Molecular background of the undesired odor of polypropylene materials and insights into the sources of key odorants

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Abstract
Screening the volatiles isolated from a standard polypropylene material consisting of a polypropylene homopolymer, the filler talcum, and a mixture of antioxidants, for odor-active compounds by application of an aroma extract dilution analysis revealed 30 odorants with flavor dilution factors ranging from 1 to 64. Eighteen odor-active compounds were subsequently quantitated by gas chromatography-mass spectrometry using stable isotopically substituted odorants as internal standards, and their odor activity values (OAVs) were calculated as ratios of the concentrations to the odor threshold values. Five odorants showed OAVs ≥1, among which were hex-1-en-3-one (OAV 12), butanoic acid (OAV 3), as well as 4-methylphenol, butan-1-ol, and 2-tert-butylphenol (all OAV 1). A comparative analysis of polypropylene materials with different additives suggested plastic-like, pungent smelling hex-1-en-3-one as an ubiquitous key odorant. Odor-active amounts of alkylphenols, in particular plastic-like, phenolic smelling 2-tert-butylphenol, were additionally formed in the presence of talcum and phenolic antioxidants. Whereas the precursors of the phenols were thus obvious, the origin of hex-1-en-3-one was unknown. Injection molding showed only little influence on odorant concentrations.

KEYWORDS
additive, aroma extract dilution analysis (AEDA), injection molding, polypropylene (PP), stable isotopically substituted odorants, undesired odor

Practical implications
Mitigation of the unpleasant odor of polypropylene products was possible by using wollastonite instead of talcum as filler or by using a combination of talcum and a mixture of antioxidants including Irgafos® 168 FF, Irganox® 1010 FF, and Tinuvin® 770 DF in high amounts. As polypropylene materials are widely used in buildings, cars, and aircrafts, the reduction in odor-active compounds will ultimately contribute to improve the indoor air quality.
1 INTRODUCTION

Polypropylene is the second most important technical polymer with 20% of the total plastic production. It is used in different industrial sectors such as packaging, consumer products, home textiles, and automotive parts. In some applications, the smell of polypropylene material can be a severe problem, particularly in indoor environments such as buildings, cars, and aircrafts. Consumers perceive the characteristic smell as rather unpleasant and tend to imply possible health implications, which often leads to the rejection of polypropylene-based products. Thus, manufacturers are in urgent need to mitigate the undesired odor of polypropylene materials. Addition of adsor- bents or absorbents can lead to a reduction in the perceived odor intensity. Nevertheless, the odor-active compounds remain in the material. Thus, preventing odorant formation would be the better alternative. However, data on the crucial processing steps leading to the characteristic polypropylene odor as well as data on the causative compounds are currently scarce. Potential odorant sources include side reactions during polymerization, impurities in additives, reactions induced by temperature, light and/or oxygen during processing (e.g., extrusion, injection molding), storage and/or use. In any case, a targeted mitigation approach requires the knowledge of the causative compounds. For this purpose, gas chromatography-olfactometry (GC-O) together with gas chromatography-mass spectrometry (GC-MS) measurements are indispensable.

In 2009, Tyapkova et al. published a comprehensive study on odor-active compounds in polypropylene samples. The application of GC-O in combination with an aroma extract dilution analysis (AEDA) revealed aldehydes and ketones such as trans-4,5-epoxy-(2E)-dec-2-enal, octanal, oct-1-en-3-one, (2Z)-non-2-enal, (2E)-non-2-enal, and 4-hydroxy-3-methoxybenzaldehyde (vanillin) with high flavor dilution (FD) factors in a standard polypropylene material. After γ-irradiation, the FD factors of some important compounds decreased, whereas the FD factors of carboxylic acids, lactones, and phenolic substances increased. Quantitation confirmed the increase in carboxylic acids.

Further GC-O studies on odor-active compounds in polypropylene material applied simultaneous distillation/extraction (SDE) and headspace-SPME as volatile sampling approaches. The compounds reported as potent odorants included aldehydes such as heptanal, octanal, nonanal, (2E)-non-2-enal, (6E)-non-6-enal, (6Z)-non-6-enal, non-8-enal, and decanal, ketones such as hex-1-en-3-one, oct-1-en-3-one, and non-1-en-3-one, and carboxylic acids such as propanoic acid and butanoic acid.

In summary of the literature overview, there was some knowledge on odor-active compounds in polypropylene materials available, but most screening data had not been substantiated by quantitative measurements and by comparison of the obtained concentrations to odor threshold values (OTVs). Furthermore, it remained unclear how these odorants are formed and how their formation could be minimized. The aims of our study therefore were (1) to characterize the key odorants in a standard polypropylene material by combining GC-O screening and AEDA with the quantitation of potent odorants and the calculation of odor activity values (OAVs; ratio of concentration to OTV), and (2) to obtain some insights into the sources of the key odorants by evaluating the effect of composition and injection molding and, based on the results, suggest potential measures for odor mitigation.

2 MATERIALS AND METHODS

2.1 Samples

The polypropylene homopolymer was obtained from SABIC; the antioxidants Irganox® 1010 FF, Irgafos® 168 FF, and Tinuvin® 770 DF were purchased from BTC Europe GmbH; the fillers Talcum CT 139 and Wollastonite CWZ 200 were from Franz Mandt GmbH & Co. KG. Irganox® 1010 FF, Irgafos® 168 FF, Tinuvin® 770 DF, and Talcum CT 139 were added to a sample of the polypropylene homopolymer. The mixture was extruded and the obtained granulate underwent an injection molding process to produce a standard polypropylene material (sample PP-1, Table 1). Further seven samples were obtained from the same polypropylene homopolymer by extrusion, either without any additives (sample PP-2), with a single additive (samples PP-3, PP-4, PP-5, PP-6, PP-8), or with a combination of additives (sample PP-7). Another three samples were commercial polypropylene granulates (samples PP-C1, PP-C2, PP-C3). Prior to the analyses, all samples were heated to 80°C for 2 h in a closed glass vessel (1 L) to be consistent with the established approach for odor evaluation of plastic materials according to VDA 270.

2.2 Reference odorants

Compounds 1-2, 5-7, 11-12, 14-23, 25, 27, 29, 31-38, 40, 42, 44, 46, and 2,6-dimethylphenol were obtained from Merck; 3, 43,

| Sample   | Composition                                                                 |
|----------|-----------------------------------------------------------------------------|
| PP-1     | polypropylene homopolymer (59.7%); Irganox® 1010 FF (0.1%); Irgafos® 168 FF (0.1%); Tinuvin® 770 DF (0.1%); Talcum CT 139 (40.0%); injection molding |
| PP-2     | polypropylene homopolymer (100.0%)                                         |
| PP-3     | polypropylene homopolymer (99.9%); Irganox® 1010 FF (0.1%)                 |
| PP-4     | polypropylene homopolymer (99.9%); Irgafos® 168 FF (0.1%)                 |
| PP-5     | polypropylene homopolymer (99.9%); Tinuvin® 770 DF (0.1%)                  |
| PP-6     | polypropylene homopolymer (60.0%); Talcum CT 139 (40.0%)                   |
| PP-7     | polypropylene homopolymer (59.7%); Irganox® 1010 FF (0.1%); Irgafos® 168 FF (0.1%); Tinuvin® 770 DF (0.1%); Talcum CT 139 (40.0%) |
| PP-8     | polypropylene homopolymer (60.0%); Wollastonite CWZ 200 (40.0%)            |
and 45 were purchased from Lancaster; 4 and 39 were from Alfa Aesar; 8, 14, and 41 were obtained from Acros Organics; 10 and 24 were from VWR. 9 was prepared by oxidation of non-1-en-3-ol (VWR) using Dess-Martin periodinane (Merck). Compounds 1312 and 3013 were synthesized as detailed in the literature. A complete list of odorants is available in the Supporting Information section (Table S1).

2.3 | Stable isotopically substituted odorants

\(^{(1H)}_2\) -4, \(^{(1H)}_2\) -16, and \(^{(1H)}_2\) -32 were obtained from Merck; \(^{(1H)}_2\) -41 was from CDN Isotopes; \(^{(2H)}_2\) -2,6-dimethylphenol was purchased from Santa Cruz Biotechnology. The following isotopically substituted odorants were synthesized as detailed in the literature: \(^{{^{13}C}_2\cdot1_{14}}\) \(^{(1H)}_2\) -3, \(^{{^{13}C}_2\cdot5_{16}}\) \(^{(1H)}_2\) -22, \(^{{^{13}C}_2\cdot27_{18}}\) \(^{(1H)}_2\) -31, \(^{(1H)}_2\) -35, \(^{(1H)}_2\) -36, \(^{(1H)}_2\) -38, \(^{(1H)}_2\) -39, \(^{(1H)}_2\) -43, \(^{(1H)}_2\) -46, \(^{(1H)}_2\) -6, \(^{(1H)}_2\) -17 were synthesized from oct-1-yn-3-ol (Merck) using lithium aluminum deuteride/deuterium oxide for the reduction to \((1,2\cdot{^2H}_2)\) oct-1-en-3-ol followed by Dess-Martin oxidation, an approach previously used for the synthesis of \(^{(1H)}_2\) -3, \(^{(1H)}_2\) -13 was synthesized from non-2-yn-1-ol (VWR) by deuteration with deuterium gas (Silantes) over Lindlar catalyst and oxidation of the obtained \((2Z)\cdot(2,3\cdot{^2H}_2)\) non-2-en-1-ol using Dess-Martin periodinane (Merck). \(^{(1H)}_2\) -17 was synthesized from the corresponding unsaturated alcohol-but-3-en-1-ol (Merck) using the approach published for the synthesis of \(^{(1H)}_2\) -19, \(^{(13C)}_2\) -21 was synthesized according to the approach published for \(^{(13C)}_2\) -23 using \((2E)\cdot(1,2\cdot{^2H}_2)\) oct-2-ena.

2.4 | Miscellaneous chemicals

Dichloromethane, diethyl ether, and pentane were purchased from VWR and freshly distilled before use. Silica gel 60 (0.040–0.063 mm) was obtained from VWR and purified as detailed previously. Silicone oil was purchased from Merck, and sunflower oil was bought in a local supermarket.

2.5 | GC-O/FID system

A Trace GC Ultra gas chromatograph (Thermo Scientific) was equipped with a cold on-column injector, a flame ionization detector (FID), and a tailor-made sniffing port. The fused silica column was either a DB-FFAP or a DB-5, both 30 m × 0.32 mm i.d., 0.25 μm film (Agilent Technologies). The Carrier gas was helium 4.6 at 90 kPa constant pressure. The injection volume was 1 μL. The initial oven temperature of 40°C was held for 2 min, followed by a gradient of 6°C/min to a final temperature of 240°C, which was held for 5 min. The column end was connected to a moving column stream switching (MCSS) device (Thermo). Employing helium 50 at 50 kPa as makeup gas, the MCSS system allowed for the time-programmed transfer of the column eluate via deactivated fused silica capillaries (0.32 mm i.d.) either simultaneously to an FID and a sniffing port used as monitor detectors or to a second fused silica column installed in a separate gas chromatograph (CP 3800, Varian). The capillary to the second column passed through a heated (250°C) hose connecting the two gas chromatographs and a liquid nitrogen-cooled trap inside the oven of the second gas chromatograph allowing for the refocusing of the heart-cut. The fused silica column in the second dimension was a DB-1701, 30 m × 0.25 mm i.d., 0.25 μm film (Agilent). The initial temperature of the second oven of 40°C was held for 2 min, followed by a gradient of 6°C/min to a final temperature of 240°C, which was held for 5 min. The end of this column was connected to a Saturn 2200 mass spectrometer (Varian) operated in the chemical ionization (CI) mode with methanol as the reagent gas.

Before a heart-cut analysis, the retention times of the target compounds in the first dimension were determined after injection of reference compounds by using the monitor detectors. During the
elution of the target compounds in the heart-cut run, the effluent of the first column was directed via the MCSS system to the column in the second dimension, and the transferred substances were cryofocused in the precooled trap. When the MCSS system had switched back to the monitor detectors, the trap cooling was turned off, and the temperature program of the second gas chromatograph was started together with the mass spectrometer. The MS Workstation software (Varian) was used for the evaluation of the mass spectra.

2.8 | GC × GC-MS system

A 6890 Plus gas chromatograph (Agilent) was equipped with a Combi PAL autosampler (CTC Analytics), a KAS4 injector (Gerstel), and a fused silica column, DB-FFAP, 30 m × 0.25 mm i.d., 0.25 μm film (Agilent). The carrier gas was helium 5.0 at 2.0 mL/min constant flow. The end of the column was connected to a second fused silica column, DB-5, 2 m × 0.15 mm i.d., 0.30 μm film (Agilent). The front part of this column passed through a liquid nitrogen-cooled dual stage quad-jet thermal modulator (Leco). The modulator was used to collect the volatiles eluted from the first column in discrete portions (4 s), which then were rechromatographed on the major part of the second column. This part was installed in a secondary oven mounted inside the primary oven of the gas chromatograph. The end of this column was connected via a heated (250°C) transfer line to the inlet of a Pegasus III time-of-flight (TOF) mass spectrometer (Leco). The temperature program of the second gas chromatograph was started together with the mass spectrometer.

2.9 | Isolation of volatiles

PP-1 was cut into pieces of ~4 mm diameter with a knife. The granulates of PP-2 to PP-8 were directly used for volatiles isolation. Dichloromethane (250 mL) was added to the samples (100 g). Extraction was performed by stirring for 24 h in the dark. Nonvolatiles were removed by solvent-assisted flavor evaporation (SAFE) at 40°C. Acidic volatiles were extracted with aqueous sodium carbonate solution (0.5 mol/L) in three portions (400 mL total). The organic phase containing the neutral and basic volatiles was washed with saturated aqueous sodium chloride solution (3 × 100 mL) and dried over anhydrous sodium sulfate. This fraction was concentrated to 1 mL by using a Vigreux column (50 × 1 cm) and a Bemelmans microdistillation device (fraction NBV). The aqueous phase was acidified (pH 2) with hydrochloric acid (32%), and the acidic volatiles were reextracted with dichloromethane in three portions (200 mL total). The combined organic phases were dried over anhydrous sodium sulfate and concentrated to 1 mL (fraction AV). The fraction NBV was further fractionated. To remove dichloromethane, hexane (0.5 mL) was added and the mixture was concentrated to 0.5 mL. The concentrate was applied onto a slurry of purified silica gel (9 g) in pentane in a water-cooled (12°C) glass column (1 cm i.d.). Elution was performed with 50 mL pentane and 100 mL diethyl ether. Both eluate portions were concentrated to 1 mL (fractions NBV1 and NBV2).

2.10 | AEDA

The polypropylene volatile fractions (NBV2; AV) were repeatedly subjected to GC-O analysis (DB-FFAP column) by three trained and experienced panelists. This was continued until for each panelist run-to-run variations disappeared and the results were reproducible. Then, the polypropylene volatile fractions were stepwise diluted 1:4 with solvent to obtain 1:4, 1:16, 1:64, 1:256, 1:1024, and 1:4096 dilutions, and each diluted sample was also subjected to GC-O. Each odorant was assigned an FD factor, representing the dilution factor of the highest diluted sample in which the odorant was detected during GC-O analysis by any of the three panelists.

2.11 | Odorant quantitation

For the quantitation of the compounds 1, 3−6, 13, 15−17, 21−22, 27, 31−32, 35−36, 38−39, 41−43, and 46, dichloromethane (50−250 mL) and stable isotopically substituted odorants (0.004−53 μg) were added to the polypropylene samples (1−100 g). Extraction was performed by stirring for 24 h in the dark. Nonvolatiles were removed by SAFE at 40°C. Acidic volatiles were extracted with aqueous sodium carbonate solution (0.5 mol/L) in three portions (60−150 mL total). The organic phase containing the neutral and basic volatiles was washed with saturated aqueous sodium chloride solution in three portions (60−150 mL total). The aqueous phase was acidified (pH 2) with hydrochloric acid (32%), and the acidic volatiles were reextracted with dichloromethane in three portions (80−200 mL total). Further workup was performed as described above, and the extracts were concentrated to final volumes ranging from 0.2 μL to 4 mL. Concentrates were analyzed by using the heart-cut GC-GC-MS system (17, 22, 35) or the GC × GC-MS system (1, 3−6, 13, 15−16, 21, 27, 31−32, 36, 38−39, 41−43, 46). Peak areas corresponding to the analytes and the internal standards were obtained from the extracted ion chromatograms using the quantifier ions detailed in the Supporting Information section (Table S2). The concentration of each target compound in the polypropylene samples was then calculated from the area counts of the analyte peak, the area counts of the standard peak, the amount of polypropylene sample used, and the amount of standard added, by employing a calibration line equation (cf. Supporting Information section, Table S2). To obtain the calibration line equation, mixed dichloromethane solutions of analyte and standard in different concentration ratios were analyzed under the same conditions followed by linear regression.

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2.12 | Sensory evaluations

All sensory analyses were performed in a specially designed room with controlled temperature (23 ± 1°C) and individual booths. The sensory panel consisted of 15–20 trained panelists (male and female, aged 24–55 years). Training included weekly sensory evaluation sessions with solutions of reference odorants.

2.13 | OTVs

OTVs were determined according to the American Society for Testing and Materials (ASTM) standard practice for determination of odor and taste thresholds by a forced-choice ascending concentration series method of limits. All threshold values were determined orthonasally in low-odor sunflower oil.

2.14 | Odor reconstitution

An individual ethanolic stock solution was prepared for each odorant. The absence of odor-active impurities was confirmed by GC-O. Dilutions of each stock solution were prepared with odorless silicone oil. Aliquots (1 mL) of the dilutions were combined, and the mixture was made up to 100 g with silicone oil to obtain final concentrations representing the concentrations previously determined. The final ethanol concentration in this odor reconstitution model was below the OTV of ethanol in oil.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the key odorants in a standard polypropylene material

3.1.1 | Odorant screening

The antioxidants Irganox® 1010 FF, Irgafos® 168 FF, and Tinuvin® 770 DF as well as the filler Talcum CT 139 were added to a polypropylene homopolymer. The extruded mixture underwent an injection molding process to obtain a standard polypropylene material (sample PP-1, Table 1). The sample exhibited a strong plastic-type odor considered as characteristic for polypropylene items with an additional slight phenolic note. Volatiles were isolated by solvent extraction and SAFE. To facilitate the GC-O screening, the distillate was fractionated into acidic volatiles (AV) and neutral and basic volatiles (NBV). The latter were further fractionated into nonpolar (NBV1) and polar volatiles (NBV2). GC-O indicated the major part of the volatiles in the fraction NBV1, but no odor-active compounds were detected. GC-MS showed that the fraction NBV1 basically consisted of hydrocarbons, which typically exhibit rather high OTVs. A total of 30 odor-active compounds were present in the fractions AV and NBV2. Application of an AEDA resulted in FD factors ranging from 1 to 64 (Table 2). Preliminary structural assignments were achieved by comparing the RIs and odor descriptions of the odorants recorded during AEDA to published data compiled in a free internet database. Structure proposals were confirmed by analyzing the corresponding authentic reference compounds in an appropriate dilution by GC-O in parallel with the PP-1 volatile fractions on two separation systems of different polarity (DB-FFAP and DB-5 column). Further confirmation was obtained by GC-MS. The approach allowed for the structural assignment of 29 out of the 30 odor-active compounds listed in Table 2. Despite all efforts, compound 26 remained unknown. With an FD factor of 64, the most potent odorant in the sample PP-1 was fatty smelling (2E)-non-2-enal (15). The study of Tyapkova et al. had also reported a high FD factor for this compound. Odorants with an FD factor of 16 included 2,3-diethyl-5-methylpyrazine (12; earthy), (Z)-non-2-enal (13; fatty), phenol (29; phenolic), 4-methoxybenzaldehyde (31; sweet woodruff-like), 4-methylphenol (32; fecal, phenolic), 4-ethylphenol (35; phenolic), 2-tet-butylphenol (36; plastic-like, phenolic), 4-tet-butylphenol (41; phenolic), and 2,4-di-tet-butylphenol (42; phenolic, leather-like). Further 19 odorants were detected with FD factors ranging from 1 to 4, among them, hex-1-en-3-one (3; plastic-like, pungent; FD factor 4), butan-1-ol (4; malty; FD factor 4), and butanoic acid (17; sweaty, cheesy; FD factor 4). Most of the compounds mentioned above have been reported as polypropylene odorants before (3, 12, 13, 17, 29, 32, 35, 42). The compounds 4, 31, 36, and 41 were identified for the first time as polypropylene odorants in our study.

3.1.2 | Odorant quantitation, OAV calculation, and odor reconstitution

Eighteen volatiles identified as odor-active compounds by AEDA were subsequently quantitated by using heart-cut GC-GC-MS or GC × GC-MS. Stable isotopically substituted odorants (cf. Supporting Information section, Table S2) were employed as internal standards to compensate for workup losses and workup variance. The results (Table 3) revealed odorant concentrations ranging from 50.5 ng/kg (hex-1-en-3-one, 3) to 5.56 mg/kg (2,4-di-tet-butylphenol, 42). Next to 2,4-di-tet-butylphenol, high concentrations were also found for 4-tet-butylphenol (41; 581 μg/kg), butan-1-ol (4; 527 μg/kg), and butanoic acid (17; 118 μg/kg).

To assess the importance of the individual odorants for the overall odor of the polypropylene material, an OAV was calculated for each compound as ratio of its concentration to its orthonasal OTV. OTVs in polypropylene were approximated by using OTVs in low-odor sunflower oil, which were taken from the LSB@TUM odorant database or, for some compounds, were determined by using the same approach. Low-odor sunflower oil was considered an appropriate approximation for the nonpolar polypropylene matrix. For five odorants (3, 17, 32, 4, 36), an OAV ≤1 was determined (Table 3); thus, their concentrations in the sample PP-1 exceeded their respective OTV. With an OAV of 12, hex-1-en-3-one (3) with a plastic-like,
Pungent odor showed the highest value. An OAV of 3 was calculated for sweaty, cheesy smelling butanoic acid (17), and an OAV of 1 was determined for 4-methylphenol (32; fecal, phenolic), butan-1-ol (4; malty), and 2-tert-butylphenol (36; plastic-like, phenolic). The concentrations of 13 compounds, however, were below their OTVs. Among them were compounds such as (2E)-non-2-enal (15) and (2Z)-non-2-enal (13), for which high FD factors were determined in the AEDA, whereas for example the FD factor of hex-1-en-3-one was 4.

### Table 2: Odorants in the volatile fractions obtained from a standard polypropylene material (sample PP-1)

| No. | Odorant                      | Odor          | RI<sup>c</sup> DB-FFAP | FD factor<sup>e</sup> |
|-----|------------------------------|---------------|-------------------------|-----------------------|
| 1   | butyl acetate                | fruity, banana| 1055                    | 1                     |
| 3   | hex-1-en-3-one               | plastic, pungent| 1081                    | 4                     |
| 4   | butan-1-ol                   | malty         | 1131                    | 4                     |
| 5   | octanal                      | citrusy, soapy| 1280                    | 4                     |
| 6   | oct-1-en-3-one               | mushroom      | 1290                    | 1                     |
| 8   | nonanal                      | citrusy, soapy| 1384                    | 4                     |
| 11  | acetic acid                  | vinegar       | 1443                    | 4                     |
| 12  | 2,3-diethyl-5-methylpyrazine | earthy        | 1480                    | 16                    |
| 13  | (2Z)-non-2-enal              | fatty         | 1496                    | 16                    |
| 15  | (2E)-non-2-enal              | fatty         | 1523                    | 64                    |
| 17  | butanoic acid                | sweaty, cheesy| 1616                    | 4                     |
| 18  | 2-methylbutanoic acid<sup>f</sup> | sweaty     | 1657                    | 1                     |
| 19  | 3-methylbutanoic acid<sup>f</sup> | sweaty     | 1657                    | 1                     |
| 21  | (2E,4E)-nona-2,4-dienal      | fatty         | 1722                    | 4                     |
| 22  | (2E)-undec-2-enal            | soapy        | 1740                    | 4                     |
| 24  | geosmin                      | beetroot      | 1811                    | 4                     |
| 25  | hexanoic acid                | sweaty        | 1834                    | 1                     |
| 26  | unknown                      | geranium      | 1911                    | 16                    |
| 29  | phenol                       | phenolic      | 1987                    | 16                    |
| 30  | trans-4,5-epoxy-(2E)-dec-2-enal | metallic     | 1996                    | 4                     |
| 31  | 4-methoxybenzaldehyde        | sweet woodruff| 2020                    | 16                    |
| 32  | 4-methylphenol               | fecal, phenolic| 2070                    | 16                    |
| 35  | 4-ethylphenol                | phenolic      | 2163                    | 16                    |
| 36  | 2-tert-butylphenol           | plastic, phenolic| 2179                    | 16                    |
| 37  | 2-ethylenol                  | phenolic      | 2192                    | 1                     |
| 39  | 3-propylphenol               | plastic, leather| 2259                    | 1                     |
| 41  | 4-tert-butylphenol           | phenolic      | 2294                    | 16                    |
| 42  | 2,4-di-tert-butylphenol      | phenolic, leather| 2310                    | 16                    |
| 44  | 3-methyl-1H-indole           | fecal         | 2490                    | 1                     |
| 46  | 4-hydroxy-3-methoxybenzaldehyde | vanilla     | 2557                    | 4                     |

<sup>a</sup>All polypropylene odorants reported in this paper were consecutively numbered according to their retention time on the DB-FFAP column.

<sup>b</sup>Each odorant was identified by comparing its retention indices on two fused silica columns of different polarity (DB-FFAP, DB-5), its mass spectrum obtained by GC-MS, as well as its odor quality as perceived at the sniffing port during GC-O to data obtained from authentic reference compounds analyzed under equal conditions.

<sup>c</sup>Odor quality as perceived at the sniffing port during GC-O.

<sup>d</sup>Retention index; calculated from the retention time of the compound and the retention times of adjacent n-alkanes by linear interpolation.

<sup>e</sup>Flavor dilution factor; dilution factor of the highest diluted sample prepared from the concentrated volatile fractions in which the odorant was detected during GC-O by any of three panelists.

<sup>f</sup>2-methylbutanoic acid and 3-methylbutanoic acid were not separated on the fused silica column used for AEDA; GC-MS(EI) indicated a mixture of both compounds; the flavor dilution factor refers to the mixture.
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To verify the crucial role of the five odorants, for which OAVs \( \geq 1 \) had been determined (3, 17, 32, 4, 36), they were dissolved in oil in the concentrations previously determined, and this odor reconstitution model was orthonasally compared with the standard polypropylene material PP-1. Despite higher costs in comparison with sunflower oil, silicone oil was used for the odor reconstitution model, because it was absolutely odorless. The odor of the model reflected the characteristic plastic-type odor of the sample PP-1, indicating that the key odorants were successfully identified.

3.2 Insights into the sources of the key odorants in polypropylene materials

3.2.1 Influence of the composition of polypropylene material

Different additives were added to a polypropylene homopolymer individually (samples PP-3, PP-4, PP-5, PP-6, Table 1) and in combination (sample PP-7). The obtained mixtures were extruded. A sample extruded without additive served as reference (sample PP-2). The polypropylene homopolymer contained minor amounts of Irganox® 1010 FF and Irgafos® 168 FF indispensable for a basic stabilization. Volatiles from the individual samples were isolated as described before and subjected to a comparative AEDA. The results revealed 46 odorants, among which 44 could be identified (Table 4).

### Table 3: Concentrations, OTVs, and OAVs of major odorants in a standard polypropylene material (sample PP-1)

| No. | Odorant                              | Concentration b (μg/kg) | OTV c (μg/kg) | OAV d |
|-----|--------------------------------------|-------------------------|---------------|-------|
| 3   | hex-1-en-3-one                       | 0.0505                  | 0.0042        | 12    |
| 17  | butanoic acid                        | 118                     | 34            | 3     |
| 32  | 4-methylphenol                       | 2.87                    | 2.3           | <1    |
| 4   | butan-1-ol                           | 527                     | 520           | 1     |
| 36  | 2-tert-butylphenol                   | 66.5                    | 69            | 1     |
| 39  | 3-propylphenol                       | 0.772                   | 1.9           | <1    |
| 35  | 4-ethylphenol                        | 32.1                    | 270           | <1    |
| 13  | (2Z)-non-2-enal                      | 0.412                   | 3.6           | <1    |
| 6   | oct-1-en-3-one                       | 0.603                   | 6.9           | <1    |
| 46  | 4-hydroxy-3-methoxybenzaldehyde      | 9.90                    | 140           | <1    |
| 41  | 4-tert-butylphenol                   | 581                     | 8900          | <1    |
| 5   | octanal                              | 5.40                    | 140           | <1    |
| 31  | 4-methoxybenzaldehyde                | 0.500                   | 16            | <1    |
| 42  | 2,4-di-tert-butylphenol              | 5560                    | 330000        | <1    |
| 21  | (2E,4E)-nona-2,4-dienal              | 0.173                   | 30            | <1    |
| 15  | (2E)-non-2-enal                      | 0.508                   | 140           | <1    |
| 1   | butyl acetate                        | 2.44                    | 1000          | <1    |
| 22  | (2E)-undec-2-enal                    | 0.987                   | 7700          | <1    |

a All polypropylene odorants reported in this paper were consecutively numbered according to their retention time on the DB-FFAP column.
b Mean of triplicates; standard deviations were <15%.
c Orthonasal odor threshold value in oil.
d Odor activity value; calculated as ratio of concentration to odor threshold value.
### Table 4: Odorants in the volatile fractions obtained from polypropylene (PP) samples with different additives

| No. | Odorant                        | Odor | Rf² DB-FFAP | FD factor⁶ | PP-2 | PP-3 | PP-4 | PP-5 | PP-6 | PP-7 |
|-----|--------------------------------|------|-------------|------------|------|------|------|------|------|------|
| 1   | butyl acetate                 | fruity, banana | 1055        | 4          | <1   | 1    | <1   | <1   | 1    | 1    |
| 2   | hexanal                       | green, grassy | 1069        | <1          | 1    | 1    | <1   | 1    | <1   |
| 3   | hex-1-en-3-one                | plastic, pungent | 1081       | 64          | 16   | 4    | 16   | 64   | 1    | 1    |
| 4   | butan-1-ol                    | malty | 1131        | 1           | <1   | 1    | <1   | 1    | <1   |
| 5   | octanal                       | citrusy, soapy | 1280       | 16          | 1    | <1   | 16   | 1    | 1    |
| 6   | oct-1-en-3-one                | mushroom | 1290  | 64          | 16   | 4    | 16   | <1   | 16   |
| 7   | hexan-1-ol                    | grassy | 1360        | <1          | <1   | <1   | <1   | <1   | 1    |
| 8   | nonanal                       | citrusy, soapy | 1384  | 1          | <1   | <1   | 1    | 4    | <1   |
| 9   | non-1-en-3-one                | mushroom | 1393  | 1          | 1    | 4    | 16   | <1   | 1    |
| 10  | 2-methoxy-3,5-dimethylpyrazine | earthy | 1419  | 1          | 4    | 1    | <1   | <1   | <1   |
| 11  | acetic acid                   | vinegar | 1443  | 4          | 4    | 1    | 4    | 1    | 4    |
| 12  | 2,3-diethyl-5-methylpyrazine  | earthy | 1480  | 1          | 4    | 1    | 1    | <1   | <1   |
| 13  | (2Z)-2-enal                   | fatty | 1496  | 4          | 1    | <1   | 4    | 4    | 1    |
| 14  | 3-isobutyl-2-methoxypyrazine  | bell pepper | 1513 | <1          | <1   | 1    | 1    | <1   | 1    |
| 15  | (2E)-2-enal                   | fatty | 1523  | <1          | <1   | <1   | <1   | <1   | 16   |
| 16  | propanoic acid                | sweaty | 1530  | 16          | <1   | 1    | 1    | <1   | 1    |
| 17  | butanoic acid                 | sweaty, cheesy | 1616  | 4          | 16   | 1    | 4    | 1    | 1    |
| 18  | 2-methylbutanoic acid         | sweaty | 1657  | 16          | 1    | 1    | <1   | 4    | 1    |
| 19  | 3-methylbutanoic acid         | sweaty | 1657  | 16          | 1    | 1    | <1   | 4    | 1    |
| 20  | neral                         | citrusy, soapy | 1692  | <1          | <1   | <1   | <1   | 1    | <1   |
| 21  | (2E,4E)-nona-2,4-dienal       | fatty | 1722  | 1          | 4    | 1    | 1    | <1   | <1   |
| 22  | (2E)-undec-2-enal             | soapy | 1740  | 16          | 1    | 4    | 64   | 1    | 1    |
| 23  | (2E,4E)-deca-2,4-dienal       | fatty | 1800  | <1          | 4    | <1   | 4    | 1    | 1    |
| 24  | geosmin                        | beetroot | 1811  | <1          | <1   | 1    | 1    | 1    | 1    |
| 25  | hexanoic acid                 | sweaty | 1834  | 1          | <1   | <1   | <1   | <1   | <1   |
| 26  | unknown                       | rubber | 1911  | 64          | <1   | 16   | 64   | <1   | 16   |
| 27  | 1,3-benzothiazole             | rubber | 1948  | 1          | 64    | <1   | 16   | 4    | 4    |
| 28  | unknown                       | phenolic | 1972  | <1          | 64   | 16   | 4    | 16   | 64   |
| 29  | phenol                         | phenolic | 1987  | 1          | 1    | <1   | <1   | 16   | <1   |
| 30  | trans,4,5-epoxy-(2E)-dec-2-enal | metallic | 1996  | 16          | 16   | 16   | 16   | 64   | 16   |
| 31  | 4-methoxybenzaldehyde         | sweet woodruff | 2020  | 4          | 4    | 1    | 4    | <1   | <1   |
| 32  | 4-methylphenol                | fecal, phenolic | 2070  | 1          | 1    | 1    | 4    | 16   | 16   |
| 33  | 2-methoxy-4-propylphenol      | phenolic | 2115  | 1          | 1    | <1   | <1   | 1    | <1   |
| 34  | γ-decalactone                 | peach | 2136  | <1          | 1    | <1   | <1   | <1   | <1   |
| 35  | 4-ethylphenol                 | phenolic | 2163  | 1          | 16   | <1   | <1   | 256  | <1   |
| 36  | 2-tet-butylphenol             | plastic, phenolic | 2179  | 4          | <1   | <1   | <1   | 1024 | 256  |
| 37  | 2-ethylphenol                 | phenolic | 2192  | 1          | <1   | <1   | <1   | <1   | <1   |
| 38  | 2-aminoacetophenone           | foxy | 2213  | 1          | 1    | 1    | 1    | 16   | <1   |
| 39  | 3-propylphenol                | plastic, leather | 2259  | 1          | 1    | <1   | <1   | 1    | <1   |
| 40  | decanoic acid                 | soapy, musty | 2266  | <1          | 1    | 1    | 1    | <1   | <1   |
| 41  | 4-tert-butylphenol            | phenolic | 2294  | 64          | 16   | <1   | <1   | 4096 | 64   |
| 42  | 2,4-di-tert-butylphenol       | phenolic, leather | 2310  | 16          | <1   | <1   | 4    | 256  | 4    |
| 43  | 4-vinylphenol                 | phenolic | 2385  | 1          | <1   | 1    | <1   | 4    | 1    |
| 44  | 3-methyl-1H-indole            | fecal | 2490  | 4          | <1   | 1    | <1   | <1   | <1   |

(Continues)
The samples PP-2, PP-3, and PP-7, which were ~10–70 µg/kg and concentrations by far exceeded the concentrations determined in the sample PP-6. With 3100 µg/kg and 40600 µg/kg, their concentrations of 4-ethylphenol (36) and 4-tert-butylphenol (41) were clearly odor-active in the sample PP-6 (OAVs 45 and 5), whereas their OAVs were <1 in the samples PP-2, PP-3, and PP-7. The concentrations of 4-ethylbenzoic acid (35) and 2,4-di-tert-butylphenol (42) were also highest in the sample PP-6 and, however, still remained below the OTVs (data not shown). Thus, the data confirmed the crucial role of talcum for the degradation of phenolic antioxidants into odor-active alkylphenols.

Different from the phenolic compounds, with 32.1–79.6 ng/kg the concentrations of hex-1-en-3-one (3) did not show such large differences between the four samples. Thus, hex-1-en-3-one (3) is unlikely a degradation product of antioxidants.

### 3.2.2 Changes during injection molding

To visualize the impact of injection molding, OAV data obtained for the samples PP-7 and PP-1 were compared. Both samples were extruded after addition of Irganox® 1010 FF, Irgafos® 168 FF, Tinuvin® 770 DF, and Talcum CT 139. The sample PP-1 additionally underwent an injection molding process.

Of 22 quantitated compounds (cf. section 3.2.1), 17 showed OAVs <1 in both samples, and five compounds exhibited an OAV ≥1 (Table 6). These compounds were hex-1-en-3-one (3), butanoic acid

### TABLE 4 (Continued)

| No. a | Odorant b | Odor c | RI d DB-FFAP | FD factor e |
|-------|-----------|--------|--------------|-------------|
| 45    | tridecanolic acid | soapy | 2550         | 16 16 <1 1 <1 <1 |
| 46    | 4-hydroxy-3-methoxybenzaldehyde | vanilla | 2557         | 16 16 1 4 1 4 |

*a All polypropylene odors reported in this paper were consecutively numbered according to their retention time on the DB-FFAP column.

*b Each odorant was identified by comparing its retention indices on two fused silica columns of different polarity (DB-FFAP, DB-5), its mass spectrum obtained by GC-MS, as well as its odor quality as perceived at the sniffing port during GC-O to data obtained from authentic reference compounds analyzed under equal conditions.

*c Odor quality as perceived at the sniffing port during GC-O.

*d Retention index; calculated from the retention time of the compound and the retention times of adjacent n-alkanes by linear interpolation.

*e Flavor dilution factor; dilution factor of the highest diluted sample prepared from the concentrated volatile fractions in which the odorant was detected during GC-O by any of three panelists.

To visualize the impact of injection molding, OAV data obtained for the samples PP-7 and PP-1 were compared. Both samples were extruded after addition of Irganox® 1010 FF, Irgafos® 168 FF, Tinuvin® 770 DF, and Talcum CT 139. The sample PP-1 additionally underwent an injection molding process.

Of 22 quantitated compounds (cf. section 3.2.1), 17 showed OAVs <1 in both samples, and five compounds exhibited an OAV ≥1 (Table 6). These compounds were hex-1-en-3-one (3), butanoic acid...
(17), 2-tert-butylphenol (36), 4-methylphenol (32), and butan-1-ol (4). Among these, four showed an increase during injection molding, only 2-tert-butylphenol (36) remained unaffected. With OAVs of 8 and 12, plastic-like and pungent smelling hex-1-en-3-one (3) was clearly the most potent odorant in both samples.

3.2.3 | Effect of an alternative filler

Since the previous results indicated the highest impact on odorant formation in polypropylene materials for talcum (cf. Table 5), wollastonite was tested as an alternative filler. Lederer et al. reported the degradation of phenolic antioxidants in the presence of talcum and observed that polypropylene made with wollastonite showed less smell. The crucial compounds responsible for the different odor intensity, however, were not clarified. To fill this gap, the polypropylene sample PP-6 consisting of polypropylene homopolymer and the filler talcum was compared with a polypropylene sample that was prepared in the same manner, but using the filler Wollastonite CWZ 200 (sample PP-8, Table 1).

Of 22 quantitated compounds (cf. section 3.2.1), 18 showed OAVs <1 in both samples, and four compounds exhibited an OAV >1 (Table 7). These compounds were 2-tert-butylphenol (36), hex-1-en-3-one (3), butanoic acid (17), and 4-tert-butylphenol (41). The biggest differences between both samples were observed for 2-tert-butylphenol (36) and 4-tert-butylphenol (41). 2-tert-Butylphenol (36), which exhibited an OAV of 45 in the sample PP-6 containing talcum, was clearly lower in the sample PP-8 made with wollastonite resulting in an OAV <1. Similarly, the OAV of 4-tert-butylphenol (41) decreased from 5 to <1. Thus, these data indicated that 2-tert-butylphenol (36) and 4-tert-butylphenol (41) were not odor-active in the sample PP-8. A degradation of phenolic antioxidants to odor-active amounts of alkylphenols as observed in the presence of talcum did not occur when wollastonite was used as filler. This result was able to explain the observations of Lederer et al. on the molecular level. OAV data suggested that the odor of the sample PP-8 was due to hex-1-en-3-one (3) and butanoic acid (17), the only two compounds, which were present in concentrations exceeding their OTVs.

4 | CONCLUSION

Plastic-like and pungent smelling hex-1-en-3-one was identified as major odor-active compound in polypropylene materials. Its concentrations in six different polypropylene materials were within a rather narrow range, namely 0.0321–0.0796 µg/kg corresponding to OAVs of 8–19, in spite of differences in additives and processing. Its relevance was further confirmed by the analysis of three commercial polypropylene granulates intended to be used for injection molded

### Table 6

Concentrations, OTVs, and OAVs of major odorants in polypropylene samples without (sample PP-7) and with (sample PP-1) injection molding

| No. | Odorant         | Concentration (µg/kg) | OTV (µg/kg) | OAV |
|-----|-----------------|-----------------------|-------------|-----|
|     | PP−7 PP−1      |                       |             |     |
| 3   | hex-1-en-3-one  | 0.0321 0.0505         | 34          | 8   |
| 17  | butanoic acid  | 63.5 118              | 34          | 2   |
| 36  | 2-tert-butylphenol | 68.4 66.5          | 69          | 1   |
| 32  | 4-methylphenol  | 0.991 2.87            | 2.3         | <1  |
| 4   | butan-1-ol      | 294 527               | 520         | <1  |

*All polypropylene odorants reported in this paper were consecutively numbered according to their retention time on the DB-FFAP column.

*Mean of triplicates; standard deviations were <15%.

*Orthonasal odor threshold value in oil.

*Odor activity value; calculated as ratio of concentration to odor threshold value.

### Table 7

Concentrations, OTVs, and OAVs of major odorants in polypropylene (PP) samples with different fillers

| No. | Odorant         | Concentration (µg/kg) | OTV (µg/kg) | OAV |
|-----|-----------------|-----------------------|-------------|-----|
|     | PP−6 PP−8      |                       |             |     |
| 36  | 2-tert-butylphenol | 3100 23.4           | 69          | 45  |
| 3   | hex-1-en-3-one  | 0.0792 0.0458        | 0.0042      | 19  |
| 17  | butanoic acid  | 157 196              | 34          | 5   |
| 41  | 4-tert-butylphenol | 40600 153          | 8900        | 5   |

*All polypropylene odorants reported in this paper were consecutively numbered according to their retention time on the DB-FFAP column.

*Mean of triplicates; standard deviations were <15%.

*Orthonasal odor threshold value in oil.

*Odor activity value; calculated as ratio of concentration to odor threshold value.
or extruded goods. These samples showed even higher hex-1-en-3-one concentrations of 0.609–1.01 µg/kg corresponding to OAVs of 145–240 (Table 8). Despite its importance, the source of hex-1-en-3-one is yet unknown. Considering the small differences between the samples with and without antioxidants and fillers in our study, an origin from additives is unlikely. Furthermore, hex-1-en-3-one has been detected as major odorant not only in polypropylene samples, but also for example in a polyvinyl chloride-based material. Thus, it most likely neither originated from the polymer backbone. Alkylphenols, among which 2-tert-butylphenol was the most potent, represented the other important odorants in the polypropylene materials. Our results suggest that they were formed via degradation of phenolic antioxidants initiated by talcum. Consequently, none of the key odorants could be linked to the methyl-branched basic polymer.

Mitigation of the phenolic odorants was possible by using wollastonite as alternative filler or by using a combination of talcum and a mixture of antioxidants including Irganox® 1010 FF, Tinuvin® 770 DF, and Tinuvin® 777 DF in high amounts. As polypropylene materials are widely used in buildings, cars, and aircrafts, a reduction in odor-active compounds will ultimately contribute to improve the indoor air quality.

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NOMENCLATURE
2-aminoacetophenone
γ-decalactone
trans-4,5-epoxy-(2E)-dec-2-enal
geosmin
Irgafos® 168 FF
Irganox® 1010 FF
eral
Tinuvin® 770 DF

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TABLE 8 Concentrations, OTV, and OAVs of hex-1-en-3-one in commercial polypropylene (PP) samples

| Sample   | Concentrationa (µg/kg) | OTVb (µg/kg) | OAVc |
|----------|------------------------|--------------|------|
| PP-C1    | 1.01                   | 0.0042       | 240  |
| PP-C2    | 0.925                  | 0.0042       | 220  |
| PP-C3    | 0.609                  | 0.0042       | 145  |

aMean of triplicates; standard deviations were <15%.
bOrthonasal odor threshold value in oil.
cOdor activity value; calculated as ratio of concentration to odor threshold value.

CONFLICT OF INTEREST
The authors declare that they have no conflict of interest.

AUTHOR CONTRIBUTIONS
VM and UM conceived the study. UM provided the samples. SF and KR conducted the experiments and analyzed the data. MS supervised the experiments. SF, KR, VM, and UM contributed to project administration. SF and MS wrote the manuscript.

COMPLIANCE WITH ETHICS REQUIREMENTS
This article does not contain any studies with human or animal subjects.
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