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Development of disposable filtering mask recycled materials: impact of blending with recycled mixed polyolefin and their ageing stability

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Abstract

A survey on Covid-19 protecting masks habits carried out on the Italian population at the end of 2020 revealed that disposable face masks are the most used, thus resulting in a considerable quantity of waste. Therefore, a separate collection of these devices based on local platforms such as schools, offices and factories is proposed. This would limit collecting costs, ensure the origin and quantity and simplify the sanitizing treatment of the masks, in order to allow their introduction into the industrial recycling stream of plastic materials.

In this scenario, an urban separate waste collection material (namely mixed polyolefin) was selected and melt blended in several ratios with the disposable filtering masks. Two recycling solutions have been envisaged: the use of the filtering part alone or the joint introduction of the ear loops.

Compared to the mixed polyolefin, the resulting recycled materials from filtering face masks have lower viscosity but comparable toughness and superior stiffness and strength. The presence of ear loops in the recycled improves the rigidity but slightly decrease the viscosity and worsen both the strength and toughness. Furthermore, conceiving an outdoor application, the stability to photo oxidation was investigated through an accelerated ageing process. The elaborated degradation rate of the masks material is similar to a commercial polypropylene, while for the mixed polyolefin is greatly reduced. The mixed compounds have intermediate degradation rates.

Key words

Face mask; mechanical recycling; recycled mixed polyolefin; mechanical properties; photo degradation; waste.

1. Introduction

An updated published research on recycling of plastic packaging, reported that in Europe only 32% of polymers were collected for recycling, while 25% were sent to landfill and 43% were incinerated (Schyns and Shaver, 2020). It is therefore clear the need to develop and promote methods that increase the recycling fraction compared to the other two solutions recognized as less sustainable (Bora et al., 2020; Gu et al., 2017; Sharma et al., 2020). Due to the currently pandemic situation, one of the main challenges is represented by disposable face masks, which mostly ended up in landfills or incineration (Armentano et al., 2021; Cesaro and Pirozzi, 2020; Rhee, 2020; Selvaranjan et al., 2021). The main constituent material was found to be polypropylene (PP) (Battegazzore et al., 2020). According to a study conducted in Japan by Narita et al. (Narita et al., 2002), the CO_2 emissions from the production of 1 kg of PP would be1.4 kg. The main body of the surgical mask is made up of just some grams, however, must be multiplied by the huge number of people who use them globally and by the fact that are single use devices.

The most sustainable scenario in this field is to mechanical recycle the waste to obtain a regenerated material that can be used in place of a first use material and possibly recycle it over and over again (Bora et al., 2020).

In a recent article it was shown that the materials with which most disposable masks are made, are potentially recyclable between 78 % and 91 % of the total weight (Battegazzore et al., 2020). However, the same article also highlighted the variability of the materials used by many producers on the market and the difficulty in mechanically recycling the different components all together. In addition, other types of masks, such as FFP2, can be collected and recycled but have a further heterogeneity of materials (Crespo et al., 2021). Therefore, the properties of the recycled materials obtained require an adequate development to fulfil different industrial application fields. Lastly, it has to be taken into account that the accurate amount of material potentially available nowadays is still unknown (Prata et al., 2020; Singh et al., 2020).

Starting from this last aspect, forecasts in the early stages of the pandemic estimated a large use of these devices (1 billion face masks each month in Italy - on March 2020 as reported by the Politecnico di Torino (Torino, 2020). In fact, it is extremely difficult to quantify the actual use of disposable masks as there is no data on sales or quantities disposed. Due to the lack of information, the first part of the article focuses on the results of a survey that directly investigated the citizens habits. This was carried out in December 2020 in Italy and received over 1000 answers. The main result is that the majority of respondents still use disposable "surgical" masks and are willing to throw them into a separate collection system. Although no economic assessments are presented, a dedicated recycling system spread at local level must be provided. Its affordability will be directly connected to the proximity of the collection site. Moreover, the elaborated data showed that the amount of waste generated by the disposed masks is not marginal compared to the other municipal waste and therefore is worth being industrially taken into consideration. This first important result made meaningful the further development of the research.

In the study, a new recycle perspective for disposable masks is presented, together with other urban waste plastics. A mixed polyolefin (MPO) waste fraction separated using flotation sorting of plastic wastes was selected as dilution source since it requires minimal sorting and is much cheaper than neat PP and PE (Schyns and Shaver, 2020).

To get rid of the possible influence of the heterogeneity of mask material (Armentano et al., 2021), in the present article only the "surgical" masks are considered and two approaches were deepen: use only the filtering part of the masks (M) or the filtering part together with the ear loops (ME). From the first approach, filtering part consists of about 78% of the total weight and is made of polypropylene (PP), like all the masks previously analyzed (Battegazzore et al., 2020). This material can be separated by floatation in recycling plants for plastics. In the second option, all the plastic parts were considered together, reaching over 90% of the total weight but having a heterogeneous system. In this latter, the separation is not necessary except for the metal nose clip. In both cases, the recycling study was carried out using only new disposable face masks.

The materials obtained with different mixing ratio of MPO and M or ME were characterized for their rheological and mechanical properties and correlated to their morphological peculiarity. Finally, designing possible outdoor applications, the photo-oxidation ageing was investigated pointing out the differences that adding M or ME has on the MPO.

2. Materials and Methods

2.1. Materials

The disposable face masks were purchased from Xiantao Wenjun non-woven co., Ltd. (China) Standard GB/T 32610-2016.

The neat filtering face mask is used and coded as M in the paper while the filtering face mask together with the ear loop parts are coded as ME (Characterization added in the SI and Figure S1).

The recycled mix of PP and PE (MPO) obtained from municipal wastes is a commercial grade Bretene 003GR160 from Breplast S.p.a., made of 70 wt.% of PP and 30 wt.% of PE from the supplier datasheet and coded as rPP in the text.

2.2. Survey

The online survey was created with “Google Forms” and consisted of 15 multiple choice questions in Italian language, 9 of them were compulsory while the others requested only if relevant. All the question have been translated and listed in the Supporting Information.

The survey was promoted via local newspaper, social networks and word-of-mouth, in order to achieve the larger spreading possible. Data collection lasted for one month before Christmas holiday when in Italy were witnessing the second wave of the pandemic. During this period the on-site working was allowed, even though remote working was encouraged. The activities of the catering were allowed only until 6.00 pm and the school were open with alternation of on-site and distance learning.

2.3. Face mask mechanical recycling process

To have a uniform and homogeneous starting material, a primary recycling step was performed using an internal mixer Brabender. A quantity of about 50 g of the mask filtering part were separated manually from the other parts and cut in squares of about 10 mm, then processed at 190°C and 30 rpm for 10 minutes. The second recycling phase involved the mixing of the material obtained in the first step with a co-rotating twin screw micro extruder DSM Xplore 15 ml microcompounder. The screw speed was maintained at 50 rpm for the feeding time and increased up to 100 rpm for the residence time, fixed for all runs at 2 min. The heating temperature was selected at 190°C.

The mixing of different concentrations of M or ME in the rPP was investigated: the first number in the material code is the weight ratio of rPP and the last part of the name is the weight ratio and type of material from the recycled mask (e.g. 25rPP75M is the formulation with 25 wt.% of rPP and 75wt.% of M).

The extruded materials were manually pelletized and placed inside a mold made of a 0.1 mm thickness aluminum foil with a 100x100 mm^2 hole inside two metal plates. Using a hot compression molding press Collin P200T at 190°C for 2 min under a pressure of 5 MPa the thin film was obtained. The same conditions were adopted for the discs for rheology tests, with a diameter of 25 mm and a thickness of 1 mm.

2.4. Ageing

UV ageing of films has been carried out by irradiations in air in a SEPAP 12/24 unit (Atlas Material Testing Technology LLC) at a wavelength > 300 nm. The apparatus was equipped with four medium-pressure mercury lamps with borosilicate envelope able to filter wavelengths below 300 nm. It was designed for accelerated artificial UV ageing tests in conditions comparable to natural outdoor weathering. Samples were homogeneously exposed on a rotating support in the center of the chamber. The surface temperature of the samples was accurately controlled and maintained at 60°C ± 1°C through a thermocouple placed behind a reference film with similar chemical composition as the exposed samples.

2.5. Analyses

The thermal properties have been evaluated by Differential Scanning Calorimetry (DSC) and Thermogravimetric analyses (TGA). DSC measurements have been performed by a DSC TA Q20, using 8±1 mg of sample and the chamber has been purged by nitrogen. Each sample has been heated from -50°C to 300°C at 10°C min^{-1}. The melting temperature, as well as the melting enthalpy have been obtained from the peak maximum and as the integral of the area under the heat flow curve, respectively.

TGA were carried out in air, from 50 to 700°C with a heating rate of 10°C/min. The used equipment is a Discovery thermo balance (TA Instruments) (experimental error: ±0.5 wt.%, ± 1 °C) with samples of approximately 10 mg placed in open alumina pans and fluxed with air at 25 mL/min.

The morphologies of the film cross sections of rPP and compounded materials were examined after mechanical tests and gold-metallization using a EVO 15 Scanning Electron Microscope (SEM) from Zeiss (beam voltage: 20kV working distance: 8.5 mm). Elemental analysis was carried out by EDS (Energy Dispersive X-ray spectroscopy) using an X-ray probe (Oxford Ultim Max, model 40).

Attenuated Total Reflection (ATR) was used to investigate chemical composition of the rPP and ME using a Frontier FT-IR spectrophotometer (16 scans and 4 cm^{-1} resolution, Perkin Elmer) equipped with a universal ATR sampling accessory and a diamond crystal.

The rheological properties of the melt blended materials were analyzed using an ARES rheometer fitted with a 25 mm parallel plate geometry. The gap between the plates was set to 1 mm. Dynamic strain sweep tests were carried out to confirm the linearity of the viscoelastic region up to 10% strain at 100 rad/s frequency. Frequency sweeps were carried out to determine the complex viscosity (η^*) over a frequency range of 0.1–100 rad/s at 10% strain. Tests were performed under a nitrogen atmosphere to avoid any degradation.

The complex viscosity curves of materials have been fitted using a modified Carreau model (Filippone et al., 2015):

$$\eta^*(\omega) = \frac{\eta_0}{[1 + (\lambda\omega)]^{(1-n)}} + \frac{\sigma_0}{\omega}$$

Where σ_0 is the melt yield stress, η_0 is the zero shear viscosity, λ is the relaxation time and n is the dimensionless power law index.

Tensile tests were performed at room temperature using a loading cell of 50 N (error <0.25%), a strain rate of 1 mm/min and a gauge length of 20 mm with an Instrom 5966 model machine equipped with 250 N rubber face pneumatic grips. The specimens for the stress–strain analyses were 40x10x0.1 mm^3 obtained by cutting the compression-molded films with scissors. Three specimens were used for each formulation and the average values and corresponding standard deviations of the tensile modulus (E), elongation at break (ε) and maximum tensile strength (σ_M) were calculated and reported.

The samples for the mechanical tests were conditioned at 23°C and 50% of relative humidity before analyses.

The compression molded films were subjected to accelerate ageing using a SEPAP 12/24 unit and monitored with a Frontier FT-IR spectrophotometer (16 scans and 4 cm^{-1} resolution, Perkin Elmer) equipment. The photo-oxidation has been followed by monitoring the intensity of the maximum absorbance in the 1800-1690 cm^{-1} range (C=O vibration stretching band range) as a function of exposure time. In order to avoid differences due to film thickness absorption, the degradation peak has been normalized to the absorption peak at 2723 cm^{-1} (C-H vibration stretching band of PP). The Oxidation Induction Time (OIT) has been calculated as the time at which the C=O peak starts to increase linearly with time and the slope of the line after the OIT has been indicated as the degradation rate.

3. Main results and implications of the survey on the use of disposable face masks

The survey was published online in December 2020 via Google's web platform and consisted of several questions with multiple choice answers. The main cross-section of respondents focused on young people (more than 60% are under 40 and the 35 % is in the 20-30 age group - Figure 1a) from the North of Italy (84%).

According to the 2020 Italian population census (ISTAT), the amount of citizens between 15 and 20 years old was the 4.8% of the population, while the age group 20 - 40 represented the 22%, the range 40-60 years was the 31% and the over 60 reached approximately the 30 % of the overall population. Lastly, the under 15 years old group accounted for the 13% but does not have entirely the legal obligation to wear masks and has not been greatly reached by the presented survey.

Considering that more than 80 % of respondents are in the age group 20-60 and that on the overall Italian population the same range accounts for over 50% (about 30 million people), the survey on the use of masks could be taken as particularly reliable of this subset of population.

Also, in this type of interview it is important to consider if a statistically significant sample is reached. The general rule is that the larger the sample size, the greater its validity. The confidence interval, also called margin of error, is the plus-or-minus figure usually reported in opinion poll results. The confidence level, expressed as a percentage, represents the value of the total population that is within the confidence interval. For a sample size of 800 people (the interviewed in this survey in the 20-60 age group), a population of 30 million and a standard confidence level of 95%, the confidence interval is from 1 to 3%. This means that all the data subsequently reported can be considered with a plus-or-minus value of 1-3%.

Considering all the interviewed, more than 55% declared that they are working or studying at the workplace where, about half of them, receive the personal protective equipment.

Referring to the masks, 78% of respondents declared to use disposable surgical masks and 47% of those questioned replaced it after 4-8 hours of use. Moreover, 45% of the interviewed used less than 3 masks per week, but 37% said they use between 3 and 7 masks and 15% between 7 and 14 (main data are reported in Figure 1, more data in the SI Figure S2). By making a rough statistical calculation in which the frequency found is multiplied for each sampling class, an average of 4.5 masks per week can be estimated. Multiplying this number by 0.78 (the percentage that declared to use this kind of masks) and assuming the survey representative of about half of the Italian population (30 million of people), it is possible to estimate the use of 105 million masks per week and therefore about 5 billion per year. This estimated value is still relevant, even though is less than half of that estimated in March 2020 by the Politecnico di Torino and published in a document used by the Italian Ministry as reference for the device supply (Torino, 2020).

The last part of the survey referred to the habit of masks dispose after use. 79% declared to dispose them in the unsorted waste collection at home, while 6% directly in the unsorted bins on the streets and 14% in special bins in the workplace or schools, 1% in another way (Figure 1d). Finally, the last question in the survey, probably the most important related to the theme of this scientific article, stated: "If there would be the possibility to collect the after use masks in a dedicated bin in your city, would you do it?" 93% answered yes. This important propensity makes a strategic recycling program more likely to be designed.

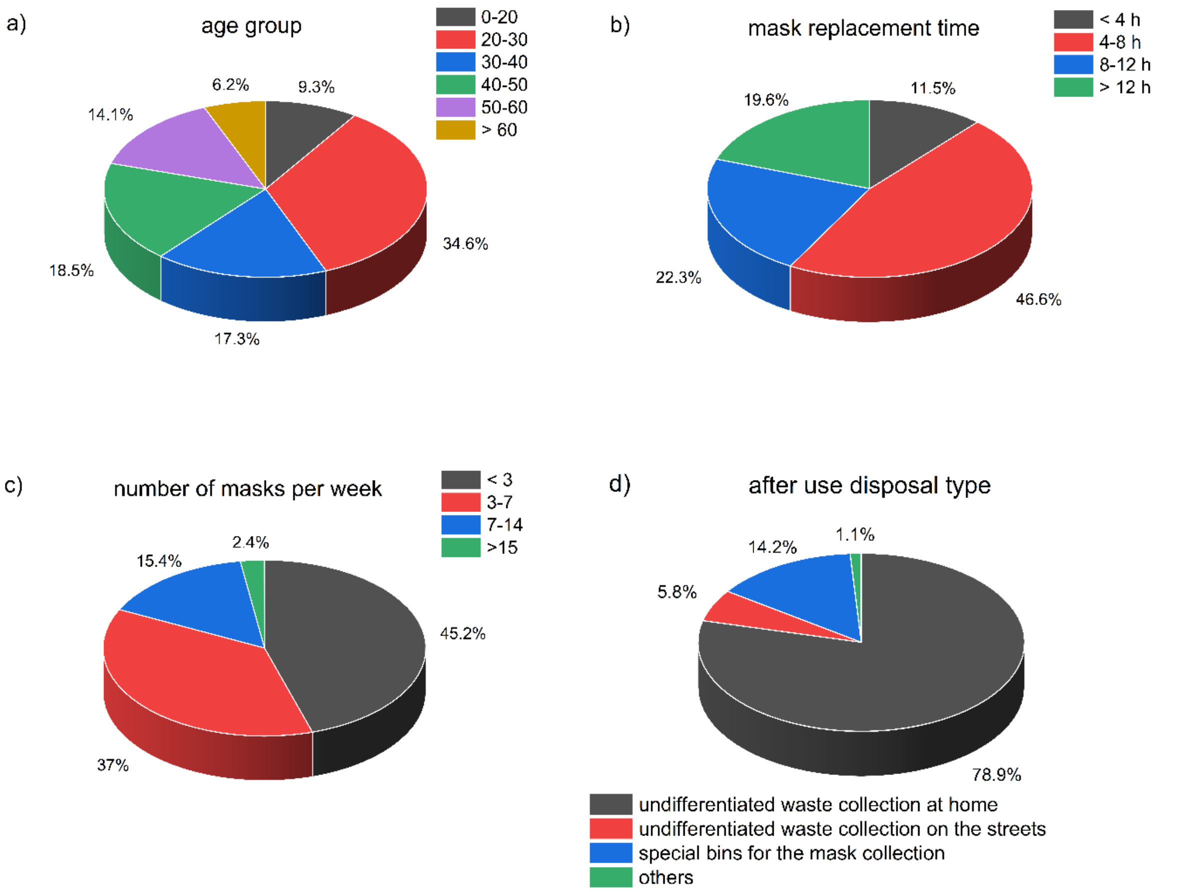

Figure 1. Online survey results regarding the use of masks: age groups of participants (a), time declared for "surgical" mask replacement (b), number of disposable "surgical" masks used per week individually (c), habit of mask disposing after use (d).

Based on the previous data and considering only the weight of the filtering part, with an average use of 4.5 masks per week, a quantity of 600 g/year per capita is generated. This value has then been compared to the current waste situation in Italy.

From the data on separate collection it can be deduced that in 2019 the percentage of municipal waste per capita was 500 kg/year (Frittelloni et al., 2019) and around 20 kg/per capita of these are plastics sent to recycling plants (2020). In this regard, the previously calculated quantity of possibly recycled masks material (0.6 kg/per capita) would be only 0.1% of the all municipal solid waste, but about 3% of the total quantity of recyclable plastic material. In addition, taking into account that PP is only a fraction of all recycled plastic (Ragaert et al., 2017), this percentage would still be much higher.

In addition to this evaluation, it is also necessary to consider how to carry out the collection. Due to the need to sanitize the masks (Armentano et al., 2021; Rubio-Romero et al., 2020; Schwartz et al., 2020), it is evident that they must be collected separately from other wastes. Thus the specific mask collection can be easily arranged only in densely populated centers e.g. in a city with 50000 inhabitants or in factories and schools where such devices are distributed, in order to have a predictable quantity and homogeneity over time. Only after sanitization they could be delivered to recycling plants and treated as the polyolefin fraction found in urban separate waste collection.

As an example, the numbers referring to students in public schools will be discussed. According to the data published by the Italian Ministry of Education (MIUR, 2020) in 2020-21, the number of students in primary and secondary schools is 6.6 million people. Because of the fact that on both scholastic levels is mandatory to wear masks, these students are provided with a disposable face mask every day. Considering about 200 days of attendance per year, this results in over 1.3 billion masks disposed, corresponding to 4000 tons per year produced throughout Italy. Even considering a scholar year as 2020-21 where the days in attendance were about half of the total (Marcello, 2021), the quantity remains high. This material, not only would be relatively constant and easy to recover, but is actually already collected in each school and thrown into the unsorted wastes. The before discussed separate collection at local level, is even more likely to be designed if considering the regional numbers of wasted masks in school. Considering only a region like Piedmont, there are approximately half a million students generating about 1 ton per day of used masks (300 tons per year). Such quantity could power a regional recycling plant which usually would processes over 100 kg per hour. The amount would be grater if also universities and factories would adopt the same collection strategy.

4. rPP characterization

A physical-chemical characterization of the recycled MPO was obtained through DSC, TGA, FTIR and SEM investigations. Through these analyses it was possible to determine that, in addition to the two main materials declared in the technical data sheet, other plastic materials and fillers are present. As can be seen from the DSC analysis (Figure 2a), in addition to the two peaks related to the crystalline part of PE (127°C) and PP (166°C), there are two other peaks centered at 209 and 249°C that can be hypothesized as PVC or PA and PET. By deep evaluating the proportions of the enthalpy areas, the crystalline quantity of the latter appears to be much smaller than the peaks assigned to PP and PE. Therefore, even if this evaluation is limited to the crystalline part of the materials, a presence of around 6% of these can be estimated.

The FTIR spectroscopy shows the presence of the typical peaks of PE and PP in addition to the ones distinctive of PET and calcium carbonate (Figure 2b). The attributions are detailed in the SI Table S1 (Battegazzore et al., 2020 Gopanna et al., 2019 Socrates, 2004 Kanelli et al., 2015).

From the TGA analysis in air (Figure 2c), it can be seen as the thermal degradation of the material follows two main degradation phases centered at the temperature of 377 and 461°C. The residue at 550°C is 7.3 % and can be attributed to the inorganic filler present.

In the morphological and elementary analyses carried out on a section of the material (Figure 3), a multiphase structure has been observed. The presence of the inorganic filler (e.g. point 1 in Figure 3) was confirmed thanks to the backscattered electrons images and the elementary analyses, of which the results are: C (~38% atomic), O (~44% atomic) and Ca (~16% atomic). Moreover, an XRD analysis was also carried out on the residues after thermo-oxidation at 600°C (reported in the SI Figure S3) to confirm the identification of the filler as calcium carbonate. In addition to the inorganic filler, the morphology presents a second phase in spheroid shape within the matrix (Figure 3 point 2): C (~99% atomic) and Ca (<1% atomic). Probably, the second phase is the PE as already reported in the literature for blend of PP/PE

(Lin et al., 2015) and the presence of Ca is due to the penetration of the EDS into the bulk of the material where calcium carbonate particles may be present.

An accurate observation of the fracture portions of the material revealed the presence of other phases different from those already reported within the matrix. Such morphologies resemble fibers or result of crushing of packaging. The elemental analysis detected the presence of C (~ 75% atomic) and O (~ 25% atomic) (Figure 3 point 3) which, considering the results reported by the DSC and ATR analyses (Figure 2a and b), can be assimilated to PET.

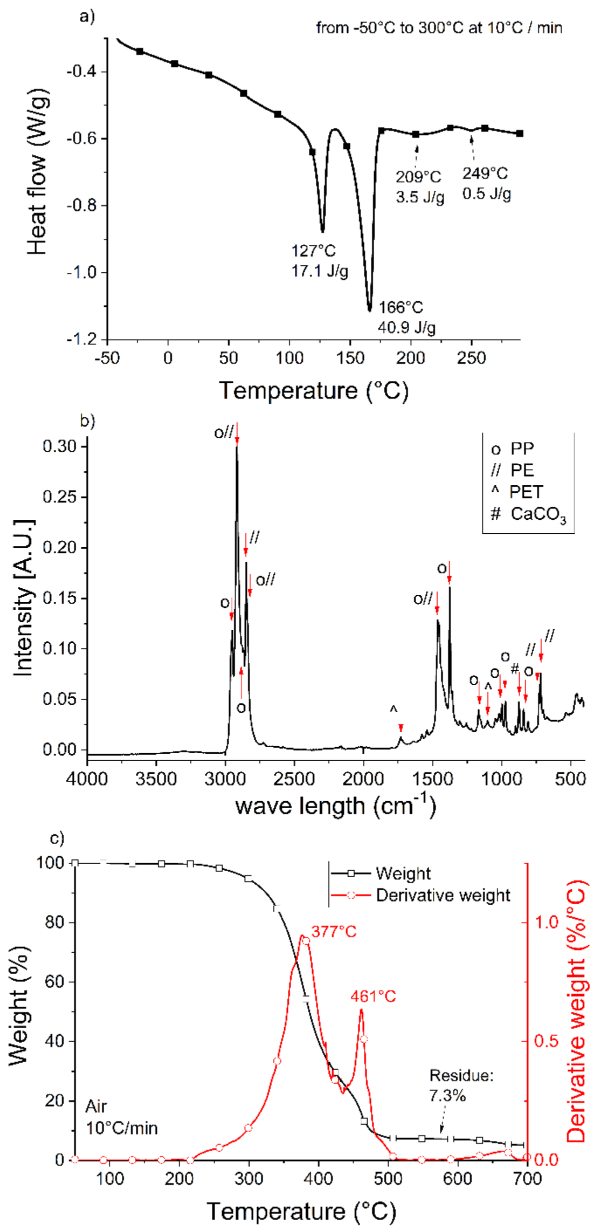

Figure 2. rPP characterization with DSC from -50°C to 300°C at 10°C min^{-1} (a); ATR from 4000 to 400 cm^{-1}, where the peaks associated to PP (Gopanna et al., 2019) are

high lined with (o), PE (Socrates, 2004) with (//), PET (Kanelli et al., 2015) with (^), calcium carbonate (Battegazzore et al., 2020) with (#) (b) and TGA from 50 to 700°C at 10°C/min in air (c).

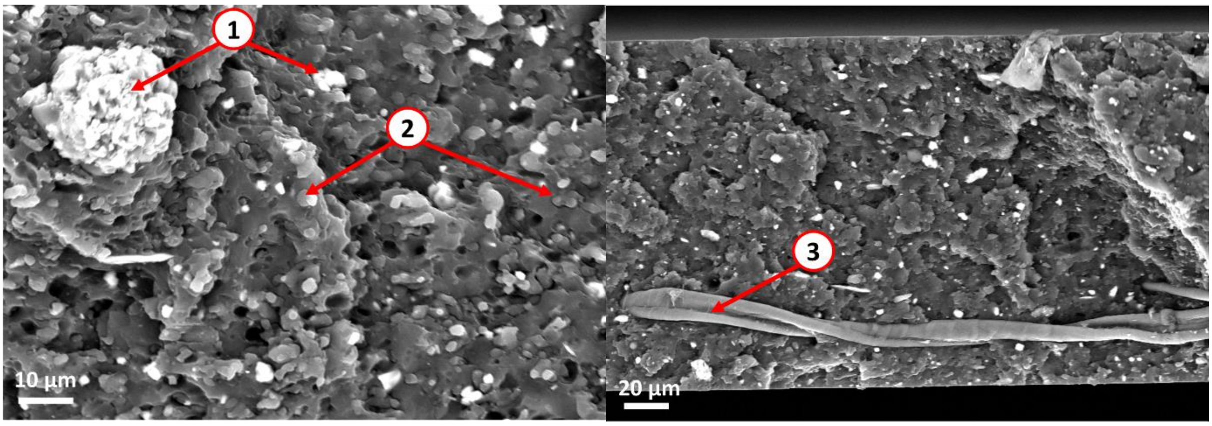

Figure 3. SEM magnifications of rPP cross-section and three characteristic points where EDS analyses were carried out.

5. Properties of the compounded materials (rPPM and rPPME systems)

In a previous article (Battegazzore et al., 2020), the recycling of the disposable mask materials separated from other recycled plastics was assumed. Conversely, in this new investigation, the influence on the main properties of a commercial material obtained from the recycling of urban waste with the masks was assessed.

5.1. Morphology

The first analysis carried out concerns the morphology of all the formulations. The purpose of this analysis is to verify the distribution of the filler and the ear loops in the compounded materials. The rPPM series shows both the gradual dilution of calcium carbonate and the progressive disappearance of the second spherical polymer phase (PE) with the increasing in the mask content. On the other hand, the rPPME series clearly shows the fibers of the ear loops when not uniformly distributed in the matrix. In fact, as the presence of material deriving from ME is diluted, the fibers are less frequent but always concentrated in some areas. Moreover, can be appreciated that the adhesion between the fibers and the matrix is poor, indeed, there are gaps between the fibers and the matrix as well as imprint left by fibers pulled out or detached.

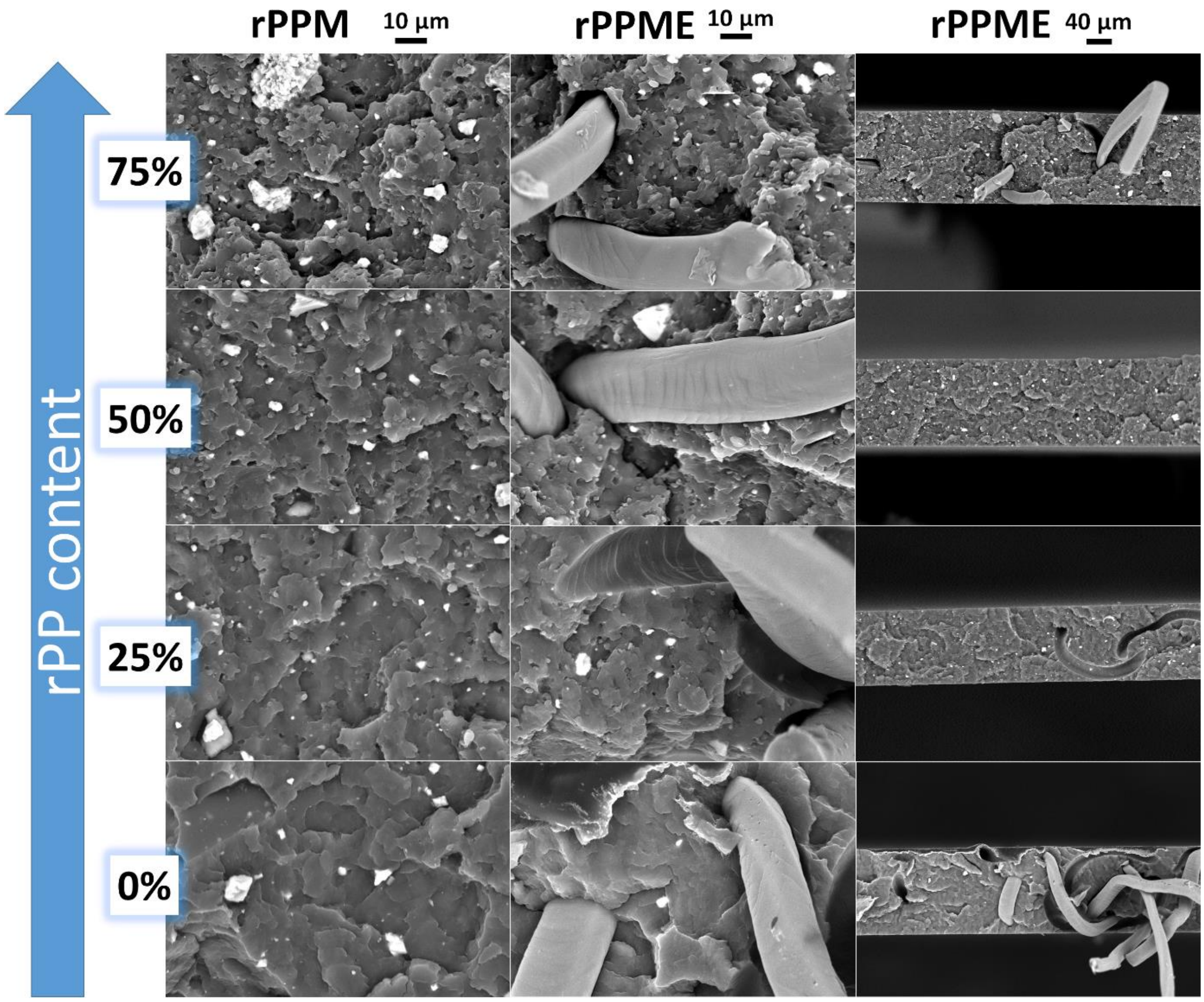

Figure 4. SEM magnifications of rPPM and rPPME formulations. From bottom to top, the figures show an increasing amount of rPP as indicated by the band on the left side. The first column reports the rPPM formulations, while the second and third ones the rPPME formulations at two different magnifications.

5.2. Rheology

The graphs of the complex viscosity of formulations based on rPPM as a function of the frequency are shown in the SI Figure S4.

M sample shows a typical PP-like behavior with a Newtonian plateau in the low frequency range and a shear thinning behavior as the frequency increases. As already reported in the literature (Battegazzore et al., 2020), the viscosity of this material is extremely low. Conversely, the rPP material has higher viscosity than M and present a yield stress behavior in the low frequency region. This is mainly attributable to the largest amount of filler present in this material if compared to M.

These two aspects can be numerically evaluated thanks to the fitting with the Carreau-like equation, in which η_0 and σ_0 parameters represent the apparent viscosity at zero shear and the yield stress, respectively.

Observing the values listed for all the formulations in Table 1, it can be noted that at 190 °C the η_0 progressively increases from 171 Pa s of M to 3397 Pa s of rPP, while σ_0 changes from 0 Pa to 234 Pa. A similar behavior was observed also at the highest temperature studied (230°C) as reported in the SI Figure S4 and Table 1.

This trend is due to the uniform distribution of the filler in the matrix of all the formulations investigated, which allows to have a progressive and predictable behavior.

Thanks to this first analysis campaign, it was found that mixing M with rPP can improve the potential low viscosity problem of M. Indeed, the rheological properties are progressively shifted towards those of the rPP and therefore a formulation can be designed to have certain tailored rheological characteristics.

Table 1. Data from Carreau like fitting of rPPM system.

Name	**190°C**				**230°C**			
	η_0 [Pa.s]	λ [1/s]	n	σ_0 [Pa]	η_0 [Pa.s]	λ [1/s]	n	σ_0 [Pa]
rPP	3397	0.78	0.53	234	1810	0.74	0.62	148
75rPP25M	1810	0.50	0.57	81	992	0.25	0.60	52
50rPP50M	788	0.28	0.63	12	435	0.22	0.69	5
25rPP75M	346	0.13	0.67	3	184	0.09	0.73	1
M	171	0.05	0.66	0	88	0.02	0.67	0

Table 2. Data from Carreau like fitting of rPPME system.

Name	190°C				230°C			
	η_0 [Pa.s]	λ [1/s]	n	σ_0 [Pa]	η_0 [Pa.s]	λ [1/s]	n	σ_0 [Pa]
rPP	3397	0.78	0.53	234	1810	0.74	0.62	148
75rPP25ME	1471	0.71	0.53	156	1042	0.72	0.59	125
50rPP50ME	1341	0.84	0.54	181	886	0.78	0.60	161
25rPP75ME	1736	1.15	0.53	396	1545	2.14	0.58	183
ME	1852	2.59	0.55	299	1377	2.47	0.54	136

Considering the ME materials, the most impressive rheological characteristic to be highlighted is the higher viscosity compared to M samples and, consequently, the recycled system rPPME has a higher viscosity compared to the rPPM counterpart (see η_0 in Table 2 versus Table 1). This is due to the ear loops that remain intact without melting at these temperatures. In fact, differently to what was studied in the previous article (Battegazzore et al., 2020), the ear loops are based on PET fabric and this increases the viscosity of the recycled material. In addition, a yield stress behavior (σ_0) is already present in the neat ME material as was observed in the rPP (Figure S4 and Figure S5).

However, it has to be noted that the properties of the intermediate formulations are not strictly proportional to that of the two boundaries (ME and rPP). Indeed, they have both viscosity and yield stress lower than expected.

These variations could be due to the heterogeneity of the materials as highlighted in the SEM observations. A greater local concentration of ear loops fibers would actually increase or lower both the viscosity and the yield stress.

Despite these limitations in the accurate determination of rheological properties of the rPPME system, it is evident that both the viscosity and the yield stress of all materials are in the same order of magnitude as neat rPP (SI Figure S5).

Furthermore, the "crossover point", which defines the boundary between mainly viscous and mainly elastic behavior, for rPP is at ω=51.2 rad/s with a value of G’=G” of $2.1*10^4$ Pa at 190°C (details in the SI Figure S6).

By mixing the material with the masks, the crossover point is shifted to higher frequencies due to the lower molecular weight of the latter polymer.

This shifting is less intense in the rPPME formulation than in the rPPM, as can be seen for the 25% of mask content formulations. In the first case, it is still possible to find the crossover point (75rPP25ME 65.4 rad/s $1.1*10^4$ Pa @190°C Figure S6) while in the second case no crossover is detected.

Summing up, both the solutions adopted are therefore suitable to improve limitations due to the low viscosity of the recycled mask material alone, and the rPPME system represents the better solution.

5.3. Mechanical properties

In Figure 5 the tensile tests data on films for both the rPPM and rPPME based formulations are summarized.

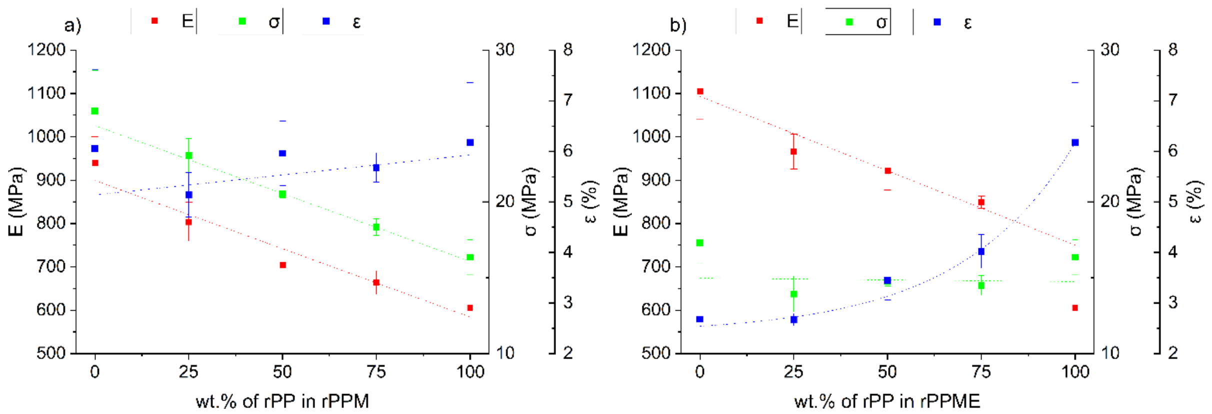

Figure 5. Mechanical main properties of rPPM (a) and rPPME (b) formulations with fitting curves.

The mechanical properties of rPP does not differ much from the ones of M or ME. In particular, M has a higher modulus (940±60 MPa) and strength (26.0±2.7 MPa) than rPP (605±57 and 16.4±1.1 MPa) while the elongation at break is comparable (6.1±1.5 %). On the other hand, ME has the highest modulus (1105±65 MPa) and a strength similar to rPP (17.3±1.4 MPa) but lower than M, as well as the worst elongation at break (2.7±0.3 %). The overall lower properties of the ME compared to the M formulation were predictable from the SEM observations (Figure 4), in which the poor adhesion between the matrix and the fibers has been observed. This generates stress concentration points in the matrix which, inevitably, decrease the strength and the elongation at break of the specimen. In fact, the Figure S7 in the SI shows the plastic deformation areas of the matrix near the fibers, after the mechanical tests. Moreover, the fibers result not evidently deformed but detached from the matrix. In addition, the separation surface between matrix and fiber is smooth, indicating poor adhesion. All these facts confirm the supposed fracture mechanism in which the load is sustained only by the matrix.

Comparing the results with the ones obtained by Crespo et al. (Crespo et al., 2021), who studied the FFP2 face masks material, it can be noted that the overall mechanical properties of the recycled material M are similar to the ones from the FFP2 masks (modulus 1.4±0.3 GPa; strength 23.6±0.2 MPa; elongation at break 7.2±0.4 %).

Regarding the compounded materials, the dilution of M or ME in rPP produces intermediate behaviors. Again, thanks to the homogeneity, rPPM formulations are much more regular so that trend lines can be obtained both for the elastic modulus and stress, basically following the rule of mixtures between the two components (dotted lines in Figure 5a). The toughness of the system seems not to be greatly influenced by the diluting of M in rPP, the trend line is indeed quite horizontal. The result is predictable also in this case because both M and rPP have a similar elongation at break.

For rPPME formulations the values are so fluctuating that only the modulus shows a clear trend with the variation of the dilution ratios (red dotted line in Figure 5b). The strength seems essentially indifferent to the composition due to the presence of defects in the sample originated by not melted inclusions. These could be ear loop fibers for ME or impurities of the rPP material as reported in the SEM magnifications (Figure 3 and Figure 4). The defects are statistically present in the tested specimens and differs in size, causing variance in the results.

On the other hand, the toughness is definitely dependent on the quantity of ME introduced. It indeed seems to follow an exponential proportionality as presented by the dotted blue curve in Figure 5, where the ME increasing amount results in a great detrimental effect.

This result is also highlighted by the comparison of the SEM images after the mechanical tests reported in Figure S7 of SI. An evident extensive deformation of the matrix is observed for neat rPP sample while a reduced one for neat ME sample. In the intermediate formulations, therefore, the ME fracture mechanism dominates.

In conclusion, M has mechanical properties as good as or better than the rPP. For this reasons, it can be used as rPP replacement for the same applications. Furthermore, the mixing with rPP does not substantially affect its characteristics in none of the percentage ratio. On the other hand, ME has lower characteristics. In order not to bring important variations in the mechanical properties, ME has therefore to be introduced in small percentages only (lower than 25 wt.%).

5.4. Ageing

One of the possible exploitation of the recycled PP is in outdoor applications. In order to verify whether the materials can be used directly or requires the addition of stabilizing additives, a light accelerated ageing study was performed. Moreover, the masks have also been compared to a commercial PP analyzed in a previous study in the same conditions (Battegazzore et al., 2014).

The FTIR analysis on samples have been carried out every 10 hours of exposure and in Figure 6 the variation of the intensity at 1717 cm^{-1} normalized to the peak at 2723 cm^{-1} is shown. According to the literature, the normalized value of the absorbance in this area is related to the formation of photo-degradation products, namely carbonyl groups (Battegazzore et al., 2014; Cerruti et al., 2009; Nanni et al., 2019; Philippart et al., 1999).

Generally, PP is characterized by an Oxidation Induction Time (OIT) during which no oxidation of the polymer is observed. This value is calculated by superimposing the two trend lines of the data obtained before and after the OIT. Their intersection defines the value of the OIT. In particular, the already mentioned stabilized commercial PP (Moplen HP500N grade) proved to have the OIT around 35h of exposure (Battegazzore et al., 2014). Similarly, the OIT calculated for the M and ME formulations was around 30h. It is thus clear that the neat materials recycled from the masks keeps the stabilizing effect of the additives generally introduced in industrial formulations.

In addition, the photo-oxidation rates were calculated as the slope of the interpolating curves (Table S2 in SI). Considering the experimental data fluctuation, it remains almost comparable for the M and ME samples (1.55×10^{-2} vs. 1.44×10^{-2}). Moreover, the rates are lower than that of commercial PP (3.13×10^{-2}). It has to be noted that probably also the typical light blue color of the external filtering part may have contributed to lower the photo-oxidation rates.

On the other hand, the photo degradation behavior of the rPP differs from the ones of the materials just described. In particular, it presents a progressive degradation with a limited slope variation between the first and second part. The OIT value is therefore not easy to define. At the same time, the degradation rate is significantly lower than that of the previous materials (0.25 x10^{-2}). The behavior may be due to the presence of fillers such as calcium carbonate or, above all, to the colorant. In fact, these formulations turns out to be black and this characteristic may have been obtained with carbon black as coloring agent. As known, it is also active as UV shield and therefore able to decrease the degradation rate (Allen et al., 1998; Horrocks et al., 1999; Pena et al., 2001).

For the evaluation of the diluted systems one intermediate formulation was studied. Like for the starting mask materials, also the ageing behaviors of 50rPP50M and 50 rPP50ME are quite similar to each other, and intermediate between the neat M or ME formulations and the rPP. In particular, the trend before the 80 h of exposure resemble the rPP ones, while the degradation rate of the second part is intermediate between that of M or ME and that of rPP (0.64-0.74 x10^{-2}) and is highlighted by dotted straight line in the graph in Figure 6.

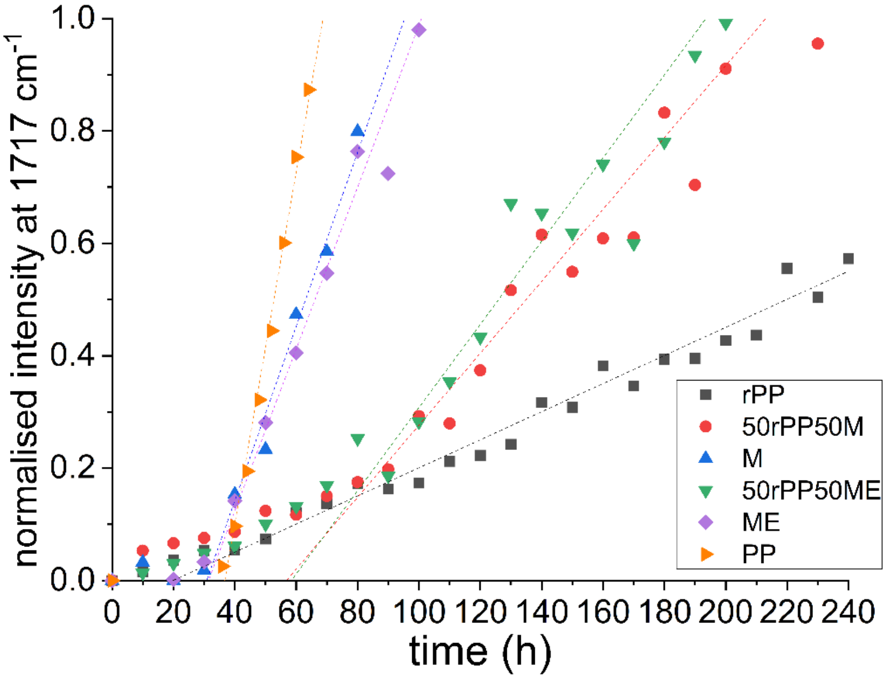

Figure 6. Ageing or M, ME, rPP, 50rPP50M, 50rPP50ME and PP (Battegazzore et al., 2014).

6. Conclusions

From the data obtained from the survey, a quantity of 0.6 kg/year per capita of waste derived from the use of disposable masks was calculated. If completely recycled, this amount would be equivalent to 3% of the actual recycled plastic materials in Italy. Even reducing the collecting area to only local realities such as regional schools, recycling plant could be envisaged.

A promising strategy would appear to mix this waste stream after sanitization with municipal recycled plastic waste. For this purpose, the physical and mechanical properties of the MPO and of the compounds containing mask materials have been compared. The joint recycling with the filtering part of the mask results in the progressive decreasing of the zero shear viscosity, in comparable toughness and superior stiffness (10-33%) and strength (12-41%). On the other hand, the additional presence of the ear loops in the recycling system gives a compounded material having low viscosity but steady for all formulations at about 50% of rPP value. The elongation and strength are lowered with respect to rPP in the range of 35-56% and 6-15%, respectively.

All the above considered, if the mechanical properties are important in the final application any concentration of the filtering part can be introduced, but only limited amounts of ear loops are accepted.

Considering the results obtained with FFP2 masks that gave mechanical results similar to those obtained in the present research, the properties reported in this study could be extended also to this type of masks or the mixture of the two.

Referring to the photo degradation ageing of the recycled filtering mask material, it is comparable to a commercial PP. Also, the presence of ear loops does not affect its behavior. Considering the compounded material instead, the photo degradation ageing is proportional to the concentration of mask and/or ear loop introduced.

The main reason is probably the lower ratio of carbon black in the material if compared to the mixed polyolefin alone. The same shielding effect of rPP would have probably reached adding carbon black to the formulations.

In conclusion, neither the waste collection and processing nor the final properties revealed any objection to the recycling of the disposable masks together with other urban waste plastic materials.

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References

Allen, N.S., Edge, M., Corrales, T., Childs, A., Liauw, C.M., Catalina, F., Peinado, C., Minihan, A., Aldcroft, D., 1998. Ageing and stabilisation of filled polymers: an overview. Polymer Degradation and Stability 61(2), 183-199.

Armentano, I., Barbanera, M., Carota, E., Crognale, S., Marconi, M., Rossi, S., Rubino, G., Scungio, M., Taborri, J., Calabrò, G., 2021. Polymer Materials for Respiratory Protection: Processing, End Use, and Testing Methods. ACS Applied Polymer Materials.

Battegazzore, D., Bocchini, S., Alongi, J., Frache, A., 2014. Plasticizers, antioxidants and reinforcement fillers from hazelnut skin and cocoa by-products: Extraction and use in PLA and PP. Polymer Degradation and Stability 108, 297-306.

Battegazzore, D., Cravero, F., Frache, A., 2020. Is it Possible to Mechanical Recycle the Materials of the Disposable Filtering Masks? Polymers (Basel) 12(11), 2726.

Bora, R.R., Wang, R., You, F., 2020. Waste Polypropylene Plastic Recycling toward Climate Change Mitigation and Circular Economy: Energy, Environmental, and Technoeconomic Perspectives. ACS Sustainable Chemistry & Engineering 8(43), 16350-16363.

Cerruti, P., Malinconico, M., Rychly, J., Matisova-Rychla, L., Carfagna, C., 2009. Effect of natural antioxidants on the stability of polypropylene films. Polymer Degradation and Stability 94(11), 2095-2100.

Cesaro, A., Pirozzi, F., 2020. About the effects of Covid-19 on solid waste management. Tema, 59-66.

Crespo, C., Ibarz, G., Saenz, C., Gonzalez, P., Roche, S., 2021. Study of Recycling Potential of FFP2 Face Masks and Characterization of the Plastic Mix-Material Obtained. A Way of Reducing Waste in Times of Covid-19. Waste Biomass Valorization, 1-10.

Filippone, G., Carroccio, S., Mendichi, R., Gioiella, L., Dintcheva, N.T., Gambarotti, C., 2015. Time-resolved rheology as a tool to monitor the progress of polymer degradation in the melt state–Part I: Thermal and thermo-oxidative degradation of polyamide 11. Polymer 72, 134-141.

Frittelloni, V., Lanz, A.M., Muto, L., 2019. Municipal Waste Report - edition 2019 - summary data. ISPRA - Istituto Superiore per la Protezione e la Ricerca Ambientale.

Gopanna, A., Mandapati, R.N., Thomas, S.P., Rajan, K., Chavali, M., 2019. Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and wide-angle X-ray scattering (WAXS) of polypropylene (PP)/cyclic olefin copolymer (COC) blends for qualitative and quantitative analysis. Polymer Bulletin 76(8), 4259-4274.

Gu, F., Guo, J., Zhang, W., Summers, P.A., Hall, P., 2017. From waste plastics to industrial raw materials: A life cycle assessment of mechanical plastic recycling practice based on a real-world case study. Sci Total Environ 601-602, 1192-1207.

Horrocks, A.R., Mwila, J., Miraftab, M., Liu, M., Chohan, S.S., 1999. The influence of carbon black on properties of orientated polypropylene 2. Thermal and photodegradation. Polymer Degradation and Stability 65(1), 25-36.

ISPRA, 2020. Rapporto rifiuti urbani. https://www.isprambiente.gov.it/files2020/pubblicazioni/rapporti/rapportorifiutiurbani_ed-2020_n-331-1.pdf. (Accessed 04/2021 Rapporti 331/2020).

ISTAT, 2020. Popolazione per età, sesso e stato civile 2020. https://www.tuttitalia.it/statistiche/popolazione-eta-sesso-stato-civile-2020/. (Accessed 22-04-2121 2021).

Kanelli, M., Vasilakos, S., Nikolaivits, E., Ladas, S., Christakopoulos, P., Topakas, E., 2015. Surface modification of poly (ethylene terephthalate)(PET) fibers by a cutinase from Fusarium oxysporum. Process Biochemistry 50(11), 1885-1892.

Lin, J.H., Pan, Y.J., Liu, C.F., Huang, C.L., Hsieh, C.T., Chen, C.K., Lin, Z.I., Lou, C.W., 2015. Preparation and Compatibility Evaluation of Polypropylene/High Density Polyethylene Polyblends. Materials (Basel) 8(12), 8850-8859.

Marcello, G., 2021. Quanti giorni di scuola in presenza hanno perso gli studenti? Napoli e Bari fanalino di coda: alle superiori saltati 2 mesi su 3. https://www.skuola.net/news/inchiesta/giorni-scuola-presenza-persi-pandemia-superiori-elementari-medie.html. (Accessed 07-2021.

MIUR, 2020. Focus “Principali dati della scuola –Avvio Anno Scolastico 2020/2021”. Governo Italiano, www.miur.gov.it.

Nanni, A., Battegazzore, D., Frache, A., Messori, M., 2019. Thermal and UV aging of polypropylene stabilized by wine seeds wastes and their extracts. Polymer Degradation and Stability 165, 49-59.

Narita, N., Sagisaka, M., Inaba, A., 2002. Life cycle inventory analysis of CO 2 emissions manufacturing commodity plastics in Japan. The International Journal of Life Cycle Assessment 7(5), 277-282.

Pena, J.M., Allen, N.S., Edge, M., Liauw, C.M., Valange, B., 2001. Studies of synergism between carbon black and stabilisers in LDPE photodegradation. Polymer Degradation and Stability 72(2), 259-270.

Philippart, J.-L., Sinturel, C., Arnaud, R., Gardette, J.-L., 1999. Influence of the exposure parameters on the mechanism of photooxidation of polypropylene. Polymer Degradation and Stability 64(2), 213-225.

Prata, J.C., Silva, A.L.P., Walker, T.R., Duarte, A.C., Rocha-Santos, T., 2020. COVID-19 Pandemic Repercussions on the Use and Management of Plastics. Environ Sci Technol 54(13), 7760-7765.

Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. Waste Manag 69, 24-58.

Rhee, S.W., 2020. Management of used personal protective equipment and wastes related to COVID-19 in South Korea. Waste Manag Res 38(8), 820-824.

Rubio-Romero, J.C., del Carmen Pardo-Ferreira, M., García, J.A.T., Calero-Castro, S., 2020. Disposable masks: Disinfection and sterilization for reuse, and non-certified manufacturing, in the face of shortages during the COVID-19 pandemic. Safety Science, 104830.

Schwartz, A., Stiegel, M., Greeson, N., Vogel, A., Thomann, W., Brown, M., Sempowski, G.D., Alderman, T.S., Condreay, J.P., Burch, J., 2020. Decontamination and reuse of N95 respirators with hydrogen peroxide vapor to address worldwide personal protective equipment shortages during the SARS-CoV-2 (COVID-19) pandemic. Applied Biosafety 25(2), 67-70.

Schyns, Z.O.G., Shaver, M.P., 2020. Mechanical Recycling of Packaging Plastics: A Review. Macromolecular Rapid Communications n/a(n/a), 2000415.

Selvaranjan, K., Navaratnam, S., Rajeev, P., Ravintherakumaran, N., 2021. Environmental challenges induced by extensive use of face masks during COVID-19: A review and potential solutions. Environmental Challenges 3, 100039.

Sharma, H.B., Vanapalli, K.R., Cheela, V.S., Ranjan, V.P., Jaglan, A.K., Dubey, B., Goel, S., Bhattacharya, J., 2020. Challenges, opportunities, and innovations for effective solid waste management during and post COVID-19 pandemic. Resour Conserv Recycl 162, 105052.

Singh, N., Tang, Y., Ogunseitan, O.A., 2020. Environmentally Sustainable Management of Used Personal Protective Equipment. Environ Sci Technol 54(14), 8500-8502.

Socrates, G., 2004. Infrared and Raman Characteristic Group Frequencies. Wiley, New York.

Torino, P.d., 2020. Rapporto: IMPRESE APERTE LAVORATORI PROTETTI. http://www.impreseaperte.polito.it/content/download/165/783/file/Rapporto%20IMPRESE%20APERTE%20LAVORATORI%20PROTETTI%20rev%203%20280420.pdf.