Supplementary Material

Impact of Thermal Stress on Abrasive Dust from a Carbon Fiber Reinforced Concrete Composite

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1. Dry-Cutting Simulation

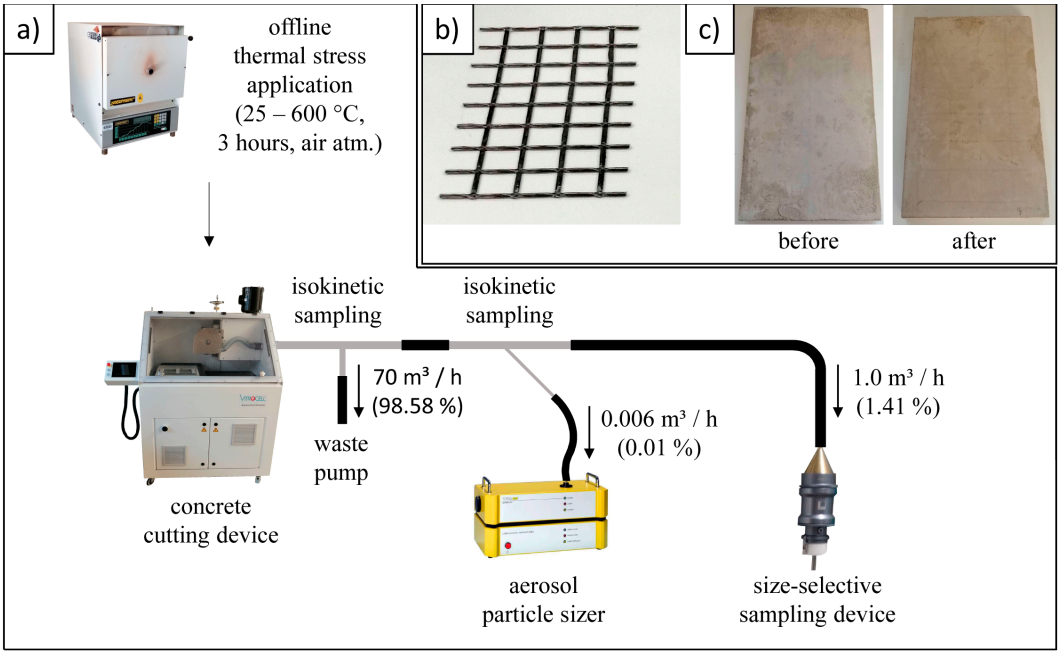


Figure S1. Illustration of the dry-cutting simulation arrangement including an offline thermal stress application step based on the arrangement described earlier by Koch et al. (2021) [1] (**a**) and pictures of the C³ reinforcement material (**b**) and a C³ sample before and after thermal exposure to 400 C (air atmosphere, 3 hours; **c**) The thermal exposure scenario ensured no cracks on the surface.

2. Homogenization of Reinforcement Materials

C³ reinforcement materials were isolated from thermally stressed concrete after a cooling period of 24 hours and homogenized using the cryomill prior to thermal analysis. The reinforcement materials were chopped into 5–10 mm long pieces and placed into a polycarbonate container together with a crushing rod. Afterward, the container was cooled in liquid nitrogen to –196 °C and crushed in two cycles of 2 minutes with a 1-minute break to obtain a homogenized powder. Homogenized reinforcement materials were stored at –20 °C until analysis.

3. Materials and Methods – Analytical Details

3.1. Pyrolysis Gas Chromatography – Mass Spectrometry

pyrolyzer:	model PY-2020iD, double-shot pyrolyzer, Frontier Laboratories
pyrolyzer program:	500°C, 1 min
gas chromatography:	SGE-BPX5 column ((30 m × 250 μm I.D. × 0.30 μm film) helium: 99.999% head pressure: 0.4 bar split: 1:10
gas chromatography program:	hold for 5 min at 40°C ramp to 330°C with 10 K/min hold for 10 min
mass spectrometry:	electron ionization (EI, 70 eV) quadrupole analyzer scan mode from *m*/*z* 40 to 500

3.2. Thermal Analysis – Mass Spectrometry

thermal analysis:	200 mL/min nitrogen (constant flow) hold 2 min isothermal at 20°C ramp to 600°C with 10 K/min hold 10 min at 600°C
transfer of evolved gases:	280°C interface 280°C transfer line (deactivated fused silica capillary, 0.53 mm ID)
mass spectrometry:	atmospheric pressure photoionization (APPI) Kr vacuum ultraviolet lamp (10/10.6 eV, 124/117 nm) Bruker Apex II ultra FTMS (7 T superconducting magnet, *m*/*z* 100 to 1000, two-second transient length (4M datapoints), resolving power: roughly 300,000 at *m*/*z* 400)

3. Organic Composition

Organic composition of reinforcement before cutting:

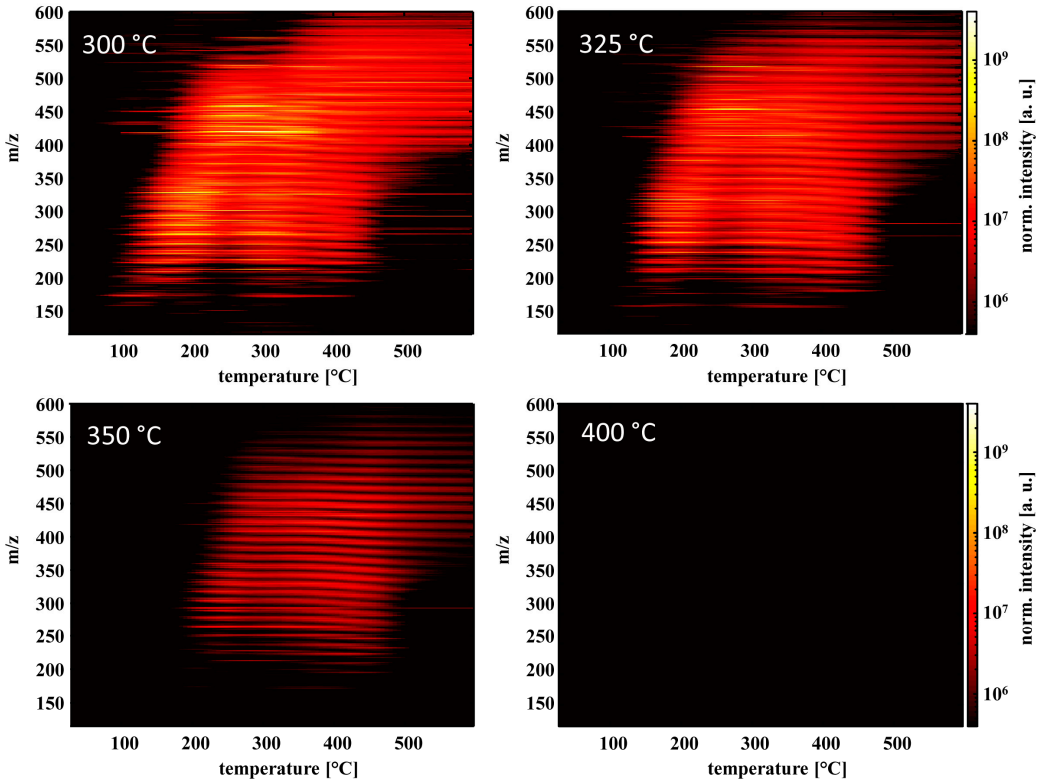


Figure S2. Comparison of the organic compositions of reinforcement materials mechanically separated from C³ exposed to elevated temperatures of 300, 325, 350, and 400 °C (air atmosphere, 3 hours) measured by TA-APPI-MS. With increasing exposure temperature, the intensities of the organic compounds decrease. At 400 °C, no organic compounds can be detected.

Organic composition of abrasive PM fractions $PM_{2.5}$ and PM_{10}

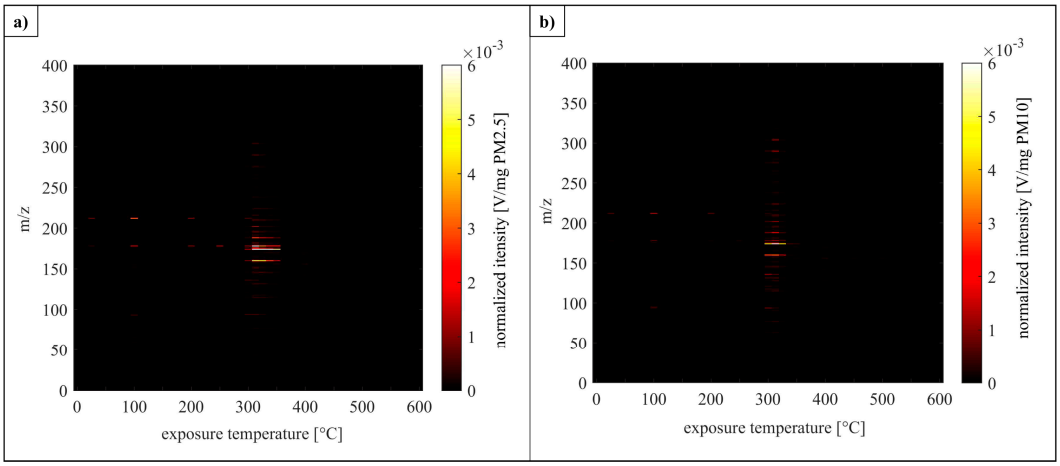


Figure S3. Averaged REMPI spectra of thermal desorption OC fraction (20-280 °C, OC1 + OC2) in $PM_{2.5}$ (**a**) and PM_{10} (**b**) released from dry-cutting of C³ exposed to elevated temperatures of 25–600 °C (air atmosphere, 3 hours) prior to abrasive machining. REMPI spectra were recorded at 14 distinct exposure temperatures.

3.1. Organic Composition of Reinforcement Before Cutting

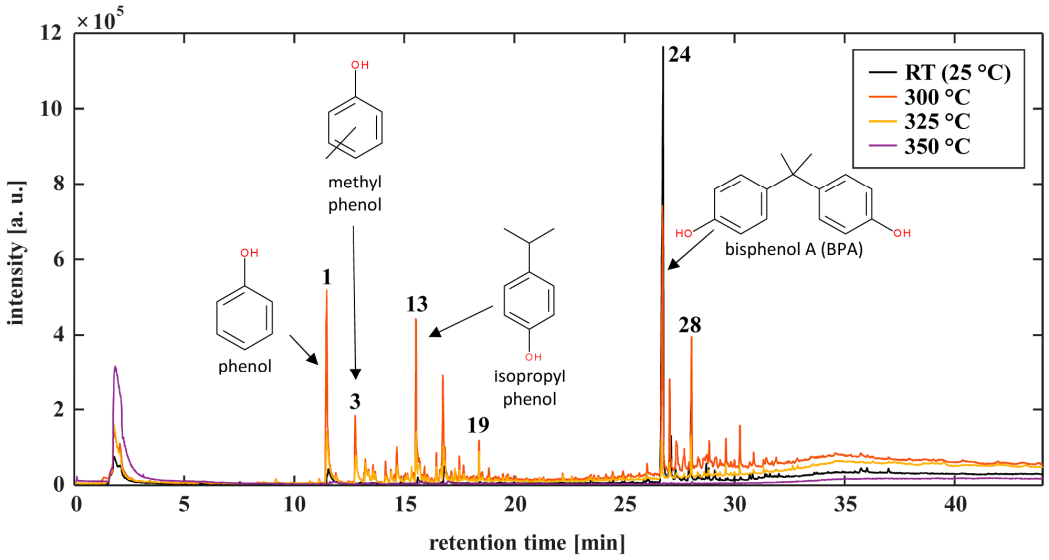


Figure S4. Total ion count (TIC) chromatogram of reinforcement material mechanically separated from C³ exposed to room temperature (RT, 25 °C), 300, 325, and 350 °C measured by Py-GC-EI-QMS. Highlighted peaks correspond to compounds summarized in Table S1. Magnified plots are illustrated in Figure S4 and S5.

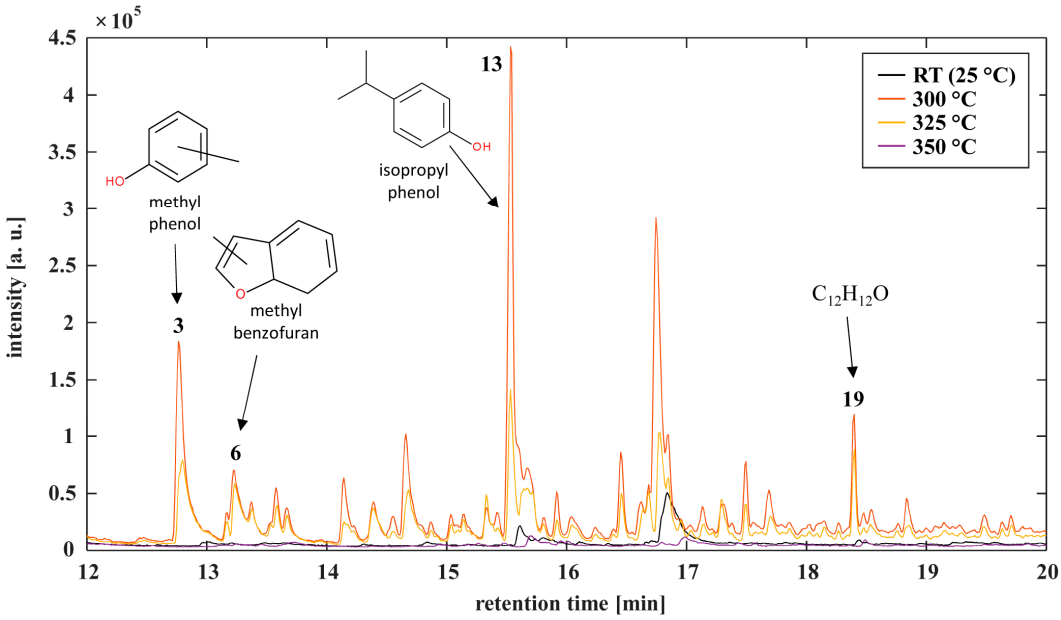


Figure S5. Magnified total ion count (TIC) chromatogram (12-20 min) of reinforcement material mechanically separated from C³ exposed to room temperature (RT, 25 °C), 300, 325, and 350 °C measured by Py-GC-EI-QMS. Several phenol derivatives, such as methyl phenol (**3**, 12.77 min), methyl benzofuran (**6**, 13.38 min) and isopropyl phenol (**13**, 15.34 min), are found due to pyrolysis during the thermal exposure period at 300 and 325 °C.

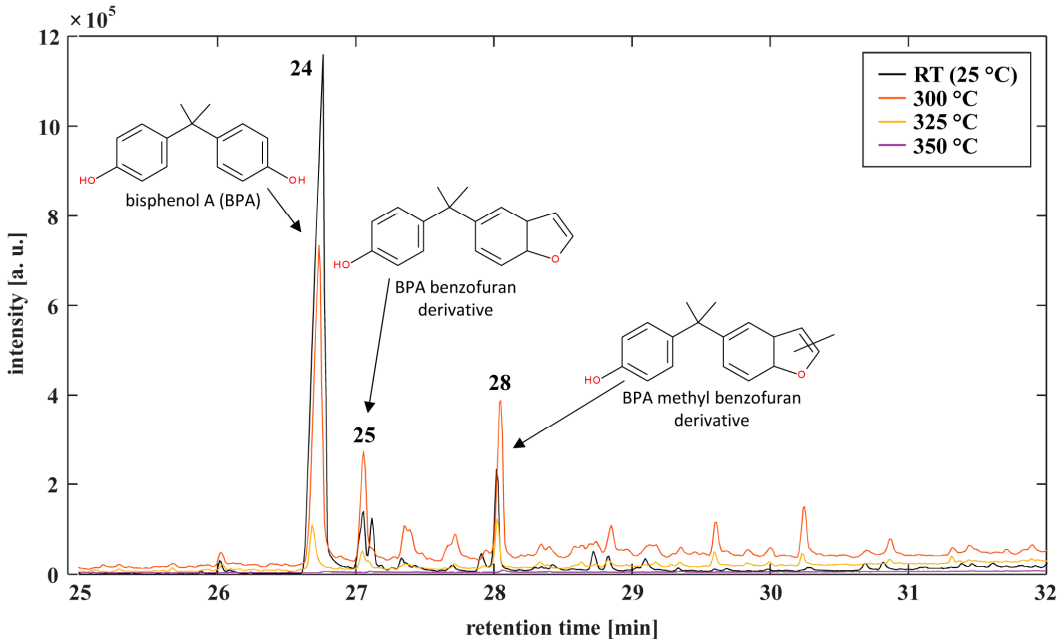
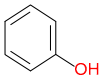
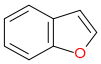
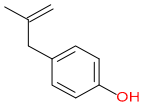
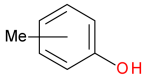
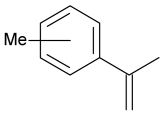
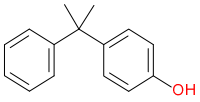
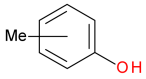
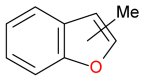
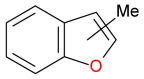
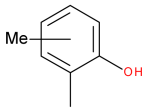
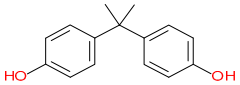
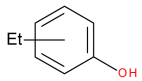
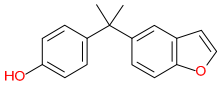
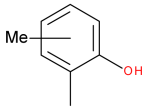
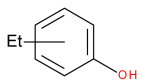
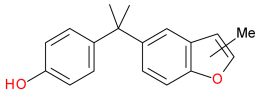
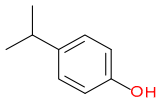
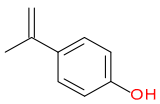


Figure S6. Magnified total ion count (TIC) chromatogram (25-32 min) of reinforcement material mechanically separated from C³ exposed to room temperature (RT, 25 °C), 300, 325, and 350 °C measured by Py-GC-EI-QMS. Several derivatives of bisphenol A (BPA, **24**, 26.74 min), such as a benzofuran derivative (**25**, 27.06 min) and a methylated benzofuran derivative (**28**, 28.05 min), are detected.

Table S1. Organic constituents in reinforcement materials mechanically separated from C³ materials exposed to 300–350 °C (air atmosphere, 3 hours) measured by Py-GC-EI-QMS. Species were assigned with NIST Library matching (NIST MS Search 2.0) and a match factor above 80 %.

#	identified substance	*m/z*	retention time [min]	#	identified substance	m/z	retention time [min]
1		94	11.48	**17**	$C_{12}H_{14}O$	174	17.49
2		118	11.62	**18**		148	17.70
3		108	12.77	**19**	$C_{12}H_{12}O$	172	18.40
4		132	13.17	**20**		212	23.49
5		108	13.23	**21**	$C_{15}H_{21}O_3$	250	24.48
6		132	13.38	**22**	$C_{14}H_{20}NO_2$	233	25.89
7		132	13.59	**23**	$C_{10}H_{25}N_3O_4$	250	26.04
8		122	13.67	**24**	 $C_{15}H_{16}O_2$	228	26.74
9		122	14.15	**25**	 $C_{17}H_{16}O_2$	252 [1]	27.06
10		122	14.39	**26**	$C_{16}H_{16}O_2$	240	27.12
11	unidentified		14.56	**27**	$C_{18}H_{20}O_2$	268	27.96
12		122	14.67	**28**	 $C_{18}H_{18}O_2$	266 [1]	28.05
13		136	15.34	**29**	$C_{19}H_{22}O$	266	28.76
14	$C_{11}H_{12}O$	160	15.92	**30**	$C_{18}H_{20}O_3$ / $C_{19}H_{24}O_2$	284	28.85
15		134	16.47	**31**	$C_{18}H_{22}O_3$	286	29.10
16	unidentified	-	16.75	**32**			

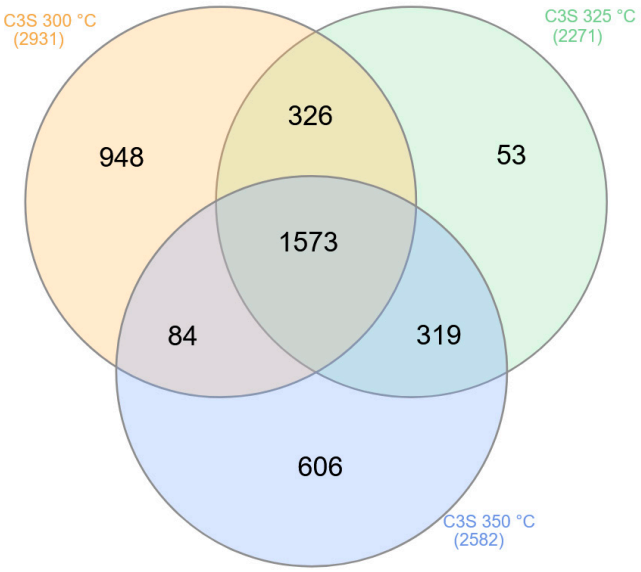


Figure S7. Venn analysis of the sum formula assignment found in the reinforcement materials mechanically separated from C³ thermally exposed to 300 (C3S 300 °C), 325 (C3S 325 °C), and 350 °C (C3S 350 °C). Most of the calculated sum formulae were found in all three samples (1573 of 3909 in total).

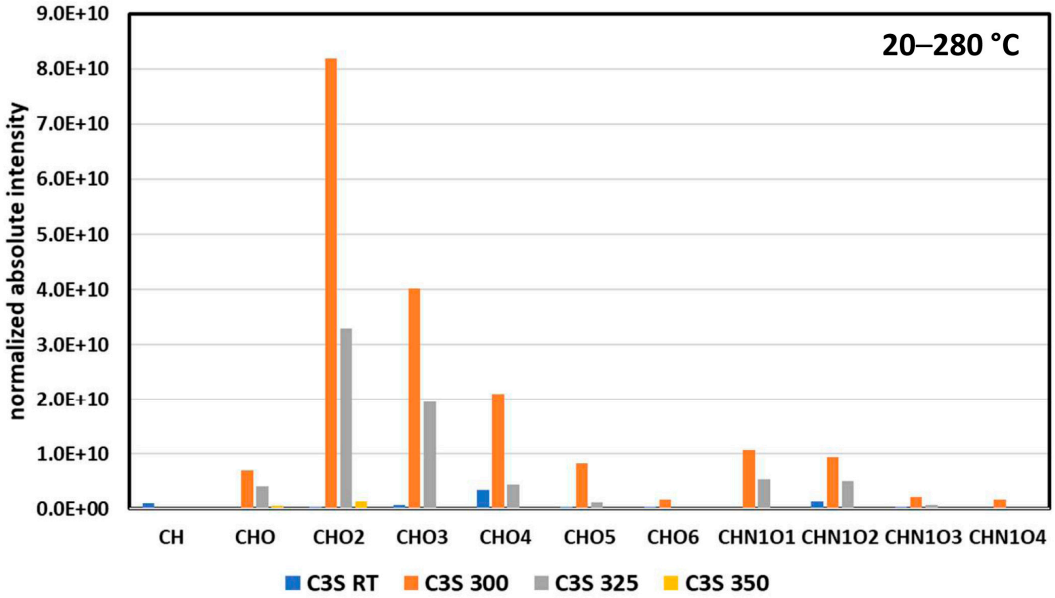


Figure S8. Absolute intensities of the individual compound classes grouped for the reinforcement materials mechanically separated from C³ exposed to room temperature (25 °C, C3S RT), 300 (C3S 300), 325 (C3S 325), and 350 °C (C3S 350) for 3 hours under air atmosphere in the thermal desorption regime (20-280 °C). Intensity is normalized to the sample mass.

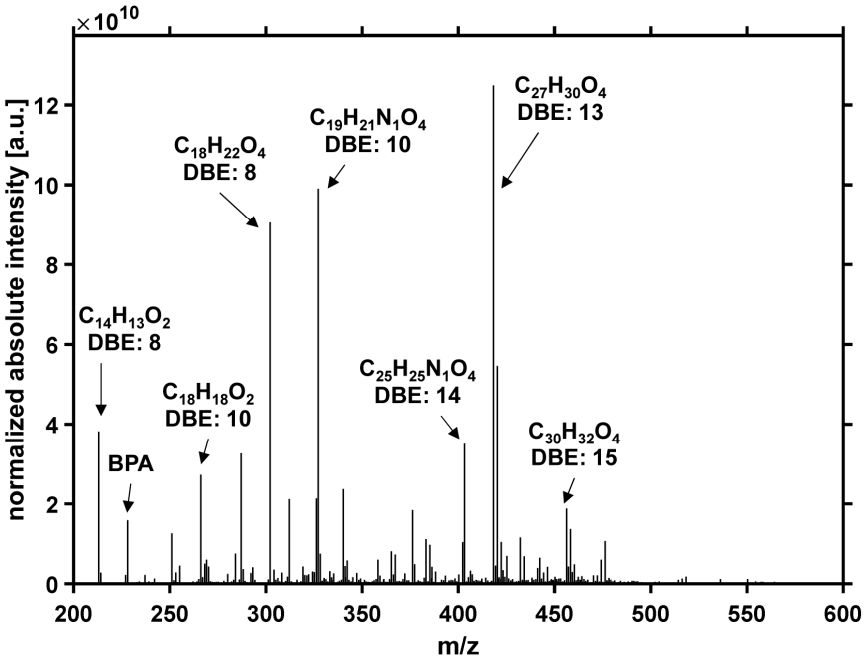


Figure S9. In-depth chemical characterization of the emitted gas mixture for the thermal analysis of reinforcement material mechanically separated from C³ exposed to room temperature (RT, 25 °C, air atmosphere, 3 hours) by APPI-MS. Average mass spectrometric response is normalized to the sample amount.

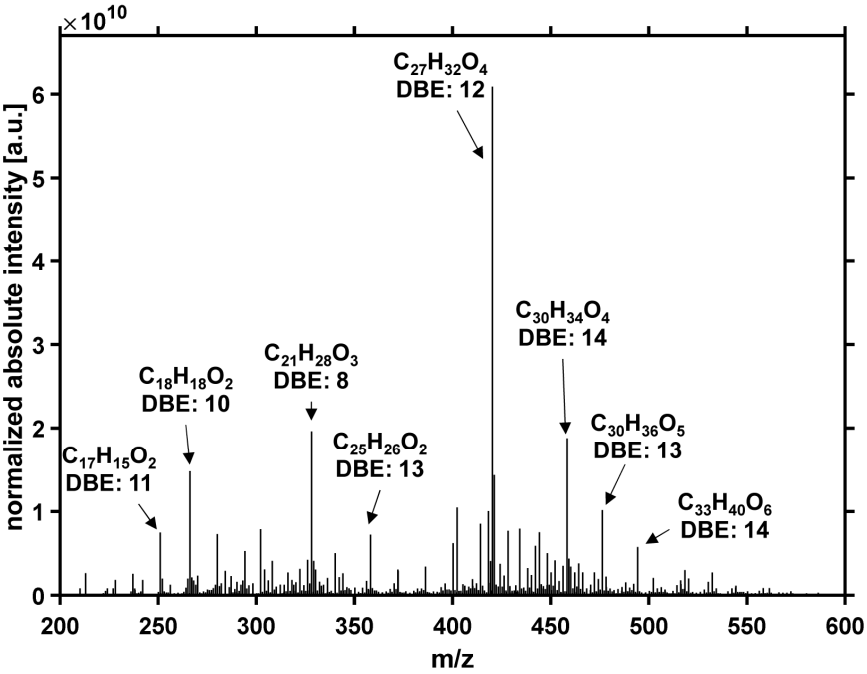


Figure S10. In-depth chemical characterization of the emitted gas mixture for the thermal analysis of reinforcement material mechanically separated from C³ exposed to 300 °C (air atmosphere, 3 hours) by APPI-MS. Average mass spectrometric response is normalized to the sample amount.

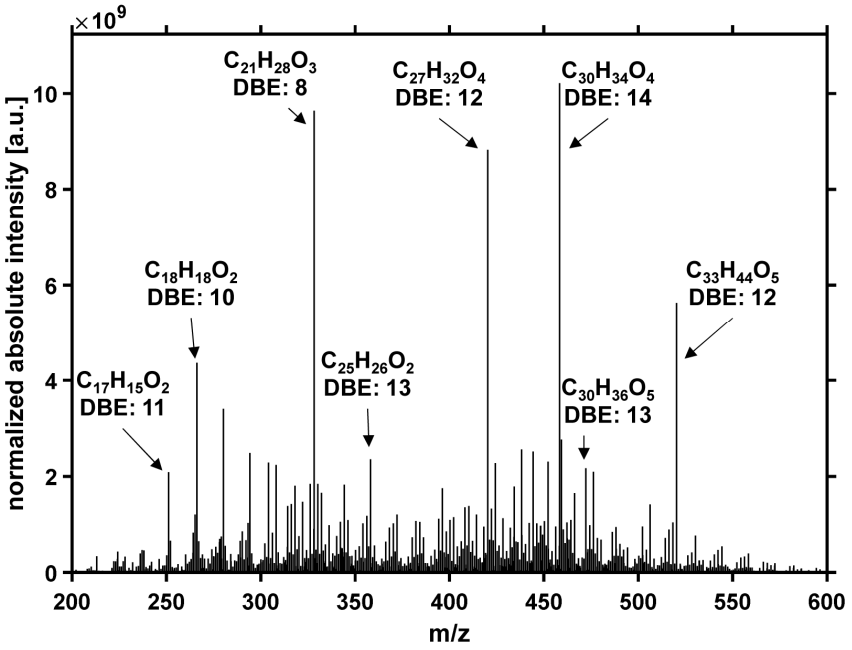


Figure S11. In-depth chemical characterization of the emitted gas mixture for the thermal analysis of reinforcement material mechanically separated from C³ exposed to 325 °C (air atmosphere, 3 hours) by APPI-MS. Average mass spectrometric response is normalized to the sample amount.

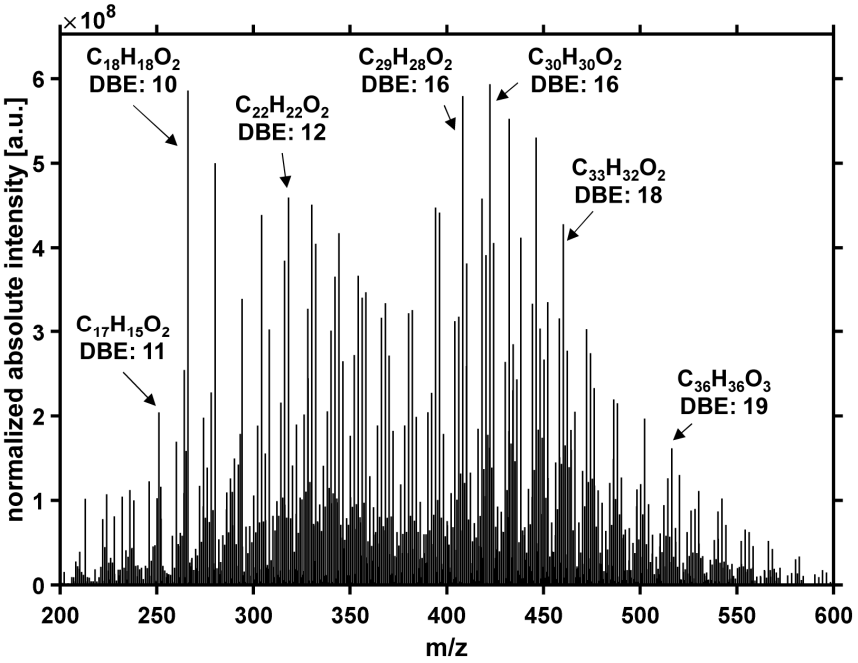


Figure S12. In-depth chemical characterization of the emitted gas mixture for the thermal analysis of reinforcement material mechanically separated from C³ exposed to 350 °C (air atmosphere, 3 hours) by APPI-MS. Average mass spectrometric response is normalized to the sample amount.

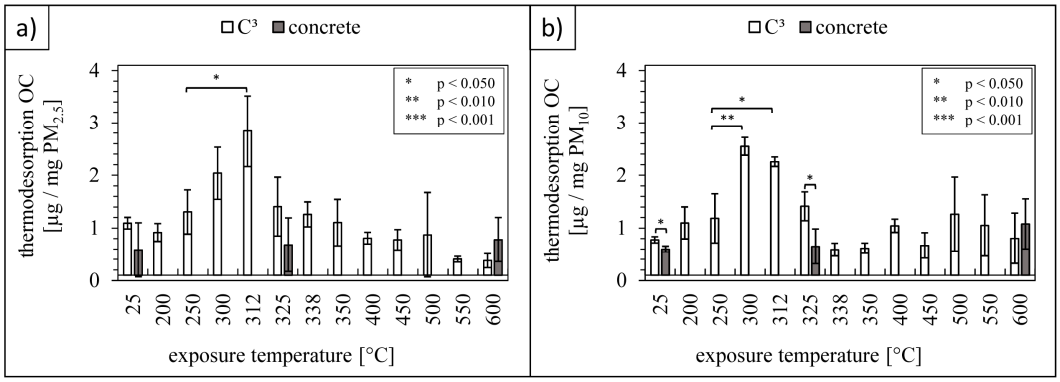


Figure S13. Concentration of thermal desorption organic carbon (OC, 20–280 °C, OC1 + OC2) in inhalable PM fractions $PM_{2.5}$ (**a**) and PM_{10} (**b**) released from dry-cutting of C^3 exposed to various temperatures between 25 and 600 °C (air atmosphere, 3 hours) prior to abrasive machining.

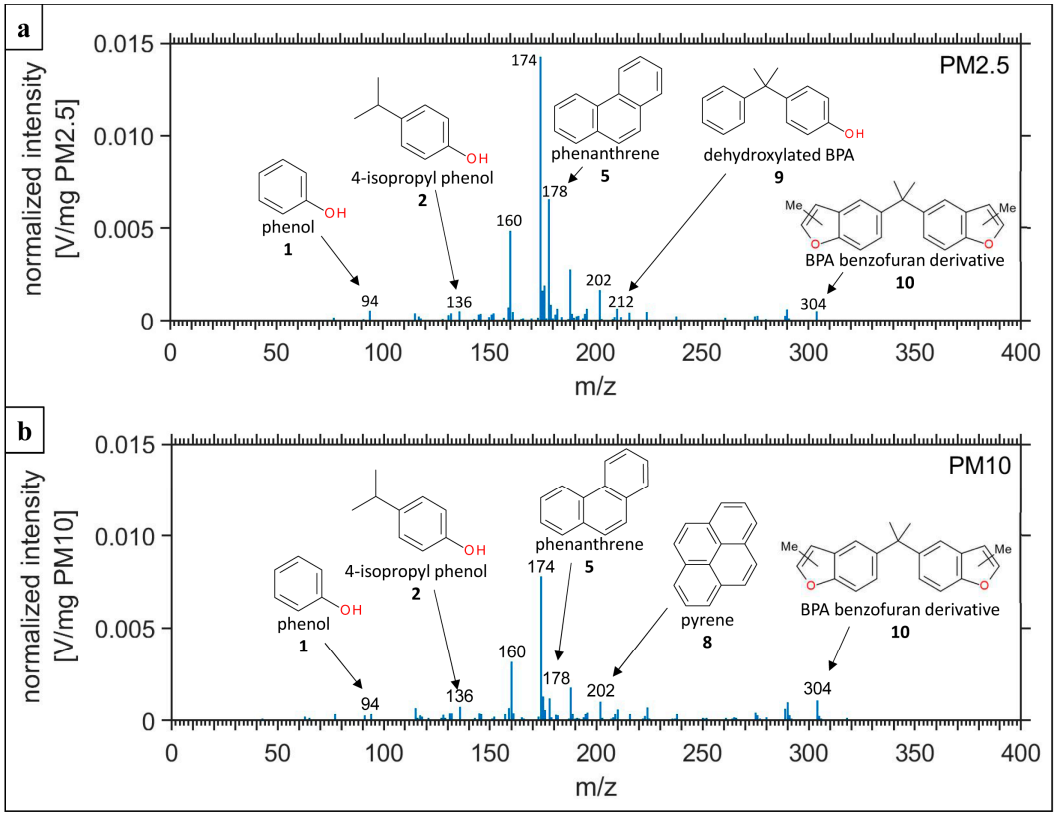


Figure S14. Averaged REMPI spectra (248 nm, 500 Hz) of thermal desorption OC fraction (20–280 °C, OC1 + OC2) of $PM_{2.5}$ (**a**) and PM_{10} (**b**) formed during dry-cutting of C^3 exposed to 312 °C (air atmosphere, 3 hours).

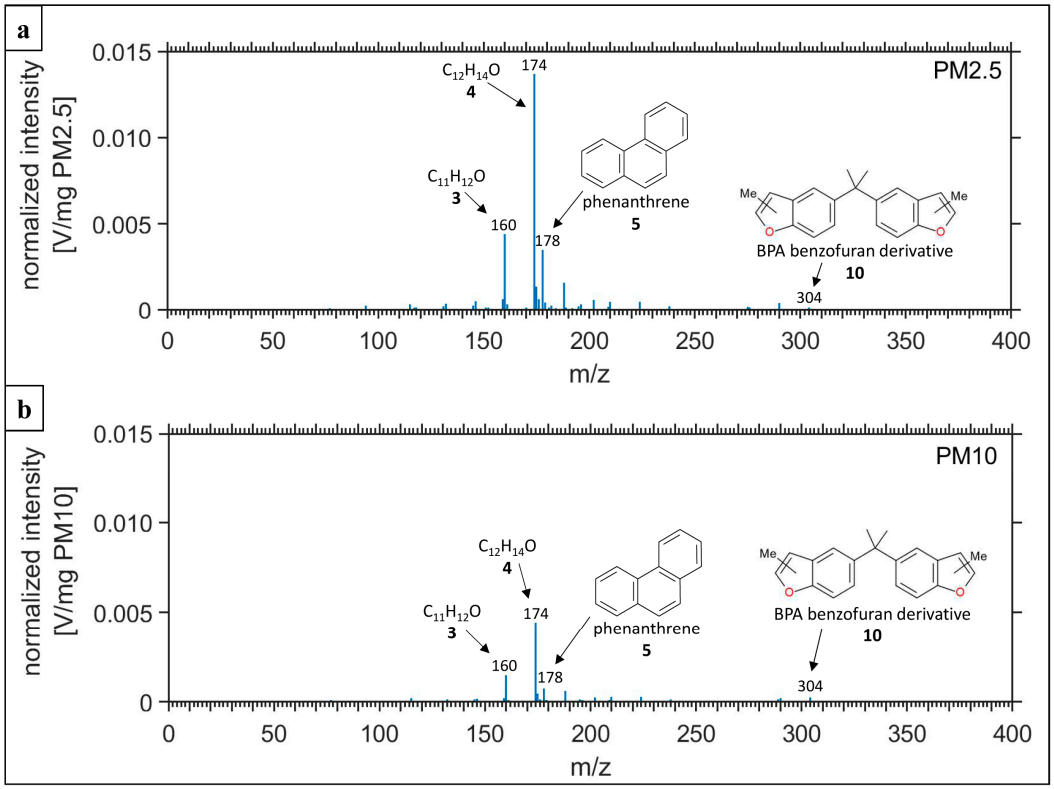


Figure S15. Averaged REMPI spectra (248 nm, 500 Hz) of thermal desorption OC fraction (20–280 °C, OC1 + OC2) of $PM_{2.5}$ (**a**) and PM_{10} (**b**) formed during dry-cutting of C^3 exposed to 325 °C (air atmosphere, 3 hours).

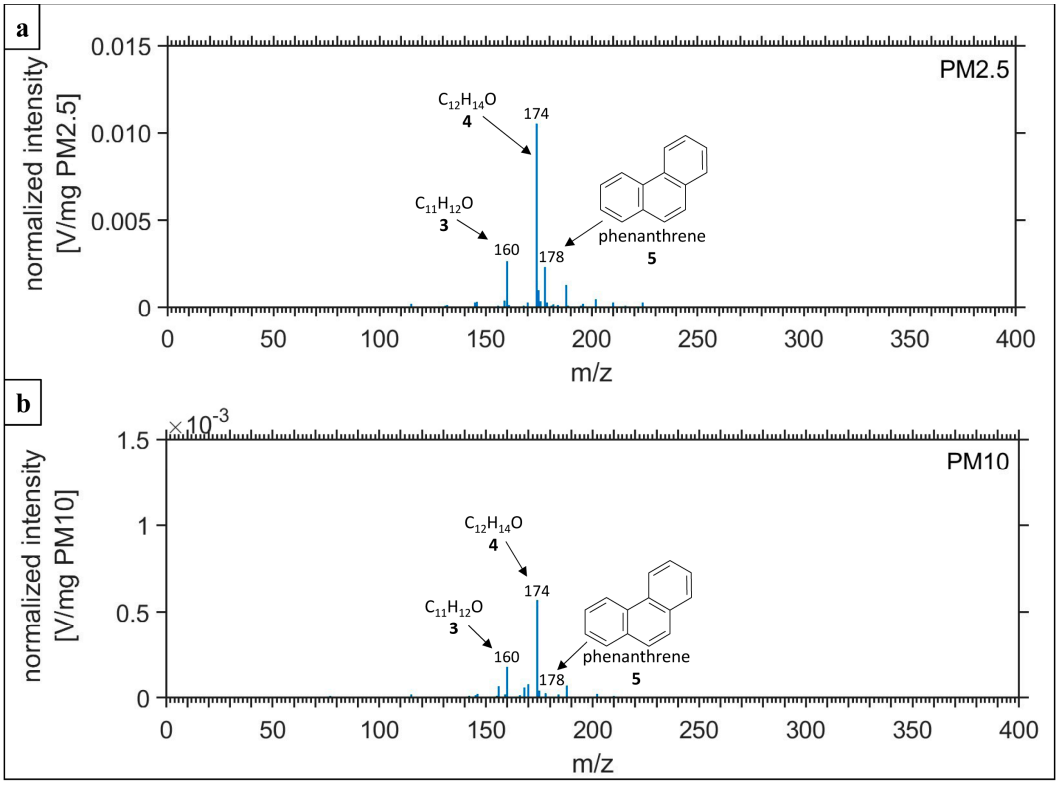


Figure S16. Averaged REMPI spectra (248 nm, 500 Hz) of thermal desorption OC fraction (20–280 °C, OC1 + OC2) of $PM_{2.5}$ (**a**) and PM_{10} (**b**) formed during dry-cutting of C^3 exposed to 338 °C (air atmosphere, 3 hours).

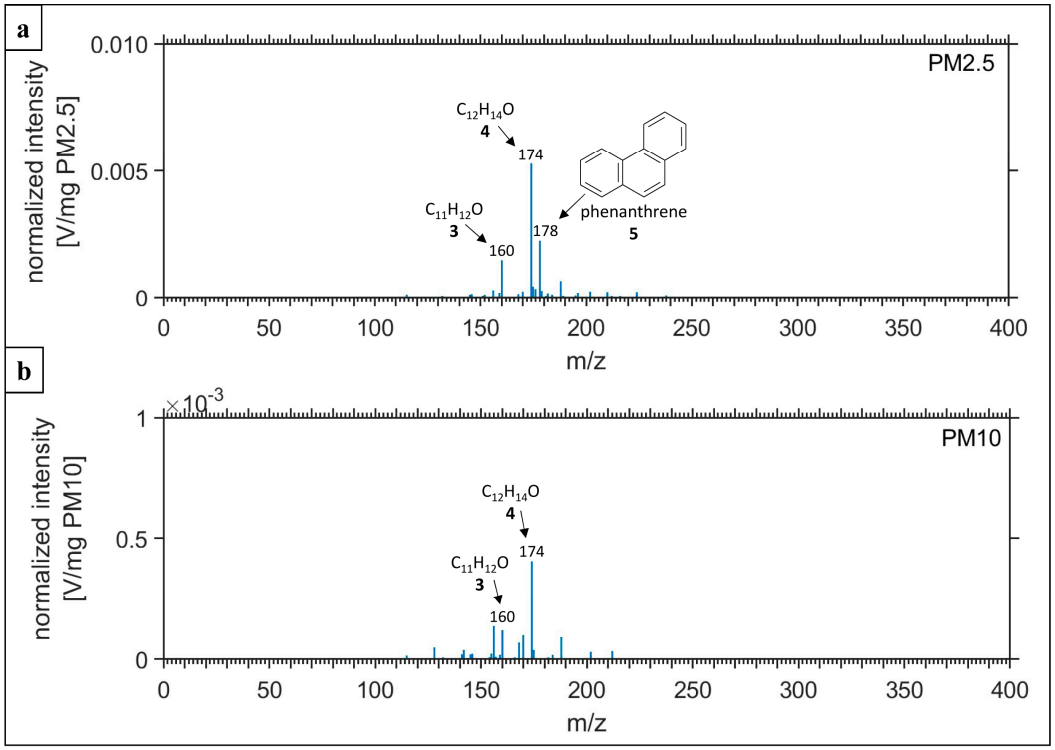


Figure S17. Averaged REMPI spectra (248 nm, 500 Hz) of thermal desorption OC fraction (20–280 °C, OC1 + OC2) of $PM_{2.5}$ (**a**) and PM_{10} (**b**) formed during dry-cutting of C^3 exposed to 350 °C (air atmosphere, 3 hours).

4. Fiber Morphology

4.1. Fiber Morphology Before Cutting

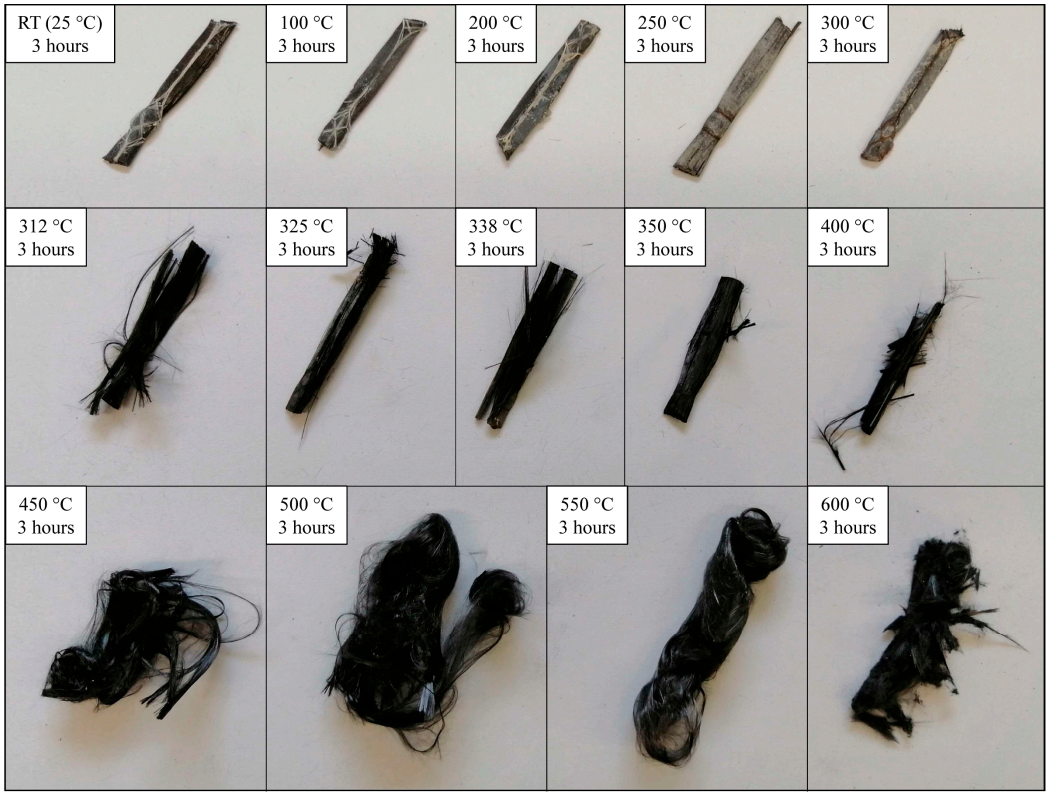


Figure S18. C^3 reinforcement material mechanically separated from C^3 exposed to various temperatures between 25 and 600 °C (air atmosphere, 3 hours). At 312 °C, the macroscopic structure of the reinforcement material starts to decompose. Fiber bundles and isolated fibers are contained. High temperatures ≥450 °C lead to a complete loss of the reinforcement structure forming a fluffy bundle of isolated fibers.

4.2. Fiber Morphology / Occurrence in Abrasive PM_{10}

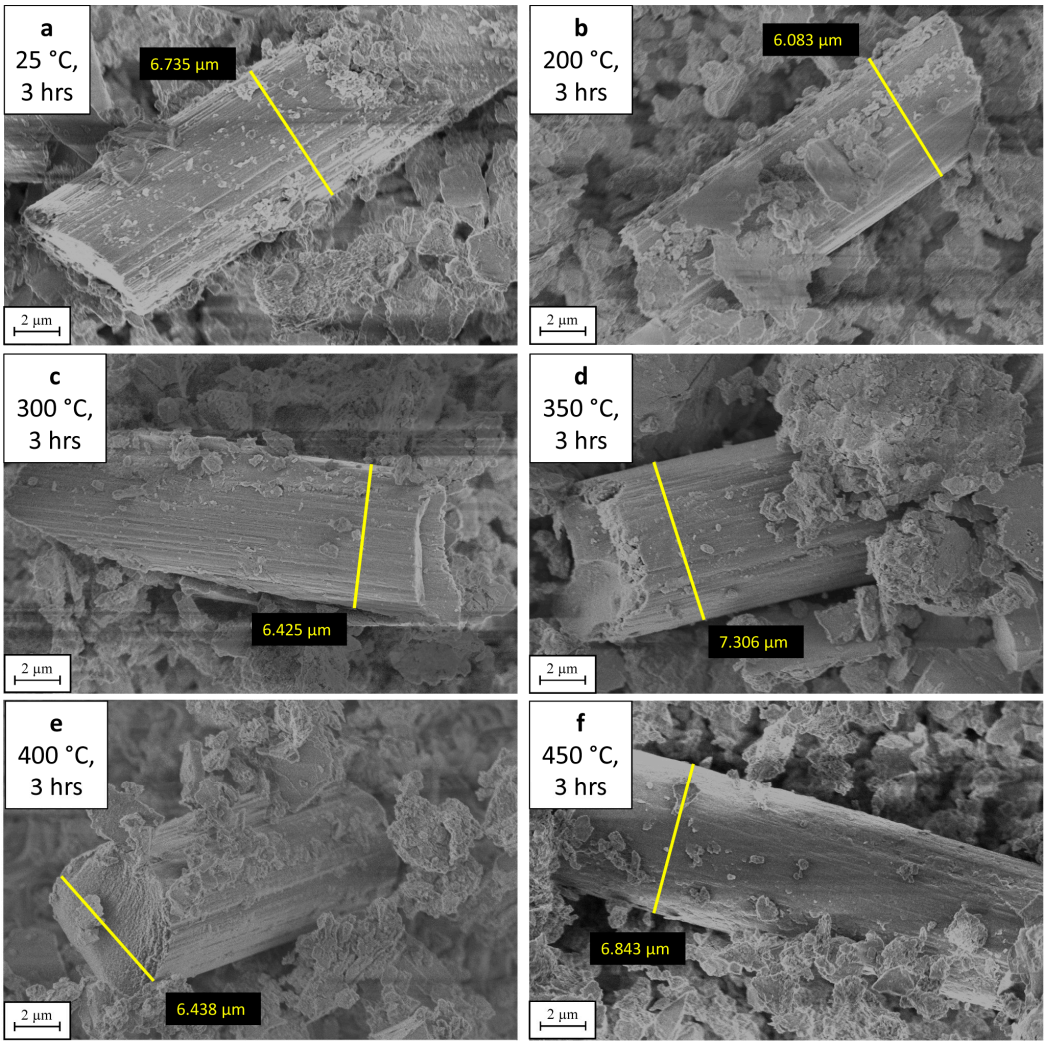


Figure S19. SEM micrographs (5000× magnification) of fibers in inhalable PM of the fraction PM_{10} formed during dry-cutting of C^3 exposed to various temperatures between room temperature (25 °C, **a**) and 450 °C, **f**, air atmosphere, 3 hours) prior to abrasive machining. The fibers all have diameters of 7 ± 1 µm due to the manufacturing process and show no degradation processes such as localized oxidation.

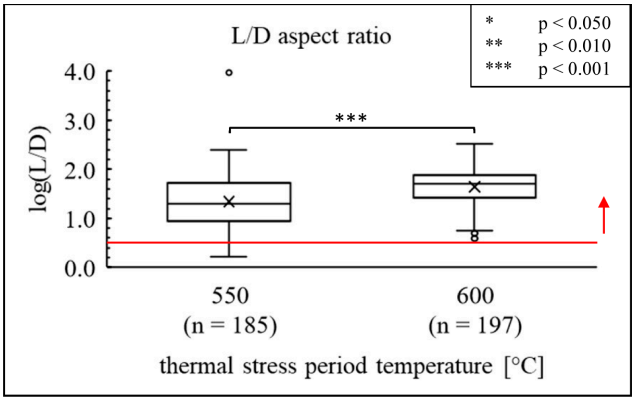


Figure S20. Length-to-diameter (L/D) aspect ratio of carbon fibers observed in the inhalable PM fraction PM_{10} from dry-cutting of C^3 thermally exposed to 550 and 600 °C (air atmosphere, 3 hours). The speciation for harmful fibers according to the WHO definition (L/D > 3) is indicated by a red line and arrow.

References

1. Koch, A.; Bergelt, P.; Fiala, P.; Käfer, U.; Orasche, J.; Bauer, S.; Di Bucchianico, S.; Stintz, M.; Gröger, T.; Streibel, T.; et al. Investigation of Chemical Composition and Fiber-Occurrence in Inhalable Particulate Matter Obtained from Dry-cutting Processes of Carbon Fiber Reinforced Concrete Composite, Concrete and the Carbon Fiber Reinforcement Materials. *Aerosol Sci Eng* **2021**, *5*, 292–306, doi:10.1007/s41810-021-00103-8.