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Probing nanoplastics derived from polypropylene face masks with hyperspectral dark-field microscopy

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HIGHLIGHTS
• UV-treated polypropylene face mask generated micrometer and sub-micrometer particles.
• Dark-field hyperspectral imaging can be used to probe mask-derived plastic particles.
• After UV treatment the distinct spectra of blue and white mask parts became similar.
• Two types of spectra could be observed for particles derived from UV-degraded mask.

Abstract

The high worldwide consumption of cheap plastic goods has already resulted in a serious environmental plastic pollution, exacerbated by piling of disposed personal protective equipment because of the recent outbreak of COVID-19. The aim of this study was to assess the feasibility of dark-field hyperspectral microscopy in the 400–1000 nm wavelength range for detection of nanoplastics derived from weathered polypropylene masks. A surgical mask was separated to layers and exposed to UV radiation (254 nm) for 192 h. Oxidative degradation of the polypropylene was evidenced by ATR FT-IR analysis. UV treatment for 192 h resulted in generation of differently shaped micro- and nano-sized particles, visualized by dark-field microscopy. The presence of nanoparticles was confirmed by AFM studies. The hyperspectral profiles (400–1000 nm) were collected after every 48 h of the UV treatment. The distinct hyperspectral features faded after prolonged UV exposure, but the assignment of some particles to either blue or white layers of mask could still be made based on spectral characteristics.

1. Introduction

The pandemic of COVID-19 resulted in high demand for personal protective equipment (PPE) and the worldwide production and consumption of disposable face masks increased accordingly (Ammendolia et al., 2021). There are several types of masks differing in their protective ability as well as materials and technologies used for their manufacture. Regardless of the type, most disposable face masks contain polypropylene formed into a non-woven meltblown or spunbond textile layer (Adanur and Jayswal, 2020). While some types of masks like medical respirators are used only by a limited number of professionals, simple surgical and procedural masks are cheaper and thus are much more widespread in population. In many countries mask wearing in public is mandatory or was mandatory for a prolonged period of time in the past two years.
Accumulation of used PPE has significantly exacerbated the problem of environmental plastic pollution, because discarded face masks, if not properly utilized, end their life in road ditches and municipal landfills and their leachates can be occasionally transferred to marine or fresh water bodies (Aragaw, 2020; Cordova et al., 2021; Hasan et al., 2021). When exposed to environmental impacts (sunlight, temperature differentials, mechanical abrasion and moisture) a discarded mask can gradually lose its integrity resulting in generation of small plastic particles, including micro- and nano-sized ones. There has been an increasing number of studies demonstrating toxic or otherwise harmful effects of micro- and nanoplastics on human and animal organisms (Silva et al., 2021; Kutralam-Muniasamy et al., 2022; Tesfaldet and Ndeh, 2022), which fuel the development of approaches to fast and high-throughput nanoplastics detection in environmental samples.

The weathering of disposable face masks was previously studied under controlled (Chen et al., 2021; Shen et al., 2021; Wang et al., 2021; Wu et al., 2022) or natural conditions (Khoirioni et al., 2020). However, in most of these studies only the plastic particles in milli- and micro-meter ranges were detected (Shen et al., 2021; Wang et al., 2021; Wu et al., 2022) with a few studies revealing particles sized <0.1 μm (Ma et al., 2021; Morgana et al., 2021; Sullivan et al., 2021). Different methods (bright-field, electron and atomic force microscopy) were applied in the above studies to detect micro- and nano-sized particles. While microplastic particles and fibers released from face masks are large enough to be observed using light microscopy (Chen et al., 2021; Rathinamoorthy and Raja Balasaraswathi, 2021; Liang et al., 2022), detection of shed nanoplastics is more laborious and requires the use of electron or atomic force microscopy (Ma et al., 2021; Sullivan et al., 2021). The main advantage of electron and atomic force microscopy methods is their high-resolution, allowing visualization of tiny nano-sized particles, but their disadvantages include a rather high cost, sample drying during preparation, and little information on the nature of the observed particles. To determine the particle chemical nature, energy dispersive X-ray spectroscopy (EDX), micro-Fourier transform infrared spectroscopy (micro-FTIR) or micro-Raman spectroscopy can be used, but a lower size of the analysed particles is limited to 20 μm for micro-FTIR and 1 μm for micro-Raman spectroscopy while EDX may give highly erroneous results (Ivelva et al., 2017). In one study (Morgana et al., 2021), fluorescent microscopy and flow cytometry were used for detecting particles <0.1 μm based on the autofluorescent properties of plastics. However, a potential problem here is that the plastics autofluorescence signals decrease with particle size (Morgana et al., 2021).

Recently, the potential of dark field hyperspectral microscopy to identify commercial micro- and nanoplastics (down to 100 nm) in biological objects was demonstrated (Nigamatzyanova and Fakhrullin, 2021). Dark-field microscopy (DFM) is advantageous over atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) because of much simpler sample preparation procedure not requiring sample drying which can potentially cause particle aggregation. Combination of DFM with hyperspectral imaging in dark-field hyperspectral microscopy allows identification of visualized nanoparticles (Fakhrullin et al., 2021). However, this method was previously used only for studying commercial polystyrene, polymethacrylate and melamin particles of narrow size ranges (Nigamatzyanova and Fakhrullin, 2021; Ishmukhametov et al., 2022) and was not applied for detection of plastics derived from real world specimens, such as face masks subjected to environmental impacts. Here we took a challenge to investigate the potential of dark-field hyperspectral microscopy to detect micro- and nanoplastics particles released from the outer blue spunbond layer, the middle white meltblown layer and the inner white spunbond layer of a disposable face mask. The nanoparticle detection and identification was supported by AFM and FTIR studies. According to the adopted classification of nanomaterials (Auffan et al., 2009), in our study the particles below 1 μm are considered nanoparticles, and those between 1 and 100 μm are considered microparticles.

2. Materials and methods

Face masks were purchased from OOO “Maska” (Russia) and, according to the manufacturer, consisted from an outer blue spunbond layer, a middle white meltblown layer and an internal white spunbond layer. All three layers were made of polypropylene.

2.1. Mask treatment and specimen preparation

The mask used was a standard size adult mask with a length of 17.2 cm and a width of 9 cm. The three layers of the mask were separated and each was cut into stripes 1 cm wide and 5 cm long to ensure the absence of folds and even irradiation of all parts. The stripes were put into a UV irradiation system (BIO-LINK, Vilber Lourmat, France) layered with aluminium foil and irradiated at 254 nm by 5 × 8-watt lamp tubes for 192 h. As the mask became evidently fragile in the course of exposure to UV light, we expected that 192 h of exposition would be enough to generate a significant number of nanoparticles. The irradiation lasted 16.5 h per day and was followed by a dark period of 7.5 h to imitate natural light conditions (Fig. 1). The maximal temperature registered in the UV camera during irradiation was 45.6 °C.

The UV-treated mask pieces (25 mg) were added to 5 ml of distilled water in a plastic tube (Eppendorf), vortexed for 1 min and an aliquot (10 μl) of the suspension was taken for microscopic analysis (DFM, AFM). The suspension was filtered through a PTFE filter (0.45 μm), pre-treated with ethanol and washed with distilled water. The pre-treatment with ethanol was used to render the PTFE filter more hydrophilic according to the general procedure recommended by PTFE filter manufacturers. The size and zeta-potential of the filtered specimen was measured (Zetazizer Nano, Malvern, UK) and an aliquot of the filtrate (10 μl) was taken for microscopic (DFM, AFM) analysis. Control specimens were prepared by using distilled water treated according to the same procedures and equipment.

To obtain a spectrum of an untreated mask, square areas (1 cm²) were cut from the blue and white mask layers of a new mask and briskly washed with distilled water. Then they were put on a glass slide with a drop of distilled water and covered with a coverslip.

2.2. Dark-field and hyperspectral imaging

Dark-field and hyperspectral microscopy was performed using an Olympus BX51 microscope (Olympus, Japan) equipped with CytoViva® high-aperture dark-field condenser (CytoViva Inc., USA) and halogen light source (Fiber-Lite DC-950, 150 W; Dolan Jenner Industries Inc., USA). The dark-field images were obtained using Exponent 7 software (Stable Microsystems, Godalming, UK). Hyperspectral data were collected at 2 nm spectral resolution in the 400–1000 nm range, using ImSpector V10E spectrograph (Specim, Finland) and a CCD camera (PCO AG, Germany). Recording of hyperspectral data and lamp-normalization of the acquired raw hyperspectral data were performed using ENVI 4.8 software (Harris Geospatial Solutions, USA). For specimen preparation extra clean dust-free Nexceler® glass slides and coverslips (Schott, Germany) were used.

At least 6–10 individual spectra collected from each specimen were used for statistical comparison. Noisy areas at the beginning and at the end of the spectra were discarded and the comparison was made in the wavelength range of 440–900. The following scheme for comparing spectra was used. Within a group of spectra belonging to one specimen, the correlation coefficient between individual spectra was calculated, and if the correlation between some spectra was weak (<0.3), such spectra were discarded. Using one-way analysis of variance (Anova), the group averages of the spectra were compared, and if they differed significantly, the average spectrum of each group was build and normalized. To compare two groups of spectra (belonging to two different specimens) the following procedure was used: (A) the correlation between the average spectra of the two groups was calculated; (B) using a z-test, the average spectra of the groups were
were recorded in the range of 600 to 4000 cm\(^{-1}\) for operation in the attenuated total reflection (ATR) FT-801 (Simex, Novosibirsk, Russia), equipped with ZnSe ATR prism.

2.4. FT-IR analysis

FT-IR analysis was performed by a Fourier transform infrared spectrometer FT-801 (Simex, Novosibirsk, Russia), equipped with ZnSe ATR prism for operation in the attenuated total reflection (ATR) mode. The spectra were recorded in the range of 600 to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) and averaged from 26 scans. The obtained spectra were CO\(_2\)- and H\(_2\)O-vapour and baseline corrected, using the FT-801 software (Simex, Novosibirsk, Russia).

3. Results

3.1. Dark-field and hyperspectral imaging of particles derived from UV-treated polypropylene mask sheets

Dark-filed images and reflected/scattered light spectra of the blue and white layers of an untreated mask are presented in Figs. 2 and 3. In dark-filed images, the mask blue layer appears as a bright-dotted material with several large pores (Fig. 2A). In the spectrum of the blue layer of a mask, a narrow peak is visible at 429 nm (Fig. 2F). After 440 nm, a steep incline of the spectral line is observed, with a secondary increase in the region of about 689 nm, developing into a sharp peak with a maximum at 745 nm. In dark-filed images, white mask layers are evenly coloured and crossing fibers of variable thickness can be distinguished (Fig. 3A,B). The internal white mask layer contained only thick fibers (Fig. 3B), while in the middle white layer both thick and thin fibers could be observed (Fig. 3A). The spectra of both white layers of a mask were similar in shape, showing some narrow peaks in the region up to 440 nm (Fig. 3G). Above 440 nm, a plateau or a gradual increase in the spectrum is observed, turning into a wide peak in the region of 700–1000 nm. Despite different manufacture processes of the two white layers, the hyperspectral profiles of the layers could not be reliably distinguished from each other, and in the following studies they were collectively regarded as a white part of mask.

First, the dynamic changes in the hyperspectral profiles of separated blue and white mask parts were studied. UV treatment for 192 h made all layers very brittle and destroyed them to small pieces of variable sizes (and even down to powder in some areas). In dark-filed images, the damage to the structure of mask fibers became clearly visible after 144 h of UV treatment for both blue (Fig. 2D) and white (Fig. 3E) layers. The distinct hyperspectral features of a blue mask layer faded after prolonged UV exposure (Fig. 2F), and the spectrum became closer to the spectrum of white mask layers.

When white and blue mask layers were exposed to UV radiation side by side for 192 h, the destroyed mask layers intermixed and it was impossible to unambiguously ascribe a certain patch to the blue or the white part. Some rather large pieces were taken for hyperspectral observations. These pieces were carefully placed on a dust-free glass slide with a drop of water, covered with a cover glass and observed with dark-field microscopy (Fig. 4A). The spectra in Fig. 3D were obtained from the areas coloured red and green in the inset of the Fig. 4D. By the appearance of the fibers, it could be assumed that green marks a fiber belonging to a blue layer (because of multiple bright dots), while red marks a fiber from a white layer. This supposition is supported by the shape of the spectra. The green spectra in Fig. 4D shows a peak at 429 nm, and an overall increase in the right half of the spectrum in the 700–1000 nm region (as it was observed for fibers from the white part). The red spectra in Fig. 4D with a peak at about 430 nm, followed by a steep decrease in the spectrum in the region of 440–689 nm resemble the spectra of the fibers from the blue layer, with the second peak at 745 nm becoming smoother or even disappearing after UV treatment of the mask. The belonging of fiber

Fig. 1. Main experimental procedures for treatment of mask sheets and detection of generated plastic particles.

compared; (C) two normalized graphs in the same coordinate system were built and (D) max difference between the two normalized average spectra was calculated. The spectra of particles from different specimens were considered similar if: in (A) the correlation was high (>0.7), in (B) the averages differed insignificantly, in (C) the graphs coincided visually, in (D) max <0.1.

2.3. Atomic force microscopy characterization

The particles derived from UV-treated mask before and after filtration through PTFE filter were dried on a clean glass slide. AFM images of particles and fibers of a mask were obtained using a Dimension Icon microscope (Bruker, USA). Scanning was performed in air in the PeakForce Tapping mode. Standard silicon nitride cantilevers ScanAsyst-Air (Bruker) (nominal length 115 μm, tip radius 2 nm, spring constant 0.4 Nm\(^{-1}\)) were used. To obtain high-quality images of topography and nanomechanical characteristics, the optimal scanning parameters were set, the scanning force was 1–2 nN at a scanning rate of 0.8–0.9 Hz. Images were obtained at a resolution of 512 scan lines. Image editing and calculation of nanomechanical characteristics were performed using Nanoscope Analysis v 1.7 software (Bruker). The quantitative calculation of roughness was carried out in the Nanoscope Analysis software in the Height Sensor channel. To obtain reliable results, the images underwent three order flattening. The calculation of the surface roughness of the fibers was made in 10 square areas of the same size (1 μm × 1 μm) for each sample.

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The green spectra in Fig. 4D shows a peak at 429 nm, and an overall increase in the right half of the spectrum in the 700–1000 nm region (as it was observed for fibers from the white part). The red spectra in Fig. 4D with a peak at about 430 nm, followed by a steep decrease in the spectrum in the region of 440–689 nm resemble the spectra of the fibers from the blue layer, with the second peak at 745 nm becoming smoother or even disappearing after UV treatment of the mask. The belonging of fiber

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fragments to either blue or white mask layer based on the apparent resemblance of the overall fragment appearances and spectral profiles was further confirmed by statistical calculations of spectra similarity (Table 1).

Then, UV-treated mask particles were added to the distilled water and filtered through a filter with the pore size of 0.45 μm. Aliquots of the particle suspensions before and after filtration were studied using dark-filed and hyperspectral microscopy. In dark filed images of the particles before filtration the size of the particles varied greatly. It was impossible to obtain data on the hydrodynamic diameter and zeta-potential of the particles in the specimen before filtration using laser Doppler velocimetry, because of the very high polydispersity of the specimen. In dark-field images, particles before filtration had various shapes and sizes, ranging from hundreds of nanometers to tens of micrometers (Fig. 4B). Spectra were separately obtained for particles sized up to 1 μm and for particles larger than 1 μm,
according to visual observations. For large particles (>1 μm), two types of spectra were observed. The first type is the spectrum with a peak at 430 nm followed by a sharp decline, with some particles also retaining (albeit a strongly smoothed) a second peak with an onset at 689 nm (Fig. 4E, “micro-1”). In spectra of this type, the left side of the spectrum is generally higher than the right side. Such spectra are similar to the spectrum of the material from the blue layer of the mask described above. The second type includes the spectrum with a peak at 430 nm and a rising right side of the spectrum (Fig. 4E, “micro-2”), similar to the spectrum of the material of the white mask layers. In some cases, the beginning of a wide peak shifted from the 700 nm region to a shorter wavelength region.

Table 1
Pairwise comparison between the spectra of particles derived from an UV-treated mask and the spectra of non-treated blue and white mask layers. Micro particles – particles sized >1 μm, and nano particles – particles sized <1 μm, according to visual observations. The number 1 or 2 indicates the form of the spectral profile shown in Fig. 4E,F.

| Spectra                      | Correlation coefficient (>0.7) | Difference between averages | Max difference (<0.1) | Conclusion               |
|------------------------------|--------------------------------|-----------------------------|------------------------|--------------------------|
| Comparison with spectra of the blue layer of an untreated mask |                                 |                             |                        |                          |
| Large piece - 1              | 0.95                           | Significant                 | 0.1                    | Spectra are similar      |
| Large piece - 2              | –0.54                          | Significant                 | 0.2                    | Spectra are not similar  |
| Micro particles before filtration - 1 | 0.95                       | Significant                 | 0.00876                | Spectra are similar      |
| Micro particles before filtration - 2 | –0.44                      | Significant                 | 0.3244                 | Spectra are not similar  |
| Nano particles before filtration - 1 | 0.92                       | Significant                 | 0.42                   | Spectra are not similar  |
| Nano particles before filtration - 2 | 0.53                       | Significant                 | 0.41                   | Spectra are not similar  |
| Nano particles after filtration - 1 | 0.89                       | Significant                 | 0.57                   | Spectra are not similar  |
| Nano particles after filtration - 2 | –0.54                      | Significant                 | 0.32                   | Spectra are not similar  |

Comparison with spectra of a white layer of an untreated mask

| Spectra                      | Correlation coefficient (>0.7) | Difference between averages | Max difference (<0.1) | Conclusion               |
|------------------------------|--------------------------------|-----------------------------|------------------------|--------------------------|
| Large piece - 1              | –0.65305                      | Significant                 | 0.22                   | Spectra are not similar  |
| Large piece - 2              | 0.97                          | Significant                 | 0.05                   | Spectra are similar      |
| Micro particles before filtration - 1 | –0.64591                | Significant                 | 0.34                   | Spectra are not similar  |
| Micro particles before filtration - 2 | 0.91063               | Significant                 | 0.14                   | Slightly similar         |
| Nano particles before filtration - 1 | –0.84559                | Significant                 | 0.76                   | Spectra are not similar  |
| Nano particles before filtration - 2 | –0.92862                | Significant                 | 0.72                   | Spectra are not similar  |
| Nano particles after filtration - 1 | –0.88846               | Significant                 | 0.57                   | Spectra are not similar  |
| Nano particles after filtration - 2 | 0.052708                | Significant                 | 0.35                   | Spectra are not similar  |
3.2. AFM characterization of mask-derived particles

For small particles (<1 μm), spectra of two types were also observed. The first is the spectrum with a peak at 430 nm and a further smooth, almost linear, decrease in the spectrum (Fig. 4E, “nano-1”). Such spectra are similar to the spectrum of the material from the blue layer of the mask. The second is an arcuate spectrum, in which the right and left parts practically do not differ in height (Fig. 4E, “nano-2”). Presumably, such a spectrum may belong to particles obtained from a white layer of the mask. The appearance of an arched spectrum in nanoparticles can be explained by an even greater shift of the broad right-hand peak to the short-wavelength region, in comparison with the spectrum of microparticles. However, there were no distinctive features in the spectral profiles of small particles obtained from UV-treated mask, and the spectra became noisier at the beginning and at the end as the particle size went down.

The sizes and zeta potentials of the particles filtered through a 0.45 μm filter were measured. The particles had a hydrodynamic diameter of 346.2 ± 10.14 nm (PDI 0.474 ± 0.052) and a zeta potential of −9.48 ± 0.193. After filtration through a 0.45 μm filter, only particles <1 μm in size were observed in the sample by dark-field microscopy. These particles demonstrated the spectra of the two types described above for small particles before filtration (“nano-1” and “nano-2”) (Fig. 4F).

To try to determine the origin of small particles from either blue or white mask layers, pairwise comparison of all the spectra with pristine blue and white layers was performed. The main criteria of spectra similarity were the correlation coefficient (>0.7) and the max difference (<0.1). In most cases, no significant correlation between the spectral features were found, not allowing one to determine with certainty the origin of small particles from either a blue or a white mask layer (Table 1). Only in case of some micro-sized particles the resemblance of spectra to that of a blue mask layer was statistically significant (Table 1). Thus, the visual similarity between some forms of spectral profiles was only apparent and was not confirmed when compared using mathematical methods.

3.2. AFM characterization of mask-derived particles

First, blue and white fibers from the three layers of an untreated mask were visualized using AFM, and the adhesion and topography properties of different mask fibers were compared (Fig. 5). The fibers differed greatly in surface topography, which is clearly seen in the topography channels and the topography plot. The white fiber from the middle layer had a more pronounced surface texture than the fibers from the other two layers, which was confirmed by the roughness measurements.

A fiber from the middle white layer had a rougher surface (Sa = 5.8 ± 1.7 nm, Sq = 7.6 ± 2.3 nm) than those from the internal white (Sa = 1.9 ± 0.5 nm, Sq = 2.2 ± 0.7 nm) and outer blue layers (Sa = 1.7 ± 0.3 nm, Sq = 2.3 ± 0.5). The higher roughness of fibers from the middle layer was observed previously (Ma et al., 2021; Wang et al., 2021) and was explained by peculiarities of meltblown and spunbond manufacture processes (Ma et al., 2021).

When the mixed particles derived from white and blue mask layers exposed to UV radiation for 192 h were analysed before and after filtration through a filter with the pore size of 0.45 μm, a large number of nanosized particles were visualized (Fig. 6). Heterogeneous particles were visible in the sample before filtration, differing both in shape (platy, round, rod-shaped, etc.) and size (up to 10 μm) (Fig. 6A), while in the sample after filtration (Fig. 6B) mostly spherical nanoparticles with sizes as small as 63 ± 25 nm were observed. When studied in the adhesion channel, the unfiltered samples were found to be more adhesive than the filtered ones (Fig. 6C,D).

3.3. Changes in the FT-IR spectra of polypropylene mask sheets in the course of UV exposure

The process of UV-induced mask degradation could be also observed by ATR FT-IR studies. ATR FT-IR spectra of non-treated blue and white mask layers did not differ (Fig. 7) and coincided with the spectrum of polypropylene published in other papers (Morent et al., 2008; Wang et al., 2021; Ullah et al., 2020). The characteristic bands at 2949 cm⁻¹, 2916 cm⁻¹, 2867 cm⁻¹, and 2837 cm⁻¹ were observed corresponding to C—H stretching vibrations in alkanes, together with the peak at 1453 cm⁻¹ corresponding to C—H scissoring vibrations in alkanes and the peak at 1375 cm⁻¹ resulting from C—H rocking vibrations in methyl. The peaks between 1200 and 700 cm⁻¹ could be attributed to C—C stretching vibrations, C—H wagging vibrations, and CH₃ and CH₂ rocking vibrations (Morent et al., 2008).

UV treatment did not significantly change the overall appearance of the IR-spectra, but two peaks at about 1730 cm⁻¹ and 1714 cm⁻¹ became more prominent as the duration of UV-exposure increased (Fig. 7B,C). The peaks at 1730 cm⁻¹ and 1714 cm⁻¹ can be assigned to C==O stretching vibrations in aldehydes and ketones. The apparent increase in the intensities of peaks corresponding to carbonyl groups can result from oxidative destruction of polypropylene and was previously observed in polypropylene pellets exposed to UV radiation in air (Cai et al., 2018).

4. Discussion

Many papers were published recently on generation of plastic particles from disposable medical masks, demonstrating that improperly discarded face masks can be a source of considerable environmental pollution. Variable numbers and sizes of released plastic particles were reported depending on the methods used and exposure conditions. It was calculated that a single 3–4 g polypropylene surgical mask could release at least 0.88 million microplastic particles after its complete decomposition (Sun et al., 2021), while >1.5 million or even 16 million microplastics released...
from one weathered mask was reported in another study (Wang et al., 2021). More than one billion of irregularly-shaped particles sized from about 5 nm to about 600 μm were released from a surgical or N95 face mask to water after rigorous shaking for 3 min (Ma et al., 2021). In another study, face masks emitted a significant amount of grain sized particles measured between 360 nm – 500 μm according to SEM analysis (Sullivan et al., 2021). When a stereomicroscope was used to estimate the release of microplastics form a face mask to water, expectedly, a much lower number of particles could be found – about 200 particles for a new masks and about 1300 particles for a used mask with sizes ranging from <100 μm to >2000 μm (Chen et al., 2021), with the number of released microplastics from one mask achieving >2000 pieces a day (Liang et al., 2022). It was found that as many as 20,000 fibers could be released from a new face mask, and the number of released fibers is even higher for a weathered mask (Rathinamoorthy and Raja Balasaraswathi, 2021). Using electron microscopy, the release of particles of up to 0.5 mm in size from naturally weathered surgical masks was shown (Shen et al., 2021). In another study, nano-sized plastic particles were detected in the leachate from surgical mask using a field-emission SEM equipped with an EDX or by AFM (Ma et al., 2021). Mask exposure to sea water resulted in significantly higher microplastic shedding compared to fresh water, which was attributed to higher pH and density of sea water (Rathinamoorthy and Raja Balasaraswathi, 2021). However, in another study, polypropylene degradation in the ultrapure water was higher than that in the simulated seawater environment, which was explained by increased refractive index of saline water (Cai et al., 2018). Exposure to UV radiation leads to cleavage of polymer chains and the degradation of the bulk material (Singh and Sharma, 2008). Moreover, the degradation degree of polypropylene in air is significantly higher than that in the solution environments, probably because of the higher access to the oxygen and higher rate of UV light utilization (Cai et al., 2018). Thus, the conditions used in our study were efficient for a rather quick degradation of a polypropylene mask, which was partly powdered after 192 h of UV exposure even without mechanical influence. It can be expected that the degradation of masks improperly disposed in urban areas where they are exposed to alternating sunlight in the air and occasional fresh-water rainfalls can be even faster. Being transferred to water, the macroscopic fragments obtained from a UV-degraded mask generated micro- and nano-sized particles of variable shapes. Similarly to our study, when the mask weathering was induced by UV treatment for up to 48 h followed by sand rubbing the leaching of plastic nano- and micro-particles from the weathered mask was also found (Wang et al., 2021). However, the authors focused only on analysis of micrometer-range particles and did not provide any details on detected nanosized plastics.

It was previously shown that fibers belonging to either internal or middle white layer differ in the number of produced microplastics (Ma et al., 2021) and the middle layer is degraded faster than the other two layers (Wang et al., 2021). In our study, different mechanical characteristics of the fibers produced by either meltblown or spunbonding process were found by AFM measurements. However, the melt-blown and spunbond
white layers were almost indistinguishable from each other by hyperspectral imaging probably because all mask layers had the same chemical composition, as was evidenced by FTIR studies.

The nano and microsized particles generated as a result of bulk plastics destruction can be harmful to humans and other living creatures. The nanoparticles can penetrate the organism through ingestion, inhalation, and dermal contact, transferring the adsorbed chemical contaminants or pathogenic microorganisms (De-la-Torre et al., 2021). The ability of human skin fibroblast to adsorb and internalize polystyrene nanoparticles was recently shown by direct observations with AFM and dark-field hyperspectral microscopy (Akhatova et al., 2022).

Various methods were proposed to date to assess microplastic and nanoplastic pollution, like fluorescent microscopy after staining with lipophilic dyes (Ranjan et al., 2021); thermal desorption-proton transfer reaction-mass spectrometry (Materić et al., 2020), inductively coupled plasma-mass spectrometry (Bolea-Fernandez et al., 2020; Jiménez-Lamana et al., 2020), X-ray photoelectron spectroscopy (Hernandez et al., 2019), micro-FTIR and micro-Raman spectroscopy (Oßmann, 2021); nanoparticle tracking analysis (Lambert and Wagner, 2016; Ekvall et al., 2019), TEM (Gigault et al., 2016), and SEM (Ranjan et al., 2021). However, most of these methods are non-specific to plastic particles or rather laborious, and thus, the development of new, more selective, techniques is desirable.

Fig. 7. FT-IR spectra of mask layers non-exposed (A) and exposed to UV radiation for different time periods (B – blue, C – white part).
In our study, AFM was capable of revealing much more nanoparticles than dark-field hyperspectral microscopy, probably because of different specimen preparation procedures. In dark-field hyperspectral microscopy, the particles are suspended in a liquid media and the limited focal plane of dark-field hyperspectral microscopy allowed the observation of only a fraction of suspended nanoparticles, while for AFM, a specimen was dried and thus all the particles deposited from a liquid column could be observed. Additionally, smaller nanoparticles were found with AFM compared to dark-field hyperspectral microscopy, because of higher resolution power of this microscopy type. Thus, AFM is a more powerful tool than dark-field hyperspectral microscopy for visual detection of very small nanoparticles, but it has a limited ability of particle identification. Identification of particles based on such properties as particle adhesion can be unreliable, as it was observed in our study where non-treated fibers, and particles obtained from UV treated mask before and after filtration all differed in their adhesion characteristics. Other measured mechanical attributes like elastic modulus also depend on the size of the object studied (Price et al., 2006; Guo et al., 2014).

The combination of direct nanoparticle visualization and its simultaneous hyperspectral characterization in dark-field hyperspectral microscopy makes this approach very useful for detection of micro- and nano-plastic pollution. As a rule, the intensity of a hyperspectrum obtained from a particle decreases with a decrease in the particle size, which limits the ability of dark-field hyperspectral microscopy to differentiate between small nanoparticles of various origins. However, dark-field hyperspectral microscopy supported by a mathematical analysis can suggest the nature of observed particles. The number of works in this field is still limited and variable spectral ranges were comprised so far for hyperspectral plastics characterization. Near-infrared hyperspectral imaging in the wavelength range of 900–1700 nm was used to obtain the spectral features of particles derived from different plastic polymers (Zhu et al., 2020) and to detect microplastics in seawater (Shan et al., 2019). Some other wavelength ranges (1000–2500 nm) were applied to assess microplastic contamination in aquatic samples (Piarulli et al., 2020) and to study the release of plastic particles from branded teabags (951–2496 nm) (Xu et al., 2021). The detection limit of 80 μm (Piarulli et al., 2020) and 100 μm (Zhu et al., 2020) for microplastic hyperspectral identification was reported in these studies. It was found that the wavelength range of 1000–2500 nm was the most suitable for recognition of polyethylene particles sized above 300 μm (Karlsson et al., 2016). In situ detection of underwater microplastics (0.5–5 mm) based on hyperspectral imaging in the wavelength range of 400–720 nm was recently proposed (Huang et al., 2021). The scarcity of the works in the field do not allow full estimation of potentiality of hyperspectral imaging for nanoplastics detection, and further development of this technique can be expected in the future. Compared to the combination of electron microscopy with EDX, usually applied for observations of nano-sized plastics, dark-field hyperspectral microscopy is much less expensive and laborious, allowing quick sample examination without complex specimen preparation.

5. Conclusions

The recent global outbreak of COVID-19 has increased the plastic pollution burden of our planet, highlighting the urgent need for elaboration of new analytical techniques for identification of synthetic polymer materials and their degradation products. The three layers of disposable polypropylene face masks were for the first time characterized using hyperspectral microscopy in the wavelength range of 400–1000 nm. The pristine blue and white mask layers had slightly different spectral profiles, while the spectra of the inner and middle white layers were indistinguishable. After UV exposure for 192 h the distinct spectral features of blue and white mask layers became less prominent. UV treatment resulted in generation of micro- and nanosized particles. The comparison of the spectra of particles derived from a degraded mask with those of the pristine mask using statistical treatment allowed the assignment of some microplastics to a certain mask layer. However, the muffling of spectral features during polymer degradation suggests that further development of mathematical and computational methods for spectral data analysis would be helpful for robust nanoparticle identification. The results of this model study can be regarded as a first step on the way to the detection of mask derived particles or other polypropylene particulate pollutants in real environmental samples using dark field hyperspectral microscopy. In the future, the method can be extended to the analysis of UV-induced degradation of other synthetic polymers potentially hazardous to the environment.
