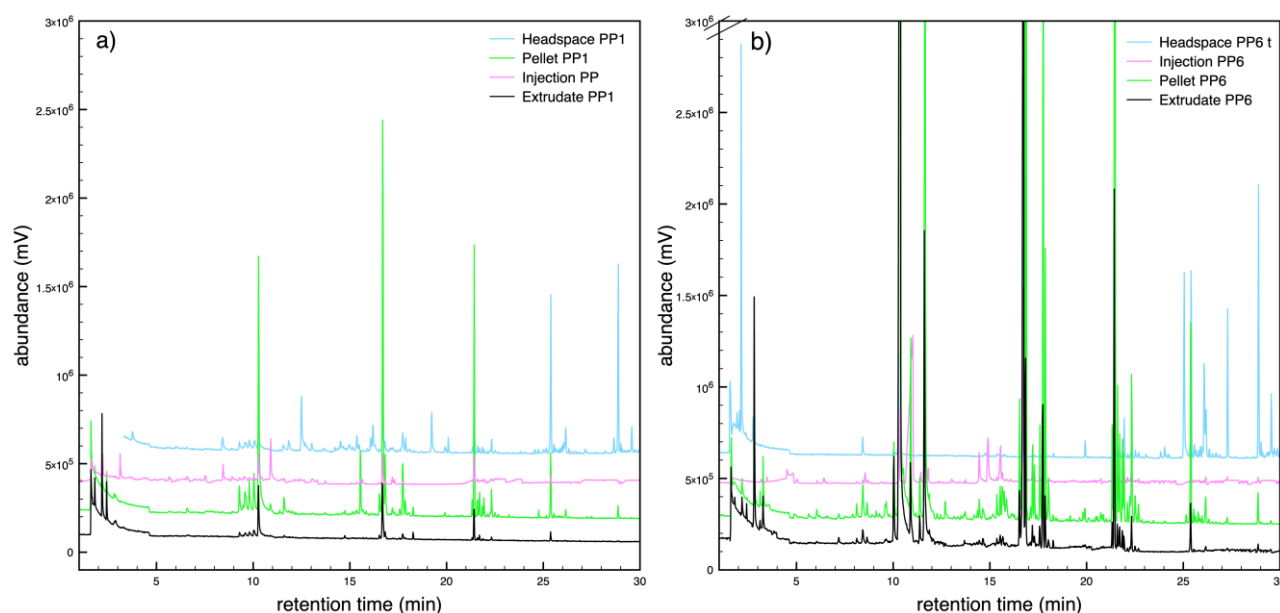


Figure 3. Chromatogram overlay of the CAR/PDMS SPME fibre extracts of the a) PP1=PP-1.6-100 and b) the PP6 = PP-DF-4-100. “Headspace” corresponds to the online sampling during the twin-screw extrusion in section 7, “extrudate” to the strand directly sampled from the twin-screw extruder, “pellet” to the sampling of the pellets after the granulator, and “injection” to the sampling of injected dumbbell shaped specimens after injection. For comparison, the ordinate of figure b is cut at 3.10^6 mV. The PP6 headspace sample was analysed with the DVB/CAR/PDMS fibre, because of experimental failure of the CAR/PDMS fibre sample. The peak intensity at larger retention times is slightly higher compared to the CAR/PDMS fibre.

The VOCs present in the PP/PP-g-MA strands, pellets and injected samples were analysed and compared to the VOCs sampled in the headspace of the extruder under different processing conditions. The chromatograms are presented in the Supporting information S5. In Figure 3, the two most distinct experimental series were chosen to illustrate the evolution of the chromatograms during processing, *i.e.* the PP-1.6-100 and PP-DF-4-100 series. Table 6 gives the attribution and semi-quantification of only the most prominent VOCs in PP and date palm fibres/PP composites. The complete information is published in the supporting information S5-Table 5.2. The quantification of compounds analysed using the SPME technique is quite tricky, because the partitioning coefficient of the absorbed molecules on the SPME fibre and the headspace are needed. Furthermore, the partitioning coefficient of a single compound can change as a function of the concentration of other molecules present in the headspace. In the

aim to compare the intensities in a qualitative manner, the percentage of a given peak area with regards to the total chromatogram area was calculated and translated into an intensity scale and normalized by the sample mass. Higher intensity number means more peak area.

The attribution of the peaks of the thermal degradation products of PP/PP-g-MA extrudates, pellets and injected samples (Table 6) revealed, non-surprisingly, the presence of known volatile degradation products of PP. Alkanes and alkenes are indeed the major volatile degradation products of PP. Ref. [49] reported in their pioneering work on the thermal degradation of PP 84.8 % (alkenes), 7.6% (alkanes), and 7.6% (alkadienes). Branched alkanes, such as 2-methyl pentane, 2-methyl pent-1-ene, 2,4-dimethyl heptane or alkenes, such as 2,4-dimethyl heptane or 2,4-dimethyl hept-1-ene, were already described [13, 14, 17, 50, 51]. 2,6-di-tert-butyl-p-benzoquinone and 2,6-di-tert-butylphenol originate from antioxidants present in PP [52]. The changes in the PP processing conditions in absence of date palm fibres had only a small impact on the VOCs fingerprint, but the relative intensity of the VOCs in the injected samples increased, indicating that this step was the most degrading for the polymer.

Alkanes and alkenes have very low odour activity, in opposition to oxygenated compounds, such as aldehydes and ketones. In particular, ketones and aldehydes with six to nine C-atoms have very low sensory thresholds in the sub-parts per billion range [14]. The identified molecules in Table 6 were consistent with oxidation products reported earlier. For example butanal, octanal, nonanal, decanal were found by [53], and butadiene, 2-pentanone, 2,4-pentadione by several other authors [14, 40, 54]. In absence of date palm fibres, only a few oxidation products were observed (octanal, nonanal), and none of them in the extrudates (Table 6).

In the presence of the date palm fibres oxidized species appeared, such as 2-pentanone, 3-methyl pentan-2-one, 4-methyl heptanone (Table 6). The comparison of the extrusion conditions showed that the condition of PP-DF-4-100, *i.e.* high flow rate and high temperatures, induced more oxidative degradation of PP, which is coherent with the macromolecular mass data in Table 4. The major impact was most probably caused by the fibre content, as the change of the flow rate of PP/PP-g-MA without fibres had no effect. The peak intensity of the oxidised species increased from the extrudate towards the injected samples. The comparison of the SPME-chromatograms of PP/PP-g-MA and PP/PP-g-MA/palm fibre composites showed that the global pattern of PP derived composites was unchanged (Figure 3), but in addition new peaks appeared which could be attributed to degradation compounds of the palm fibres (3-hydroxy-butanone, furfural, furfuryl alcohol, 5-methyl furfural). Surprisingly, in the extrudate and the pellets, the most characteristic compounds (furfural, furfuryl alcohol) associated to the

degradation of the palm fibres were absent. They were observed with high intensity in the injected samples. This observation was coherent with the morphological analysis of the date palm fibres, which showed that their length was cut by half in the injection process. We conclude that among the analysed processing steps, the injection process is the one which generates the highest quantity of VOC and contributes thus most importantly to the odour of PP/PP-g-MA/date palm fibre composites. Injection processing due to higher temperatures and shearing of the material has an important impact on the stability of the polymer (Table 6).

In the headspace of the extruder, supplementary compounds such as pentane and toluene were detected. Pentane is a described degradation product of PP [13, 55], but very volatile. It might have been lost during extrusion and therefore not sampled in the material afterwards. Toluene could be an environmental pollutant of the laboratory atmosphere or the extrusion equipment. Other supplementary compounds, such as butyrolactone, benzaldehyde, benzyl acetate were present in the analysis of heat-treated palm fibres, thus potentially already present as contaminants in the extrusion equipment regularly used for the fabrication of composites.

Conclusions

Odour emission of composites can be problematic in interior applications. It can be attenuated by the use of odour scavengers, but also by the optimization of the composite processing. With that aim, we investigated the impact of processing on fibre morphology and generation of volatile organic compounds at different stages all along the processing, i.e. during twin-screw extrusion, pelletizing and injection. Mild twin screw processing conditions with low shear rate (< 300 rpm) only moderately decreased the fibre dimensions. The most important degradation of fibre length was observed at the injection step. In coherence, the twin-screw extrusion step only contributes little to the creation of VOCs. Interestingly, only small quantities of VOCs coming from the natural fibres were observed at this stage. Among the processing parameters, the material flow rate appears to have the most severe impact on the PP and fibre degradation. Much higher emission of VOCs was observed at the injection step, where the date palm fibre length was degraded. We conclude that the important mechanical shearing which could lead to a local temperature rise in the injection machine is the most critical processing point which needs to be optimized in order to decrease the odour of biocomposites.

Table 6. Tentatively identification of volatile compounds extracted by the CAR/PDMS SPME fibre from samples during processing.

t _R (min)	Name	CAS	odour	Headspace		Extrudates		Pellets		Injection	
				PP1.6- 100	PP-DF- 4-100	PP1	PP-DF-4- 100)	PP1.6- 100	PP-DF- 4-100)	PP1.6- 100	PP-DF- 4-100
2.2	Acetone	67-64-1	strong solvent			4	2	2	1	3	
2.3	Isobutanol	78-83-1	Slightly suffocating; no residual alcoholic			3	2	2	2	2	
2.8	2-Methyl pentane	107-83-5				2	3		2	1	
3.2	2,3-Butadione	431-03-8	strong butter sweet creamy pungent caramel				1		1		1
3.9	Acetic acid	64-19-7	sharp pungent sour vinegar						1		2
4.52	2-Butenal	4170-30-3	flower								2
5.6	2-Pentanone	107-87-9	sweet fruity ethereal wine banana woody					1	1		1
6.1	2,3-Pentandione	600-14-6	pungent sweet butter creamy caramel nutty cheese						1		1
6.4	3-Hydroxybutanone	513-86-0	sweet buttery creamy dairy milky fatty						1		1
7.5	3-Methyl-2-pentanone	565-61-7							1	2	1
8.1	2-Pentenal	764-39-6	pungent green apple orange tomato				1		2		1
8.4	Toluene	108-88-3	sweet	2	1						
8.44	4-Methyl-heptane	589-53-7					1		1	3	1
8.6	1-Hydroxy-2-butanone	5077-67-8	sweet coffee musty grain malt butterscotch				1		2	2	2
9.28	1-Octene	111-66-0	gasoline	2		2		2	1	1	
9.58	2-Octene	111-67-1		2		2	1	2	1	1	
9.64	1-Hexanal	66-25-1	fresh green fatty aldehydic grass leafy fruity sweaty						1		1
10.28	2,4-Dimethylheptane	2213-23-2		3	2	3	5	4	4	3	3
10.88	2,4-Dimethyl-1-heptene	19549-87-2				1	2	2	2	4	1
11.38	heptane, 2.3 dimethyl						2	1	1		1

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