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ScienceDirect
Physics Procedia 56 (2014) 1153 – 1164
Physics Procedia

8th International Conference on Photonic Technologies LANE 2014

Laser cutting of carbon fiber reinforced plastics – investigation of hazardous process emissions

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Abstract

Carbon fiber reinforced plastics (CFRP) show high potential for use in lightweight applications not only in aircraft design, but also in the automotive or wind energy industry. However, processing of CFRP is complex and expensive due to their outstanding mechanical properties. One possibility to manufacture CFRP structures flexibly at acceptable process speeds is high-power laser cutting. Though showing various advantages such as contactless energy transfer, this process is connected to potentially hazardous emission of respirable dust and organic gases. Moreover, the emitted particles may be fibrous, thus requiring particular attention. Here, a systematic analysis of the hazardous substances emitted during laser cutting of CFRP with thermoplastic and thermosetting matrix is presented. The objective is to evaluate emission rates for the total particulate and gaseous fractions as well as for different organic key components. Furthermore, the influence of the laser process conditions shall be assessed, and first proposals to handle the emissions adequately are made.

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Keywords: laser cutting; carbon fiber reinforced plastics; respirable dust; organic gases; hazardous potential

1. Introduction

Carbon fiber reinforced plastics (CFRP) represent a remarkable group of organic composite materials with outstanding mechanical properties in relation to the comparably low specific weight. These properties result from the inner structure of the composite material. Carbon fiber rovings which have a high specific strength are arranged

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Peer-review under responsibility of the Bayerisches Laserzentrum GmbH
doi:10.1016/j.phpro.2014.08.030

as unidirectional layer, bi- or multi-axial non-woven fabrics, or woven fabrics. The matrix material consists either of a thermosetting resin, such as epoxy, or a thermoplastic polymer, such as polypropylene (PP), polyamide (PA) or polyphenylene sulfide (PPS). Due to the carbon fibers, CFRP parts have a high specific strength parallel to the composite layers, whereas the strength perpendicular to these layers is mainly determined by the matrix properties. The described properties lead to a very high potential regarding the production of lightweight structures. This was first recognized by the aircraft industry, where large parts of different aircrafts are made from CFRP (e.g. Airbus A350XWB), helping to reduce fossil fuel and energy consumption. Increasing interest in such composite materials is noticed in the automotive industry, as documented by remarkable close-to-production prototypes made mainly from CFRP (e.g. Volkswagen XL1) as well as by the efforts of major automotive companies to implement CFRP into their series production (e.g. BMW i3 or Audi R8 GT). Nowadays, relevant applications can also be found in the wind energy industry (rotor blades with structure-reinforcing CFRP parts) and in the sports segment (bicycle frames, tennis rackets, canoe paddles, or hulls and masts in boatbuilding).

The biggest challenge with respect to CFRP parts is the realization of an economically efficient processing. Due to the specific strength and hardness of the fibers and the viscoelastic behavior of the matrix material, conventional processing techniques such as milling or water jet cutting are slow, affected by substantial wear and tear of the tools, and consequently expensive (Sheikh-Ahmad (2009)). In contrast, lasers can apply the energy precisely without direct contact to the processed parts. Moreover, high cutting speeds can be achieved (see e.g. Bluemel et al. (2012)). At the same time, operating and maintenance costs of laser systems are comparably low. However, laser cutting in particular is related to the generation of a notable amount of thermal energy on the work piece due to the material-specific absorption of radiation, which is generally wavelength-dependent. As matrix and reinforcement materials have vastly different thermophysical and chemical properties, the matrix is evaporated and decomposed much faster than the carbon fibers, which causes distinctive heat-affected zones (HAZs). Nevertheless, processing results of good or even excellent quality, i.e. almost completely without defects such as delamination or formation of blow-holes or pores, can be obtained, if specific processing strategies, e.g. multipass processing using short-pulsed laser systems with high brilliance, are applied (see e.g. Jaeschke et al. (2014)).

The laser energy input causes a considerable emission of fumes and organic gases, influenced by various material and process parameters. The composition of these process emissions is complex, and they may contain a significant amount of of toxic or even carcinogenic components. Furthermore, a lot of ultrafine particles, having the potential to be incorporated into the pulmonary alveoli, may be generated (see e.g. Haferkamp et al. (1998)). So far, there is only little detailed quantitative information on the release of particulate and gaseous emissions during laser cutting and ablation of CFRP, as well as regarding the requirements for adequate measures concerning occupational safety and environmental protection. For instance, it is not known if the fumes contain fibrous particles which may behave similar to asbestos fibers in the lung tissue due to their geometry. In Germany, environmental protection is regulated by the law BImSchG (2013) and the corresponding regulation TA Luft (2002). Here, threshold limit values for hazardous substances in the exhaust air are defined, and emissions have to be reduced accordingly. Apart from the German law ArbSchG (2013), the European regulation REACH (2012) is the basis for the employees' protection against hazardous substances. The German law ChemG (2013) and the regulation GefStoffV (2013) refer to this European regulation. The exposure limit values for hazardous substances in the air at the workplace are listed in the technical rule TRGS 900 (2014). The values have to be met by adequate measures, starting from technical measures to reduce hazardous substances, to organizational measures such as preventing access to the working area, if technical measures are not sufficient, and finally to personal protective equipment for employees who have to stay in the working area in spite of hazardous substances, which cannot be reduced sufficiently due to technical reasons.

In this paper, initial investigations concerning the systematic qualitative and quantitative analysis of particulate and gaseous process emissions during laser cutting of exemplary CFRP materials are presented, taking into account the process conditions in terms of the cutting strategy. The aim was to evaluate the total emission rates of potentially dangerous organic components, the amounts of emitted particles, and the occurrence of toxicologically critical fibrous particle morphologies. The results shall be used to assess the potential hazards, to define the necessity of protective measures, and to develop strategies for adequate process management and handling of the emissions. The concentrations of the organic gases and particles and the particle morphologies in the exhaust air were measured using well-established analytical methods and commercially available instrumentation, such as flame ionization detection, infrared sensor technology, electrical low-pressure cascade impaction, and scanning electron microscopy.

2. Experimental

For the laser cutting experiments, CFRP samples of $b = 3.5$ mm thickness with thermosetting epoxy matrix (CF-Epoxy) and $b = 2.2$ mm with thermoplastic polyphenylene sulfide matrix (CF-PPS) were used (Table 1). The experiments were performed using a new 1.5 kW single-mode continuous-wave fiber laser system (type FL015C, ROFIN-SINAR Laser GmbH, Hamburg, Germany). The radiation was guided through an optical fibre to a galvanometer scanner (type intelliSCAN 25, SCANLAB AG, Puchheim, Germany), equipped with an F-Theta plane-field lens providing a focal length of 340 mm, resulting in a focal diameter of approximately 70 µm. Using this scanner, quadratic contours of 20 x 20 mm^2 with rounded edges, corresponding to contour lengths of 71.4 mm, were generated on the work piece surface.

Table 1. CFRP material characteristics.

Material	Fabric	Thickness *b* (*mm*)	Number of layers	Fiber orientation
CF-Epoxy	non-crimp fabric	3.5	11	$[(0,90)_2,0,\overline{90}]_S$
CF-PPS	5-harness satin weave	2.2	7	$[0,45,0,45,90,45,90]_T$

In order to improve the cutting quality compared to conventional contour cutting, the strategy was to reduce the heat energy input into the work piece by multipass processing. The laser beam was moved several times along the same contour with relatively high speed, each time ablating a certain amount of material, until the CFRP plate was cut completely. In addition, the order in which the quadratic contours were cut was staggered in order to maximize the cooling time of the material between the passes. A further reduction of the heat development could be achieved by defined breaks between consecutive passes to enable additional intermediate cooling-down phases. The laser power was set to the system maximum of 1.5 kW, and the energy per length was kept constant at 37.5 kJ/m. The scanning speed v_s of the laser beam and the number of passes n were adapted according to the process strategy and the material considered. An overview of the experiments is given in Table 2. The temperature distribution during the cutting process was observed with a thermocamera (type InfraTec PIR uc 180, InfraTec GmbH, Dresden, Germany), that was equipped with a telephoto lens with a focal length of 36 mm.

In order to analyze the process emissions, a specific quasi-rectangular funnel was placed close to the processed work piece (see Fig. 1) to collect the emitted fumes as completely as possible. The exhaust system worked with a volume flow of 2,500 m^3/h. Using a standard aerosol (Dräger Safety AG & Co. KGaA, Lübeck, Germany), the capture efficiency was determined to about 90%. Fumes capturing was supported by cross jets that blew compressed nitrogen across the CFRP sample in order to deflect the emissions directly into the funnel (see Fig. 1). The nitrogen also served as coolant and prevented the CFRP material from oxidation. The particle size distribution was measured in a linear part of the exhaust pipe, where a turbulent flow without notable disturbances could be assumed and isokinetic sampling was possible. Instead of a gravimetric measurement according to VDI 2066 (2006), an electrical low-pressure cascade impactor (ELPI™, Dekati, Kangasala, Finland), was used to enable online control of the results. To achieve stable measurement signals during the cutting process, an emission collection time of at least two minutes was required. Due to the fact that the cutting time for a single square was much shorter than two seconds, a series of quadratic contours was irradiated in the course of one process cycle, as indicated above.

Table 2. Scanning speed v_s of the laser beam dependent on the process strategy and the material used (n.a.: not applicable).

Material	Number of passes *n*	Scanning speed v_s (*m/min*)	Duration per pass (*seconds*)	Duration per break (*seconds*)	Effective cutting speed (*mm/s*)
CF-Epoxy	1	2.4	1.78	n.a.	39.4
CF-Epoxy	8	19.2	0.22	0.0	35.5
CF-Epoxy	8	19.2	0.22	2.0	4.0
CF-PPS	1	2.4	1.78	n.a.	39.3
CF-PPS	6	14.4	0.30	0.0	36.1
CF-PPS	6	14.4	0.30	2.0	5.1

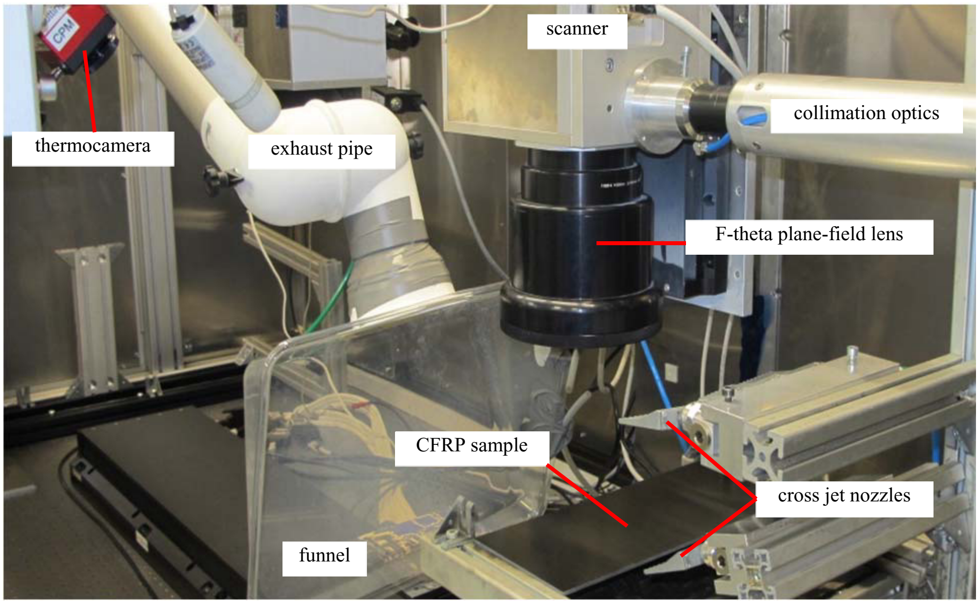

Fig. 1. Experimental setup for multipass cutting of CFRP samples with funnel to capture the emissions.

The total concentration of organic gases (volatile organic compounds – VOCs) was measured online using a flame ionization detector (FID) for mobile use (type SmartFID, ErsaTec GmbH, Barsinghausen, Germany). To avoid contamination with particles, the FID was equipped with an adequate particle filter. Simultaneously, the concentrations of the important inorganic gases carbon monoxide (CO), carbon dioxide (CO_2), and nitrogen oxide (NO_x) were determined with a spectroscopic detector (type Polytector II G750, GfG Gesellschaft für Gerätebau mbH, Dortmund, Germany). In an accredited laboratory (ProChem GmbH, Hildesheim, Germany), specific chemical analyses of the collected particles, serving as adsorbents for low-volatile organic species, gave the amount of polycyclic aromatic hydrocarbons (PAH). Further details regarding the quantitative composition of the organic gases will be investigated in future experiments using different analytical methods. So far, a qualitative determination of the most important components was performed in the course of a so-called emission prognosis, using a CO_2 laser to pyrolize small CFRP samples and a gas chromatography / mass spectrometry (GC/MS) system (type Varian Saturn® 2000, Agilent Technologies Deutschland GmbH, Böblingen, Germany), to identify the released compounds.

3. Results and discussion

The laser-induced damage was quantified by software-aided area measurement of the respective HAZ using micrographs of cross sections prepared from the laser-cut structures. Dividing the measured HAZ area by the material thickness, an average width of the HAZ was calculated (see Bluemel et al. (2012)). Consistently beginning at the cutting kerf, different HAZ types can be described, depending on the matrix material and the temperature reached. *HAZ1* is the charred area adjacent to the cutting kerf where the matrix material is assumed to be evaporated completely. Next to this, the decomposition temperature of the polymer matrix is exceeded, which leads to material deterioration in the area of *HAZ2*. The third area of *HAZ3* can only be observed for thermoplastic matrix materials. Here, the melting temperature of the thermoplastic matrix is reached or exceeded. At the same time this temperature exceeds the vaporization temperature of volatiles (e.g. water), causing porosity. In order to obtain an acceptable statistical certainty, the measurements were repeated 6 times, respectively, using different specimens for all measurements. These data were then used to calculate mean values as well as standard deviations.

As expected, the cutting strategy and thus the heat development in the process zone is a critical factor with respect to the cutting quality. This can clearly be shown by the pictures of the cross sections prepared (Fig. 2 (b)) and the corresponding results of the HAZ measurements (Fig. 2 (a)). Regarding CF-PPS, HAZ1, HAZ2 and HAZ3, all decrease if the process is switched from contour to multipass cutting, while only HAZ3 decreases further if breaks are added as cool-down periods between the single passes. Looking at CF-Epoxy, HAZ2 obviously decreases from contour to multipass cutting and finally to multipass cutting with breaks, whereas HAZ1 only decreases from contour to multipass cutting, while staying on a constant level if additional breaks are inserted between the passes.

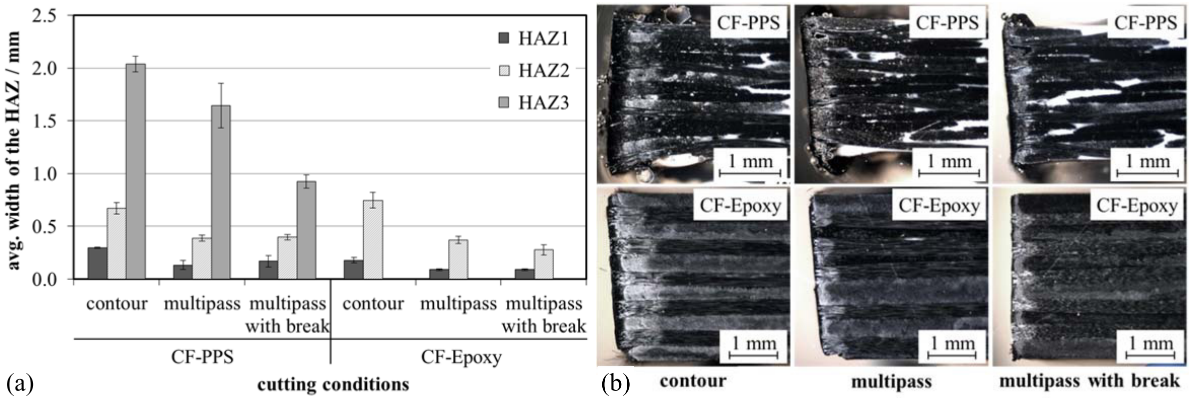

Fig. 2. Average width of the HAZs (a) and cross sections (b) of CF-PPS and CF-Epoxy cut with different strategies.

The variations in the overall heat development due to the different cutting strategies can also be demonstrated by the thermographic measurements performed. In this context, it should be noted that all temperatures given here are approximate values, because a comprehensive calibration was not performed. The emission coefficient of the CFRP materials was set to 0.95, which should be an adequate approximation. Thus, only tendencies can be shown. In order to understand the effects resulting from the different cutting strategies, the heat development was monitored in the center of single quadratic contours, located in the middle of the multiple-cut CFRP samples as shown in Fig. 3 (a). Here, falsifications due to outshining by the plasma development could be largely avoided. In Fig. 3 (b), the approximated maximum temperatures at the respective measurement points are compared for the three cutting strategies considered. It can be seen that there is a general temperature decrease and thus a reduced heat input, if multipass cutting is supplemented by additional breaks of 2 seconds between consecutive passes. Obviously, these additional breaks enable significant heat dissipation, leading to reduced damaging of the composite structure. Understanding the influence of the change from contour to multipass cutting without additional breaks is more complex. Considering contour cutting, a notable difference between CF-Epoxy and CF-PPS can be observed: the heat dissipation for CF-Epoxy is apparently much larger than for CF-PPS. One reason may be that the CF-Epoxy samples are significantly thicker than the CF-PPS samples, resulting in a higher heat capacity per surface element.

Furthermore, the varying fiber reinforcement structures and fiber volume contents contribute to different heat conductivities. If the strategy is changed from contour to multipass cutting and thus the heat input is repeated several times, both factors in combination with the increasing barriers represented by the cutting kerfs obviously lead to a concentration of the heat within the quadratic contour for CF-Epoxy, whereas the heat dissipation improves for CF-PPS. This topic is under thorough investigation. Finally, the more severe damage near the cutting edges of both materials during contour cutting in comparison to multipass cutting can be explained by the larger local overheating.

The fumes emitted during laser cutting of CFRP contain different organic substances which are of toxicological relevance. In the following sections, the different categories of hazardous substances are discussed.

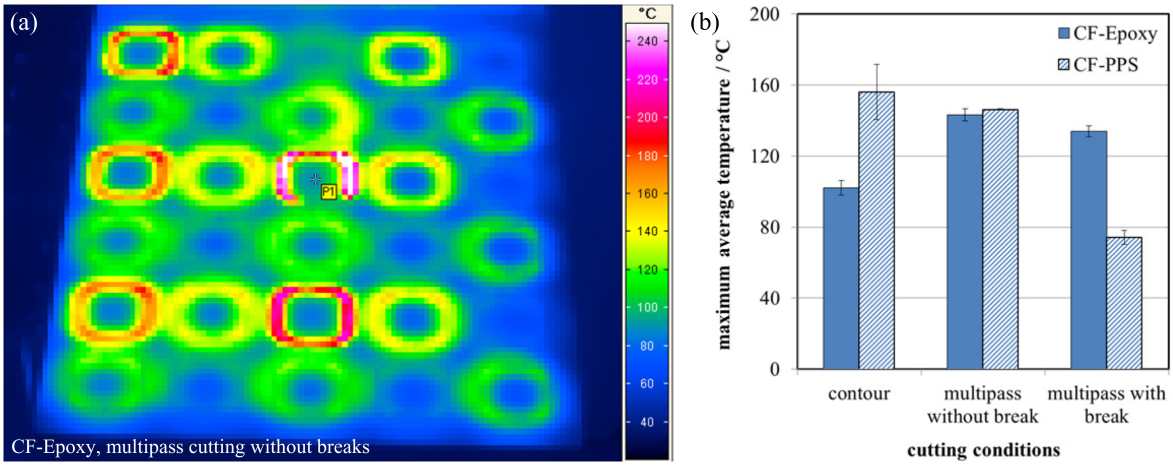

Fig. 3. Thermographic measurements: (a) exemplary thermographic picture, recorded during multipass cutting of CF-Epoxy without breaks (P1 denotes the point of measurement on the sample surface); (b) averaged maximum temperatures in the center of quadratic contours, chosen for the experiments according to Table 2. Note: temperatures given in °C are approximate values as no calibration was performed.

3.1. Emitted particles

The total aerosol concentrations were calculated from the ELPI measurements (see section 2). The aerosols were not separated into inorganic and organic components. In fact, they represent the part of the fumes that was generated due to evaporation of the different material components. The measured particle mass concentrations, the specific emission rates referred to the total kerf length generated during the complete laser cutting process, as well as the aerodynamic diameters of the emitted particles are given in Table 3.

Table 3. Averaged emission rates and aerodynamic diameters of the particles emitted during laser cutting of the CFRP materials regarded (*: referred to the total cutting kerf length, #: American Conference of Governmental Industrial Hygienists (respirable portion), Reist (1993)).

Material	Cutting process	Concentration (*mg/m³*)	Emission rate (*mg/s*)	Specific emission rate* (*mg/mm*)	Median diameter (μm)	Alveolar portion acc. to ACGIH#
CF-Epoxy	contour	24.9	5.67	0.144	6.04	36.9%
CF-Epoxy	multipass	12.6	2.87	0.081	5.87	39.5%
CF-Epoxy	multipass with breaks	1.0	0.23	0.058	5.50	44.4%
CF-PPS	contour	3.7	0.84	0.021	5.37	46.1%
CF-PPS	multipass	6.9	1.56	0.043	6.12	35.5%
CF-PPS	multipass with breaks	1.7	0.38	0.074	5.79	41.0%

As is evident from the results, the specific particle emission rate decreases from contour cutting to multipass cutting with additional breaks in the case of CF-Epoxy, whereas it increases in the case of CF-PPS. This is a significant difference between the two materials investigated in this work and clearly demonstrates that it is necessary to examine each laser process separately with respect to the potentially hazardous emissions, using optimized processing parameters. Future investigations will show if the observed behavior is a result of the matrix type or of other material properties. All measured particle size distributions were polydisperse and showed a minor mass frequency maximum close to an aerodynamic diameter of 700 nm (see sample curves in Fig. 4).

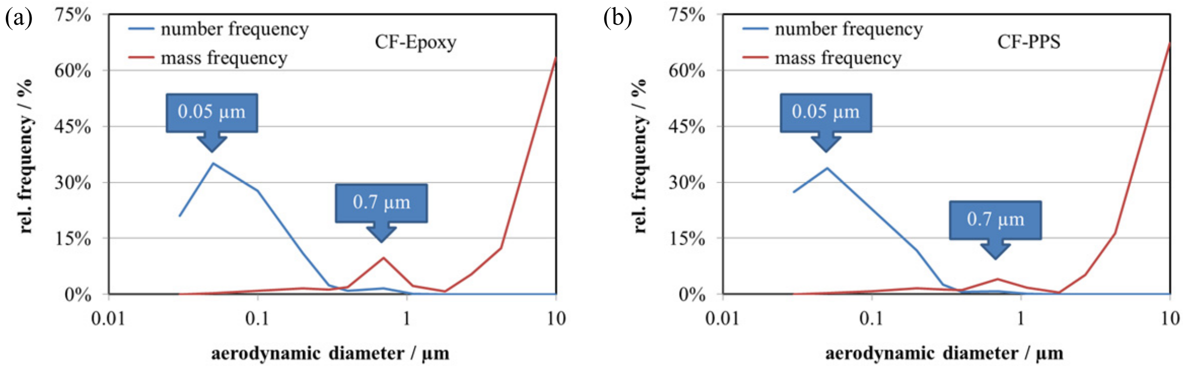

Fig. 4. Particle size distributions of aerosols emitted during multipass cutting with additional breaks ((a) CF-Epoxy and (b) CF-PPS).

The calculated median diameters were in the range from 530 to 620 nm. Therefore, the alveolar portion was smaller than 50% for all experiments performed according to Reist (1993). However, the particle size distribution curves indicate that a large portion of the emitted particulate mass can be found in relatively few large particles with aerodynamic diameters of about 10 µm. The number frequencies are slightly increasing at the corresponding ELPI stage. Scanning Electron Microscope (SEM) pictures recorded of gold filter foils, used together with a specific sampling head to capture fibers and fiber segments, confirmed that a notable amount of relatively large carbon-rich particles was emitted during the cutting processes. However, it is not yet clear if the carbon fibers and fiber segments caused falsifications at the ELPI stages due to their electrical conductivity. Nevertheless, the different CFRP materials and cutting strategies cannot be distinguished using the particle size distribution curves.

Exemplary SEM pictures of gold filter foils, covered with fiber segments and particles, are shown in Fig. 5. Here, a distinct difference between the two CFRP materials CF-Epoxy (Fig. 5 (a) and (b)) and CF-PPS (Fig. 5 (c) and (d)) is found Laser cutting of CF-Epoxy obviously generated significantly longer fibers (longer than 600 µm) than laser cutting of CF-PPS, particularly in case of multipass cutting with additional breaks. Obviously, the contour processes generally resulted in less and shorter fiber segments than multipass cutting with breaks. However, this finding has to be interpreted with caution as in fact, the overall laser energy input was kept constant for all experiments, whereas the capturing time differed strongly between the cutting strategies. According to the World Health Organization (WHO), fibers with a diameter < 3 µm, a length > 5 µm and a length-to-diameter ratio $> 3 : 1$ can penetrate the lower respiratory tract (so-called WHO fibers). Almost all fibers and fiber segments found on the gold filter foils have a diameter significantly larger than 3 µm and are therefore not classified as WHO fibers. According to the CFRP producers, the fiber diameter is in the range of 7 µm for both CFRP materials (carbon fibers type T-300).

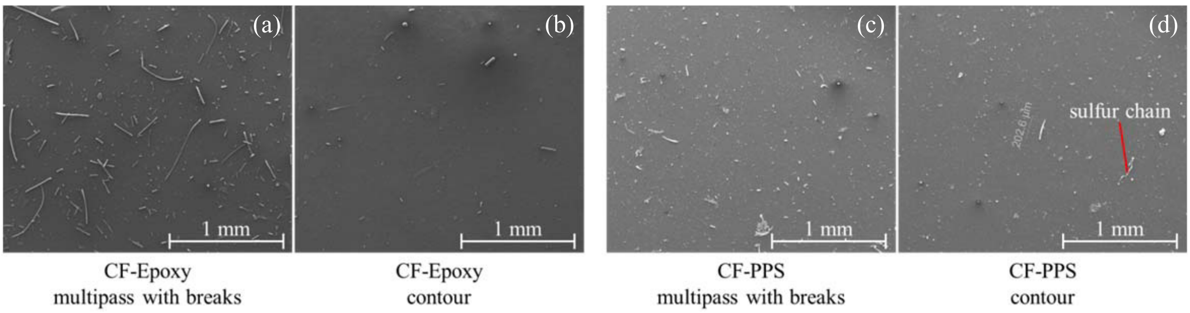

Fig. 5. SEM pictures of gold filter foils used to collect fibers and fiber segments during CFRP laser cutting. (a) CF-Epoxy, mulitpass cutting with breaks; (b) CF-Epoxy, contour cutting; (c) CF-PPS, multipass cutting with breaks; (d) CF-PPS, contour cutting.

Using energy-dispersive X-ray spectroscopy (EDX), it could be proven that almost all fiber segments and also the large spherical particles in case of cutting CF-Epoxy were composed of carbon. In contrast, a part of the fiber-like objects found on the gold filter foils during CF-PPS cutting were composed of sulfur. High-resolution pictures of these sulfur objects showed chains of agglomerated spherical particles. This finding could be expected because of the sulfur content of the PPS matrix. Unexpectedly, the EDX analysis of the CF-Epoxy emissions indicated a certain chlorine content in the captured particles. Finally, this could be explained by the use of epichlorohydrin in the course of the CF-Epoxy production process.

The chemical analysis of the emitted particles did not give any evidence for the formation of PAH, adsorbed at the particle surfaces, to a relevant degree during laser cutting of CF-Epoxy or CF-PPS. This result must not be transferred to other processes or materials, as recent investigations indicate the existence of PAH in the case of cutting specific CFRP materials with alternative matrices using a pulsed near-infrared laser system.

3.2. Organic gases

As described in Section 2, the total gaseous hydrocarbon concentrations in the exhaust fumes were detected with a flame ionization detector. The concentrations were shown as propane equivalent values in volume parts per million (ppm) as a function of time. According to ErsaTec (2013), the carbon concentrations in mg_C/m^3 are calculated from these propane equivalent values by multiplication by the constant factor 1.608 $mg_C/(m^3 \cdot ppm)$. The values calculated for the different experiments in the course of this work are listed in Table 4.

Table 4. Averaged emission rates of total hydrocarbons for the processed CFRP materials (*: referred to the total cutting kerf length).

Material	Cutting process	VOC concentration (mg_C/m^3)	Emission rate (mg_C/s)	Specific emission rate* (mg_C/mm)
CF-Epoxy	contour	14.8	3.37	0.086
CF-Epoxy	multipass	12.7	2.89	0.081
CF-Epoxy	multipass with breaks	2.8	0.64	0.161
CF-PPS	contour	7.5	1.69	0.043
CF-PPS	multipass	9.1	2.05	0.057
CF-PPS	multipass with breaks	2.3	0.53	0.104

In all cutting experiments, relevant concentrations of total hydrocarbons were found. The mean values were in a range of up to 15 mg_C/m^3. The maximum concentration measured as a peak during contour cutting of CF-Epoxy was 24.9 mg_C/m^3. For CF-Epoxy as well as for CF-PPS, the measurements yielded the largest specific emission rates in the case of multipass cutting with additional breaks. In the case of contour as well as multipass cutting without additional breaks, the specific emission rates for CF-Epoxy and CF-PPS amounted to about 50% of the respective emission rate for multipass cutting with additional breaks. The differences between the total specific emission rates for the two CFRP materials are interpreted as a consequence of the different material thicknesses. Considering the VOC emissions, a distinct difference between the behavior of CF-Epoxy and CF-PPS could not be observed.

Exemplary gas chromatograms of CF-Epoxy and CF-PPS, measured after pyrolysis of small material samples using a CO_2 laser, are shown in Fig. 6. The peak positions in these diagrams are characteristic for the specific thermosetting epoxy and for thermoplastic PPS, respectively, so that the chromatograms may serve as a form of identification instrument. Thus, the materials investigated in the course of this work can be clearly distinguished from CFRP materials with polyamide or polyetherimide matrices, for example.

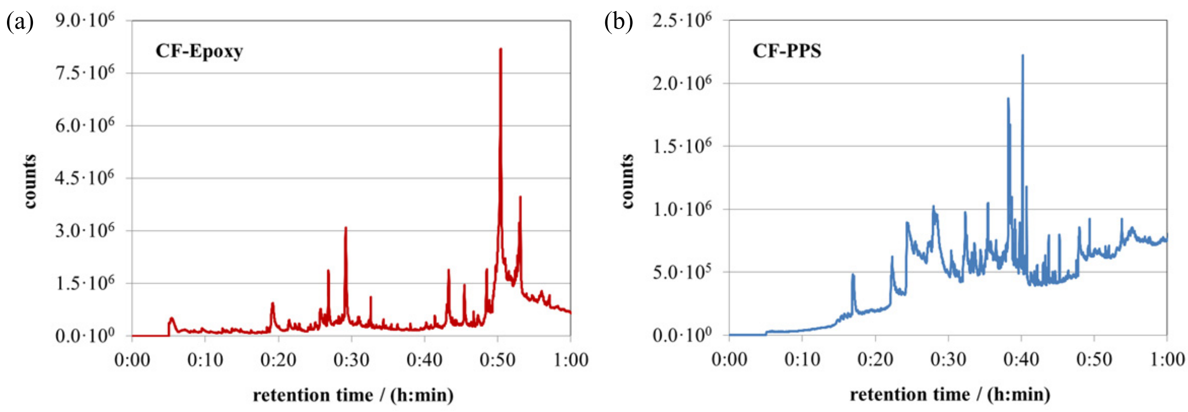

Fig. 6. Typical gas chromatograms of CF-Epoxy (a) and CF-PPS (b), pyrolized with a CO_2 laser, respectively. Note: y axes have different scales.

In Table 5, important organic components, found to a notable degree by means of mass spectrometry after pyrolysis of the two CFRP materials considered, are listed. The evaluation was performed according to NIST (2009). It should be noted that a quantitative transfer of the measured percentages to the CFRP cutting processes performed in the course of this work is not realistic. The listing merely gives some of the most important substances which are expected to be emitted during the cutting processes.

Table 5. Important components of CFRP-epoxy and CFRP-PPS determined in the course of the emission prognosis.

Organic component found by GC/MS	CFRP-epoxy		CFRP-PPS	
	Retention time (min)	Percentage	Retention time (min)	Percentage
bisphenol A	48.1	41.0%	47.9	23.4%
1,22-docosanediol	45.0	20.3%	44.7	1.8%
N,N-dimethyl-m-toluidine	27.9	5.7%	–	–
phenol	18.4	4.0%	–	–
4-(1-methyl-1-phenylethyl)-phenol	41.2	2.4%	–	–
2-(1-methylethyl)-phenol	25.6	2.0%	–	–
1,2,3,5-tetramethyl-benzene	27.8	1.6%	27.7	1.0%
diphenyl sulfide	–	–	34.7	28.4%
benzenethiol	–	–	16.9	24.4%
diphenyl disulfide	–	–	42.6	3.5%
1,2,3,4-tetrahydro-1-phenyl-naphthalene	–	–	37.2	2.6%
1-eicosanol	–	–	39.1	2.1%

Bisphenol A was found in both pyrolysis experiments. This substance belongs to the diphenylmethane derivatives and shall be classified as toxic for reproduction according to the European Chemicals Agency (ECHA), although this classification is not yet finalized. Apart from this, different long-chained alcohols as well as phenol and benzene derivatives were found in case of CF-Epoxy, whereas different sulfur compounds were measured in the case of CF-PPS, as expected. A quantization of these hazardous compounds for the real laser cutting process will be performed in future investigations.

3.3. Inorganic gases

The concentrations of CO, CO_2, and NO_x, measured as volume parts during the different CFRP laser cutting processes as described in section 2 and transformed to mass concentrations in case of CO and NO_x (measured as NO_2) are listed in Table 6.

Table 6. Concentrations of CO, CO_2, and NO_x in the exhaust air of the CFRP laser cutting processes investigated.

Material	Cutting process	CO (mg_{CO}/m^3)	CO_2 (*vol.-%*)	NO_x (mg_{NO2}/m^3)$^+$
CF-Epoxy	contour	52	0.9	< 2
CF-Epoxy	multipass	26	0.6	< 2
CF-Epoxy	multipass with breaks	< 1	0.04	< 2
CF-PPS	contour	14	0.07	< 2
CF-PPS	multipass	27	0.08	< 2
CF-PPS	multipass with breaks	< 1	0.04	< 2

$^+$: NO_x measured as NO_2

Obviously, notable concentrations of highly toxic CO were emitted unless a multipass cutting strategy with additional breaks was chosen. According to TA Luft, there is no threshold limit value for CO in the exhaust air. However, CO is highly toxic, documented by an exposure limit value of 35 mg/m^3 for the air at the workplace according to TRGS 900 (2014). Thus, the accumulation of CO in the air at the workplace must be strictly prevented. The exposure limit value would have been exceeded rapidly during the contour cutting of CF-Epoxy without the capturing of exhaust gas.

The CO_2 concentration in the exhaust air is significantly higher than the typical concentration in atmospheric air (0.03 – 0.04 vol.-% depending on the conditions). However, the observed increase is of less relevance as the hazardous potential of CO_2 is comparatively small. Finally, NO_x was not found to a significant degree, neither during contour nor multipass cutting, which indicates relatively moderate temperature regimes in the corresponding process zones or small high-temperature residence times of the oxidizable components (the formation of nitric oxides from the elements according to the so-called Zeldovic mechanism is an endothermic reaction with a relatively high activation energy; see also e.g. Beychok (1973) and Schaefer and van Basshuysen (1993)).

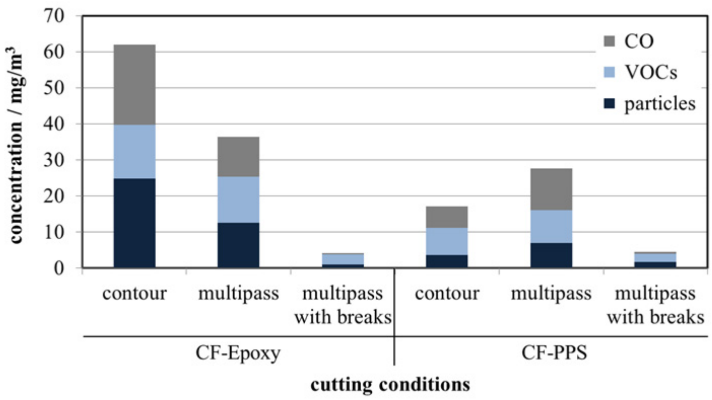

Fig. 7. Overview of the concentrations of hazardous substances measured in the exhaust air during laser cutting of CF-Epoxy and CF-PPS with the three process strategies considered here. Note: in contrast to Table 6, CO concentrations are referred to the respective carbon content in mg_C/m^3 to allow for a better comparability with the VOC concentrations given in Table 4.

In Fig. 7, the concentrations of hazardous substances measured in the exhaust air during the different cutting processes which were performed with CF-Epoxy and CF-PPS are compared. This figure summarizes the dependencies of the process emissions on the cutting strategies, which are finally a result of the varying energy input during the cutting processes as discussed above. Accordingly, multipass cutting with additional breaks is clearly favored for CFRP cutting as it yields the best cutting results and causes the smallest emission rates at the same time.

4. Conclusions

The experiments presented in this work have proven that relevant amounts of VOCs and carbon monoxide as well as of spherical and fibrous particles are emitted during laser cutting of different CFRP materials, namely carbon fiber composites with thermosetting epoxy and with thermoplastic PPS matrix, respectively. Obviously, choosing an optimized cutting strategy for these materials, i.e. multipass cutting with additional breaks to allow for sufficiently long intermediate cooling-down phases of the material, helps not only to improve the cutting qualities considerably, but also to reduce the hazardous emissions. Using a processing strategy that keeps the overall heat input into the CFRP workpiece small, threshold limit values in the exhaust air according to TA Luft (2002) can be met depending on the amount of CFRP material processed per time interval. The processing results will be implemented into the LZH Laser Safety Database (1997) to provide this information to the interested public. Future investigations will have to show to which extent the findings can be transferred to other CFRP materials.

Filtering the exhaust air with a surface filter to remove the aerosols, and then with an activated charcoal filter to absorb the VOCs and the carbon monoxide, ensures protection of the environment adequately. These methods of cleaning the exhaust air are well-established. Especially in case of CFRP, catalytic cleaning appears to be a promising alternative, as all components of the composite materials can potentially be transformed to less hazardous substances such as CO_2 and H_2O and thus no hazardous residuals have to be dealt with. This will be investigated in the course of the new German research project HoLQueSt 3D, funded by the German Ministry of Education and Research (BMBF). Here, CFRP laser cutting with short-pulsed high-power disk lasers, providing pulse durations in the nanosecond range, will be used to achieve high cutting qualities and at the same time high processing speeds.

Nevertheless, it is necessary to remove the hazardous substances from the air at the workplace during CFRP laser cutting or ablation. Otherwise, relevant exposure limit values according to TRGS 900 (2014) will probably be exceeded within short time intervals. This is valid not only for the inorganic carbon monoxide, but also for VOCs such as bishphenol A, phenol and benzene derivates as well as different sulfur compounds in the case of CF-PPS. Particular attention was paid to the emitted fibrous particles. Almost all fiber segments found in the emitted particulate matter have diameters in the range of those of the original fibers (here about 7 µm). Therefore, they are not classified according to the WHO definition of respirable fibers, i.e. they cannot easily be incorporated into pulmonary alveoli. If carbon fibers of diameters below 3 µm are used for the production of CFRP parts, the potential respirability and biopersistence of fiber segments emitted during CFRP laser processing have to be considered in detail. Biopersistence is a key factor for fiber pathogenicity (see e.g. Donaldson and Tran (2004)). According to Lockey and Ross (2011), the existing knowledge considering such WHO carbon fibers is still inadequate to provide definite answers as to their potential for causing adverse health effects.

The performed mass-spectrometric analyses indicate the emission of hazardous substances to a significant degree for which threshold limit values are defined. Nevertheless, the calculated emission rates lead to the assumption that adequate capturing and exhausting measures will allow for minimizing the corresponding hazardous concentrations in the air at the workplace, so that the exposure limit values can be met. However, a recirculating-air operation is not allowed due to the minimization requirement according to GefStoffV (2013) if carcinogenic substances of category 1 or 2 occur, unless at least 50% of fresh, non-contaminated air is supplied.

Acknowledgements

Major parts of the work presented here were performed in the course of the German national research projects “Cost Effective Laser Cutting Of Thermoplastic Composite Materials For High Performance Applications” (CO-COMPACT, reference no. 01QE1232B), funded by the Federal Ministry of Education and Research and supported by the project management organization German Aerospace Center (DLR e.V.), and “Emissions during the laser processing of plastics" (AiF-IGF reference no. 433 ZN), funded by the Federal Ministry for Economic Affairs and Energy and supported by the project management organization AiF German Federation of Industrial Research Associations "Otto von Guericke" e.V., what is gratefully acknowledged. Furthermore, the authors thank ROFIN-SINAR Laser GmbH, Hamburg, Germany, for their invaluable support of the work by temporary loan of their 1.5 kW single-mode fiber laser system.

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