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FEASIBILITY OF GAMMA OR E-BEAM IRRADIATION AS A TREATMENT FOR REUSE OF MEDICAL MASKS AFTER A FIRST USE

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Abstract

Facing the global shortage of medical facemask in the current COVID-19 crisis, the RUM (Re-Used Masks) French consortium explores the feasibility of recycling masks after a first use. Radiation processing was the first virucide technique of decontamination that was investigated in this consortium. Tests were carried out using the ^{60}Co gamma irradiator of ARC-Nucléart and with Ionisos industrial facilities, including ^{60}Co irradiation and e-beam. 20 kGy is the reference maximum dose that was mainly used in this study, as a dose able to ensure a 10 kGy minimum dose in a mass processing leading to a decontamination (-5 log reduction) as based on surrogate of SARS-COV-2. Conservation of masks performance and behavior of the materials after treatment were studied in the consortium and by commercial laboratories for standard testing. Data available at date of 12th May 2020 are compiled and discussed in this report.

Unfortunately, our results indicate a clear loss of submicronic filtration efficiency because of electric discharge of the electrostatic filter (electret) of FFP2 masks. This is believed to be due to high density of ionisation. This is confirmed whatever the operative condition tested in this study.

In the other hand, loss of efficiency is low in the micronic range. The treatment of surgical masks by ionizing radiation is still interesting but gamma irradiation in air must be avoided to prevent beginning of oxidation of PP that could lead to important delayed post-effect degradation. Care must also be taken about degradation products after consumption of antioxidant, in few amounts at doses between 10 and 20 kGy.

Generally speaking, the choice of a method in the frame of reuse of surgical masks during crisis must pass through a complete risk analysis. In this case, it must include the evaluation of the right dose and operative condition with regards of the benefit in terms of virucide reliability for instance and the potential drawback such as loss of efficiency or amount of unwanted compounds.

1. INTRODUCTION

Facing the global shortage of personal protective equipment (PPE) due to the current pandemic of COVID-19, and specifically shortage of medical facemasks, it was decided to explore the feasibility of re-using them. With this objective, the TIMC-IMAG laboratory, which gathers scientists and clinicians for medical engineering in link with the Centre Hospitalier Universitaire Grenoble-Alpes (CHUGA), was rapidly and spontaneously able to form a consortium involving many other laboratories from CNRS (Centre National de la Recherche Scientifique, the main organism of scientific research in France), CEA (Commissariat à l'Énergie Atomique et aux Énergies Alternatives, the French commission for nuclear research), INSERM (Institut National de la Santé et de la Recherche Médicale, the main research institute for health) and many universities, hospitals and industrials. The consortium is now sometime named RUM for Re-Use Masks.

We focused in this report, on the tests made in the frame of this RUM consortium with ionizing radiation, rather gamma or electron. Indeed, as known to represent around half of the global capacity of sterilization of single use medical device in the world, ionizing radiations processing was naturally designed as a potential technique for biological decontamination of the masks after a first use.

First tests were carried out using the ^{60}Co gamma irradiator of ARC-Nucléart and quickly also with the Ionisos industrial facilities, including ^{60}Co irradiation and e-beam.

Conservation of masks performance, behavior of the materials after treatment and biological effectiveness of the treatments are the main concerns. All the post tests on the masks irradiated at ARC-Nucléart and Ionisos were carried out by other French and foreign laboratories specialists, including polymer ageing under irradiation specialist at CEA-Saclay, aerosol filtration in IMT Atlantique Nantes and IRSN Saclay, together with commercial laboratories for standard testing (APAVE Grenoble, France and Centexbel, Grâce-Hollogne, Belgium).

This report is a preliminary synthesis of the work done up to the 12th May 2020, even if many data are still missing, due to still ongoing research and the difficulties of conducting them in urgent time of crisis.

2. MATERIALS AND METHODS

2.1 Masks

2 types of half-masks were considered in this study, namely FFP2 masks mainly aiming to protect the wearer from external, and surgical masks mainly aiming to prevent emission exhaled by the wearer.

FFP2 masks must meet the European standard EN 149, a Personal protective equipment (PPE) qualification. They must be able to filter more than 94% of submicronic particles in the range of hundred nanometers with side leaks less than 8%. They are very near N95 American standard masks. The tested masks were provided by CA diffusion, ref.RP2_M (only on the first campaigns), and by Valmy, réf. VR202-03C (from 3 April 2020).

Both are made of polypropylene Spunbond-Meltblown-Spunbond sandwich (SMS) with 2 internal layers of meltblown electrically charged to make an electrostatic filter, leading to a filtration that is efficient submicronic particles. This is the so-called “electret” filter.

Surgical masks are medical devices, meeting the European standard EN 14683, ensuring the bacterial filtration to be better than 98 % for the micronic dimension range. The tested masks were provided by CA diffusion, ref. CA 1960. Limited preliminary tests were also carried out with some masks provided by Kolmi, OP air type II in the first experimental campaign.

CA 1960 are high filtration efficiency 3-ply II-R type (anti-splash). They are also made of polypropylene SMS, with only one intermediate metlblown layer, and with no electret filter.

PP is of isotactic quality for both type of masks, with low amount of phenolic antioxidant (butylated hydroxytoluene (BHT), Irganox 1076).

The first test campaign was carried out on masks worn and collected after their use in CHUGA (Grenoble hospital). Following tests were made with unused masks, but some of them were washed or conditioned for instance with humid atmosphere before to be treated, to simulate some use. A new campaign has been recently launched with the idea to cumulate real wearing, real washing and different treatments.

It is noteworthy that all these masks were not sterile before use and not designed to be sterilized.



II-R

FFP2

FIG. 2.1. Surgical masks and FFP2 masks

2.2 Washing

Washing in the hospital laundry is a step that was a priori required to remove the stains on the masks already worn. CHUGA laundry uses standard condition (1 hour with 12 min of steady-state temperature of 60°C, using neutral detergent with surfactants “Ultimate mineral” (1 ml/kg) added with disinfectant based on perchloric acid and hydrogen peroxide “Ultimate Forte” (5 ml/kg)). Some washing tests were also done in Ionisos with similar conditions with the Ecolab detergent used in the Civil Hospital of Lyon.

2.3 Gamma irradiation

Most of gamma irradiation tests were performed in the ARC-Nucléart Grenoble irradiator, with dose rate of 1 kGy.h⁻¹, except some irradiations of the first campaign that were performed at 0.5 kGy.h⁻¹ and 2 kGy.h⁻¹. Dosimetry was done using routine Perspex dosimeters, Red and Amber. Masks were usually packaged in a vacuum envelope (vacuum sealing). Air renewal (40 per hour) in the irradiation chamber assures low O₃ concentration level when the irradiation was conducted with no vacuum envelope.

Tested doses range from 1 kGy to 100 kGy.

Some gamma irradiations were also achieved in Dagneux Ionisos ⁶⁰Co industrial plant, in routine conditions. Mean dose rate is 2 kGy.h⁻¹. Alanine dosimeters were used for those experiments.



FIG. 2.2. Set-up in the irradiation chamber of batches of masks before gamma irradiation in ARC-Nucléart irradiator

Tested doses range from 1 kGy to 100 kGy.

Some gamma irradiations were also achieved in Dagneux Ionisos ^{60}Co industrial plant, in routine conditions. Mean dose rate is $2 \text{ kGy}\cdot\text{h}^{-1}$. Alanine dosimeters were used for those experiments.

2.4 E-beam irradiation

10 MeV Chaumesnil Ionisos industrial electron accelerator (Mevex A29) was used for electron irradiation, in routine conditions. Dose rate reaches several hundred kGy per minute. Dose was controlled with a calorimeter in case of these trials.

2.5 Polymer characterization

Characterizations were performed in CEA-Saclay and in CERMAV, CNRS, Grenoble. They include optical and electronic (SEM) microscopy, Fourier transform infrared spectroscopy– attenuated total reflectance (FTIR-ATR), Differential Scanning Calorimetry (DSC), Thermal desorption-gas chromatography mass spectrometry (TD GC/MS) and Solid-state nuclear magnetic resonance (SS NMR).

2.6 Micronic filtration performance

Surgical masks filtration efficiency was measured with bacterial aerosols by commercial Centexbel laboratory according to EN-14683 standard, which provides a bacterial mean filtration efficiency determined for a bacterial aerosol of $3 \mu\text{m}$ mean size (aerosol size ranges from 0.65 to $7 \mu\text{m}$). IMT Atlantique - GEPEA Laboratory also set up an experimental bench allowing to measure a spectral filtration efficiency in the same conditions of EN-14683 but for a liquid aerosol of Di-Ethyl-Hexyl-Sebacat (DEHS) ranging from $0.1 \mu\text{m}$ to $5 \mu\text{m}$ (instead of a bacterial aerosol). This set-up allows determining the particulate filtration efficiency at $3 \mu\text{m}$.

2.7 Submicronic filtration performance

FFP2 submicronic performance was measured by solid NaCl aerosol and Paraffin Oil aerosol penetration according to EN-149 standard by commercial APAVE Grenoble laboratory. Results are expressed in terms of penetration, which is the complement to 100 % of the filtration efficiency.

IRSN-Saclay also set up an experimental bench using NaCl solid aerosol to measure "total filtration efficiency" (in mass, as defined in standard EN 13274-7 standard, linked with EN 149) and "spectral filtration efficiency" according to the aerosol diameter. In this bench, initial NaCl median particle size is around $0.060 \mu\text{m}$ in number and around $0.600 \mu\text{m}$ in mass.

3. EXPERIMENTS

First experiments were conducted on 16 to 23, March 2020, on 260 worn masks in real hospital condition, both FFP2 and surgical masks, collected after a first use in CHUGA [1]. One of the difficulties was to organize homogenous batches of the 7 different brands used in the hospital. The masks were separated into batches and sealed in standard vacuum bags in P3 hospital laboratory. Vacuum packaging aimed to offer tight protection against the virus, allowing an easy and safe transport and handling, but also to minimize the clutter. The idea that it could offer a protection against radio-induced oxidation during irradiation came later.

2 doses were used during this campaign, not directly chosen with respect to SARS-CoV-2 radiosensitivity that we did not evaluate at this moment:

TABLE 3.1. BATCHES OF THE FIRST IRRADIATION CAMPAIGN IN ARC-NUCLÉART

Batch	Type of masks	New / Worn	Pre-treatment	Type of treatment	Treatment parameter	
					Target dose	Conditioning
L01	Surgical	Worn	none	Gamma irradiation	50 kGy	Vacuum sealed
L02	Surgical	Worn	none	Gamma irradiation	25 kGy	Vacuum sealed
L06 to L09	Surgical	Worn	none	Gamma irradiation	50 kGy	Vacuum sealed
L10-6	Surgical	Worn	CHUGA laundry washed	Gamma irradiation	25 kGy	Vacuum sealed
L02	FFP2	Worn	none	Gamma irradiation	25 kGy	Vacuum sealed
L01	FFP2	Worn	none	Gamma irradiation	50 kGy	Vacuum sealed
L10-7	FFP2	Worn	CHUGA laundry washed	Gamma irradiation	25 kGy	Vacuum sealed

- 25 kGy as a well-known default reference in medical sterilization,
- and 50 kGy as a safer dose and as twice 25 kGy, the maximum dose that can be encountered processing 25 kGy with a Dose Uniformity Ratio (DUR) of 2.
It concerned 5 batches of surgical masks and 3 batches of FFP2. It included 2 batches of 10 masks, one of surgical masks and one of FFP2 masks, that before to be irradiated at 25 kGy (dose rate 0.4 kG/h), were passed through the hospital laundry cycle (1 hour with detergent -including 12 min steady state 60°C- + gentle drying 30°C).

In almost the same days, a first campaign was launched in Ionisos, using 48 kGy as a reference, one batch of 40 surgical masks being irradiated in gamma industrial irradiator while one batch was irradiated with e-beam.

Then, new campaigns used unworn new masks in order to dissociate the wear effect of the mask from that of its treatment, and also to remove the biologic risk during experiments. About 250 masks were irradiated in ARC-Nucléart and Ionisos facilities.

In ARC-Nucléart, gamma irradiations were performed from the 3rd to 8th April 2020 with some complement on 20-21 April. For this campaign, 10 kGy was considered as a potential reference minimum dose corresponding to a virucide decontamination, and associated to a 20 kGy maximum dose, with doses ranging from 1 to 100 kGy, and with dose rate 1 kGy.h⁻¹.

TABLE 3.2. BATCHES OF THE FIRST IRRADIATION CAMPAIGN IN IONISOS

Batch	Type of masks	New / Worn	Pre-treatment	Type of treatment	Treatment parameter	
					Target dose	Conditioning
L03	Surgical	Worn	none	Gamma irradiation	48 kGy	Vacuum sealed
L04	Surgical	Worn	none	e-beam	48 kGy	Vacuum sealed
L03	FFP2	Worn	none	Gamma irradiation	48 kGy	Vacuum sealed
L04	FFP2	Worn	none	e-beam	48 kGy	Vacuum sealed

TABLE 3.3. BATCHES OF THE SECOND IRRADIATION CAMPAIGN IN ARC-NUCLÉART

Batch	Type of masks	New / Worn	Pre-treatment	Type of treatment	Treatment parameter	
					Target dose	Conditioning
L44	FFP2	New	none	Gamma irradiation	20 kGy + thermal annealing	Vacuum sealed
L45	FFP2	New	none	None	Control	
L46	FFP2	New	none	Gamma irradiation	2 kGy	Vacuum sealed
L47	FFP2	New	none	Gamma irradiation	2 kGy + thermal annealing	Vacuum sealed
L48	FFP2	New	none	Gamma irradiation	20 kGy	Vacuum sealed
L49	FFP2	New	none	Gamma irradiation	20 kGy	Air
L60	Surgical	New	none	Gamma irradiation	2 kGy	Vacuum sealed
L61	Surgical	New	none	Gamma irradiation	2 kGy + thermal annealing	Vacuum sealed
L62	Surgical	New	none	Gamma irradiation	2 kGy	Air
L63	Surgical	New	none	Gamma irradiation	50 kGy	Vacuum sealed
L64	Surgical	New	none	Gamma irradiation	100 kGy	Vacuum sealed
L65	Surgical	New	none	Gamma irradiation	1 kGy	Vacuum sealed
L66	Surgical	New	none	Gamma irradiation	5 kGy	Vacuum sealed
L67	Surgical	New	none	Gamma irradiation	10 kGy	Vacuum sealed
L72	Surgical	New	none	Gamma irradiation	20 kGy + thermal annealing	Vacuum sealed
L73	Surgical	New	none	Gamma irradiation	20 kGy	Vacuum sealed
L76	Surgical	New	none	none	Control	
L77	FFP2	New	none	Gamma irradiation	2 kGy	Air
L78	FFP2	New	none	Gamma irradiation	20 kGy	Confined air (O ₃)

During this campaign, some thermal annealing was completed, consisting of heating in air at 95°C for 15 min before to seal again the masks under vacuum. It aimed to anneal free radical to avoid post effect radio-oxidation. Irradiations in air, and even in confined air, i.e. in a sealed box (therefore without evacuation of the ozone created by the irradiation), have also been carried out to evaluate the effect of radio-oxidation.

A third small campaign combining laundry washing and irradiation run also in following this second campaign in ARC-Nucléart, in order to check the effect of one or more complete cycle of washing and treatment on surgical masks.

TABLE 3.4. BATCHES OF THE THIRD IRRADIATION CAMPAIGN IN ARC-NUCLÉART

Batch	Type of masks	New / Worn	Pre-treatment	Type of treatment	Treatment parameter	
					Target dose	Conditioning
L213	Surgical	None	CHUGA laundry washed	Gamma irradiation	20 kGy	Vacuum sealed
L214	Surgical	None	1 cycle (washing + irradiation) + new CHUGA laundry washed	Gamma irradiation	+ 20 kGy (= 40 kGy)	Vacuum sealed
L215	Surgical	None	2 cycles (washing + irradiation) + new CHUGA laundry washed	Gamma irradiation	+ 20 kGy (= 60 kGy)	Vacuum sealed

In the same time, e-beam irradiation was also conducted in Ionisos:

TABLE 3.5. BATCHES OF THE SECOND IRRADIATION CAMPAIGN IN IONISOS

Batch	Type of masks	New / Worn	Pre-treatment	Type of treatment	Treatment parameter	
					Target dose	Conditioning
L301	FFP2	New	none	none	Control	
L302	FFP2	New	none	e-beam	10 kGy	Air
L303	FFP2	New	none	e-beam	20 kGy	Air
L304	FFP2	New	none	e-beam		
L305	FFP2	New	none	e-beam	20 kGy	Vacuum sealed
L306	FFP2	New	none	e-beam		
L307	FFP2	New	none	e-beam	60 kGy	Vacuum sealed

4. RESULTS

4.1. Results of characterization

4.1.1. Surgical masks

For first campaign in ARC-Nucléart, batches were set up in definite position after isodoses were determined using a numerical dispersive/no-diffusion model, neglecting the attenuation in this case. This calculation generally allows an approach of $\pm 20\%$.

Several routine Red Perspex dosimeters placed and both front and rear sides of the batches determinate real doses.

TABLE 4.1. MEASURED DOSES DURING THE FIRST CAMPAIGN OF IRRADIATION

Batch	Target dose	Minimum dose (rear face)	Maximum dose (front side)	Mean dose rate
L01	50 kGy	46.4 kGy \pm 10%	53.1 kGy \pm 20% *	1.8 kGy.h ⁻¹
L02	25 kGy	27.7 kGy \pm 10%	29.8 kGy \pm 10%	1.1 kGy.h ⁻¹
L06 to L09	50 kGy	48.6 kGy \pm 10%	60.3 kGy \pm 20% *	2.2 kGy.h ⁻¹
L10-6 and L10-7	25 kGy	29.5 kGy \pm 10%	32.3 kGy \pm 10%	0,5 kGy.h ⁻¹

* Between 50 and 75 kGy, i.e. over the normal measurement range of the dosimeters (5-50 kGy), we use a "home-made" calibration polynomial with a degraded uncertainty (\pm 20%).

In the 2nd and 3rd campaigns, batches were placed always exactly at the same place, in the same conditions. Therefore, dose rate was fixed, and the irradiation time has just to be adjusted to reach the target dose. Control dosimeter were used at each irradiation, routine perspex amber for low doses and red for higher doses, but best accuracy was given by multiplying the irradiation time by average dose rate. The value coming from those control dosimeters was 1.1 kGy.h⁻¹, and taking into account the measurement uncertainty, the value of 1.0 kGy.h⁻¹ -0%/+20% was selected as reference. Target dose were therefore reach for all batches with this uncertainty of -0%/+20%, as the cumulated exposure time in hour was actually set to the target dose express in kGy:

- L65 \Rightarrow 1 kGy -0%/+20%
- L46 – L47 – L60 – L62 – L77 \Rightarrow 2 kGy -0%/+20%
- L66 \Rightarrow 5 kGy -0%/+20%
- L67 \Rightarrow 10 kGy -0%/+20%
- L44 – L48 – L49 – L72 – L73 – L78 – L213 \Rightarrow 20 kGy -0%/+20%
- L214 \Rightarrow 40 kGy -0%/+20%
- L63 \Rightarrow 50 kGy -0%/+20%
- L215 \Rightarrow 60 kGy -0%/+20%
- L64 \Rightarrow 100 kGy -0%/+20%

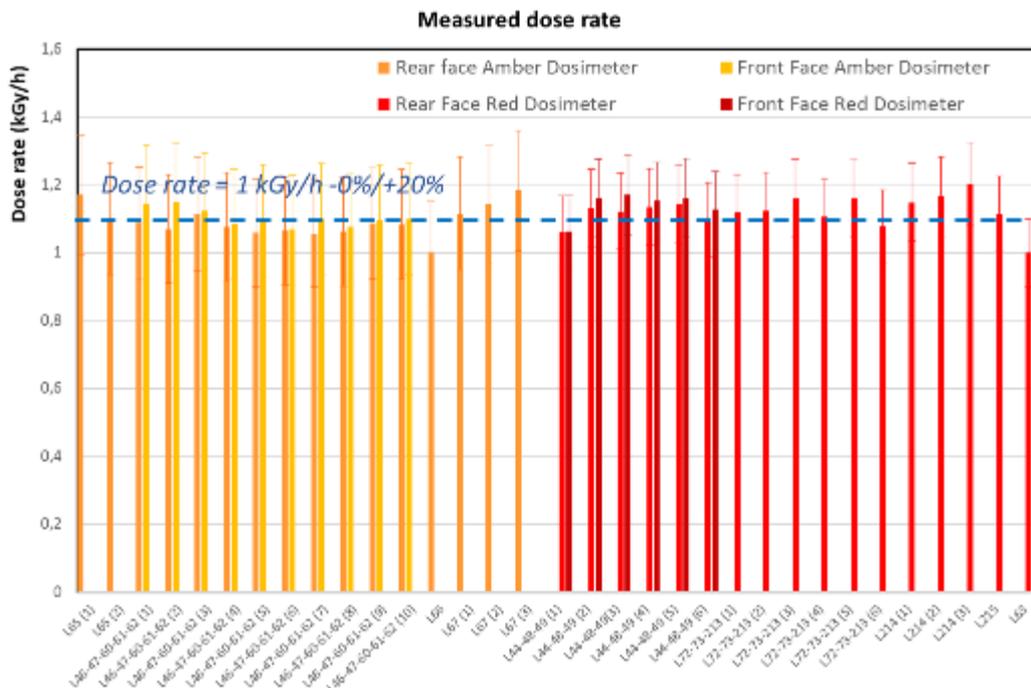


FIG. 4.1. Control measurement of the dose rate. Average dose rate, 1.1 kGy.h⁻¹, gave reference value of 1.0 kGy.h⁻¹ -0%/+20% taking into account the uncertainty.

4.1.2. Measured dose in Ionisos

4.1.2.1. Gamma rays

In Ionisos, dose delivered by gamma rays (Cobalt 60, Dagneux facility) during trials was measured with alanine dosimeters, that give a dose equivalent to dose received in water, with an uncertainty of 4,0 %.

The samples are disposed on an overhead conveyor (totes), in a parcel. Alanine dosimeters are disposed on both opposite sides of the samples' parcel in front of the incident rays. Due to several 180° rotations during radiation, the samples' parcel (very light, as containing less than 20 masks) is treated on both sides, for a homogeneous distribution of dose. Average dose rate of the facility is 2 kGy.h⁻¹.

TABLE 4.2. MEASURED DOSES DURING THE CAMPAIGN OF GAMMA IRRADIATION OF WORN SURGICAL MASKS

Batch	Dose target	Min Controlled Dose	Max Controlled Dose	Dosimetric method	Dosimetric uncertainty
L03	50 kGy	48,4 kGy	48,7 kGy	Alanine	4,0%

4.1.2.2. Electron Beam

In Ionisos, dose delivered by electron beam (10 MeV energy, dose rate of several hundred kiloGrays per minute) during trials is measured with a polystyrene calorimeter developed in Risø National Laboratory in Denmark [2], that gives a dose equivalent to dose received in water, with an uncertainty of 4,6 %.

The samples are disposed on a horizontal conveyor, perpendicular to the electron accelerator, in a way to be treated in conditions of a homogeneous distribution of dose. So, the minimum dose received by the samples is equivalent to the dose received by the calorimeter.

TABLE 4.3. MEASURED DOSES DURING THE CAMPAIGN OF BETA IRRADIATION OF SURGICAL MASKS

Batch	Dose target	Controlled Dose	Dosimetric method	Dosimetric uncertainty
L210 run 1	40 kGy	39,3 kGy	calorimeter	4,6%
L211 run 1	40 kGy	39,3 kGy	calorimeter	4,6%
L211 run 2	40 kGy	39,1 kGy	calorimeter	4,6%
L211 total dose	80 kGy	78,4 kGy		
L212 run 1	40 kGy	39,3 kGy	calorimeter	4,6%
L212 run 2	40 kGy	39,1 kGy	calorimeter	4,6%
L212 run 3	40 kGy	39,9 kGy	calorimeter	4,6%
L212 total dose	120 kGy	118,3 kGy		
L04	50 kGy	48,7 kGy	calorimeter	4,6%

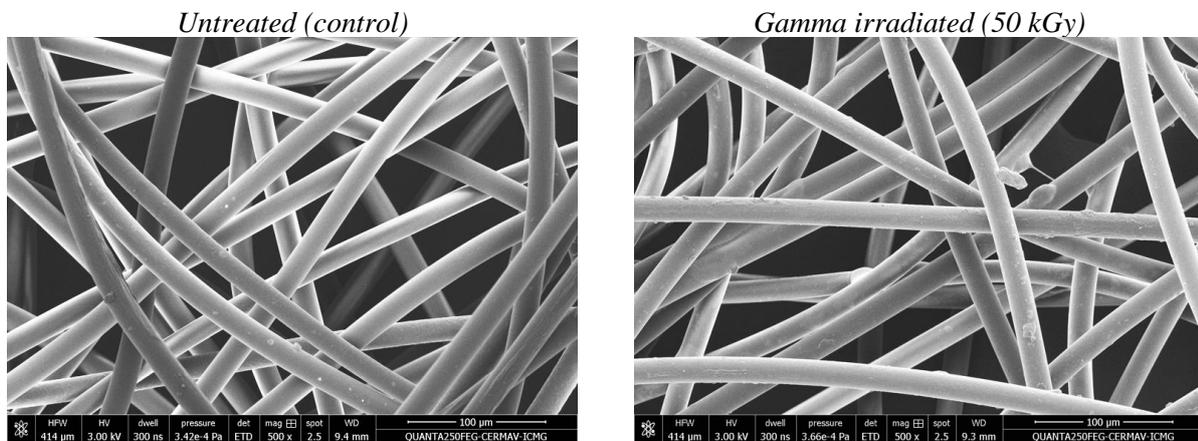
TABLE 4.4. Measured doses during the campaign of beta irradiation of FFP2 masks

Batch	Dose target	Controlled Dose	Dosimetric method	Dosimetric uncertainty
L302	10 kGy	10,4 kGy	calorimeter	4,6%
L303	20 kGy	20,2 kGy	calorimeter	4,6%
L304	10 kGy	10,4 kGy	calorimeter	4,6%
L305	20 kGy	20,2 kGy	calorimeter	4,6%
L306	40 kGy	40,4 kGy	calorimeter	4,6%
L307	60 kGy	59,1 kGy	calorimeter	4,6%
L309	10 kGy	10,4 kGy	calorimeter	4,6%
L310	20 kGy	19,7 kGy	calorimeter	4,6%
L312	10 kGy	10,4 kGy	calorimeter	4,6%
L313	20 kGy	19,7 kGy	calorimeter	4,6%

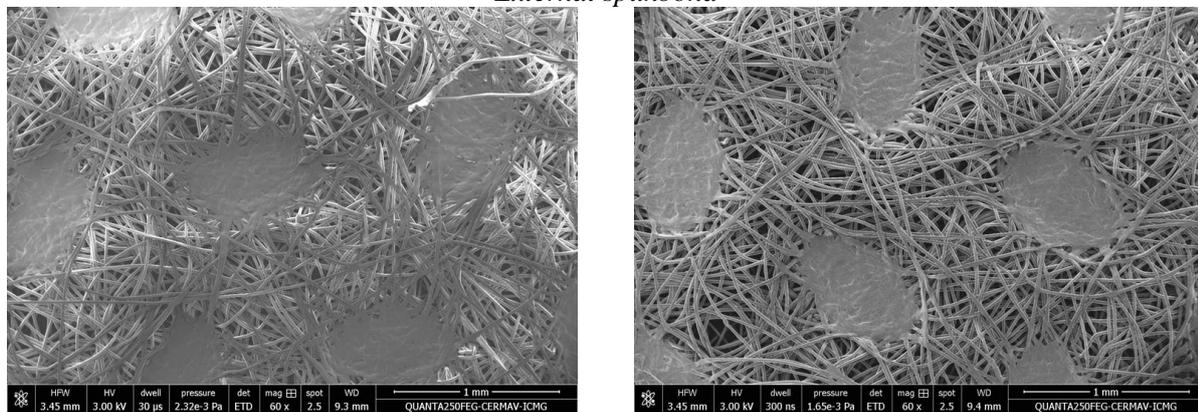
4.2. Result of characterization

4.2.1. Surgical masks

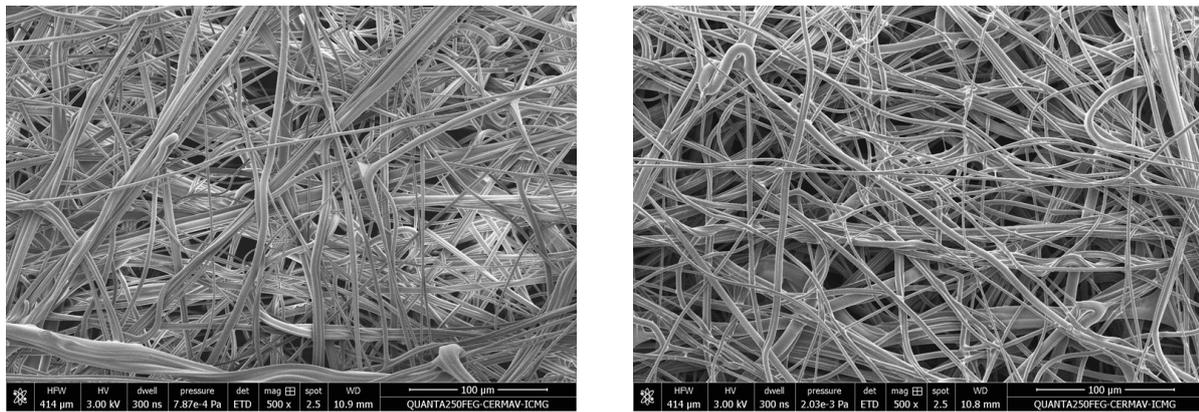
First characterizations of materials were done in CERMAV laboratory on already worn and 50 kGy irradiated surgical masks (L01) versus the same brand new and untreated mask. NMR analysis did not reveal any detectable chemical degradation in link with this technique [2] and SEM observation did not show any morphological modification [3]. Only some traces of distortion of elastic wrap were observed, surely more in link with the first wearing than with the irradiation.



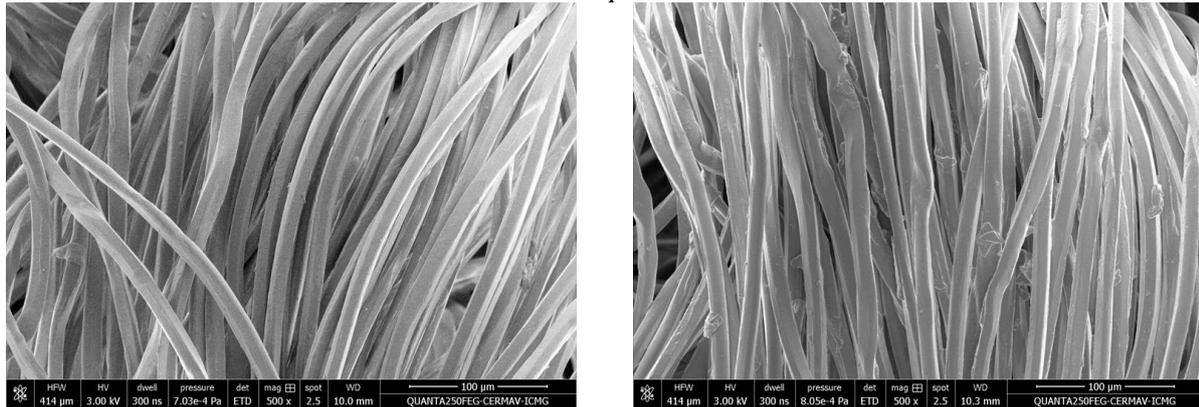
External spunbond



Intermediate meltblown



Internal spunbond



Elastic strap

FIG. 4.2. SEM observation of already worn and 50 kGy irradiated surgical masks with comparison with control untreated mask. Pictures from [3].

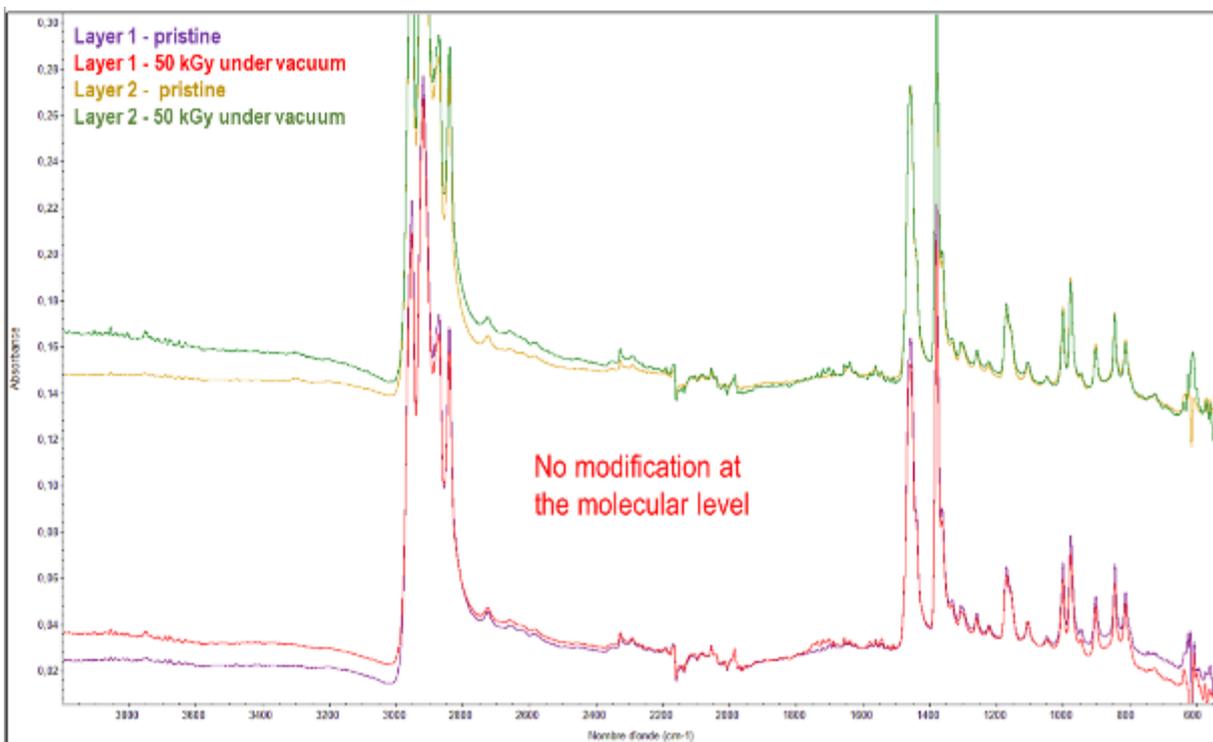


FIG. 4.3. FTIR-ATR spectra of the internal and of the meltblown layer before and after irradiation. Pictures from [5].

Following characterization were done in CEA-Saclay [4-5] in collaboration with ENSAM Paris on 25 and 50 kGy irradiated masks (L02 and L07). As for SEM observation, no morphological change was observed by optical microscopy. In addition, FTIR-ATR did not allow revealing any noticeable molecular bond nature evolution, whatever the layer under study and its face.

OIT (Oxidative-induction time) was tempted using DSC but unirradiated PP surgery mask parts began to degrade after a few minutes under oxidative atmosphere, which is a clear indication of the very low level of antioxidants in the unirradiated PP fibers.

TD-GC/MS allowed to the volatile compounds to be separated and identified during heating. After irradiation, approximatively 90 products are present, much more than when compared to unirradiated masks. Even if still in low quantities, the amount increases with the dose. The main degradation products are coming from the degradation of phenolic primary antioxidants.

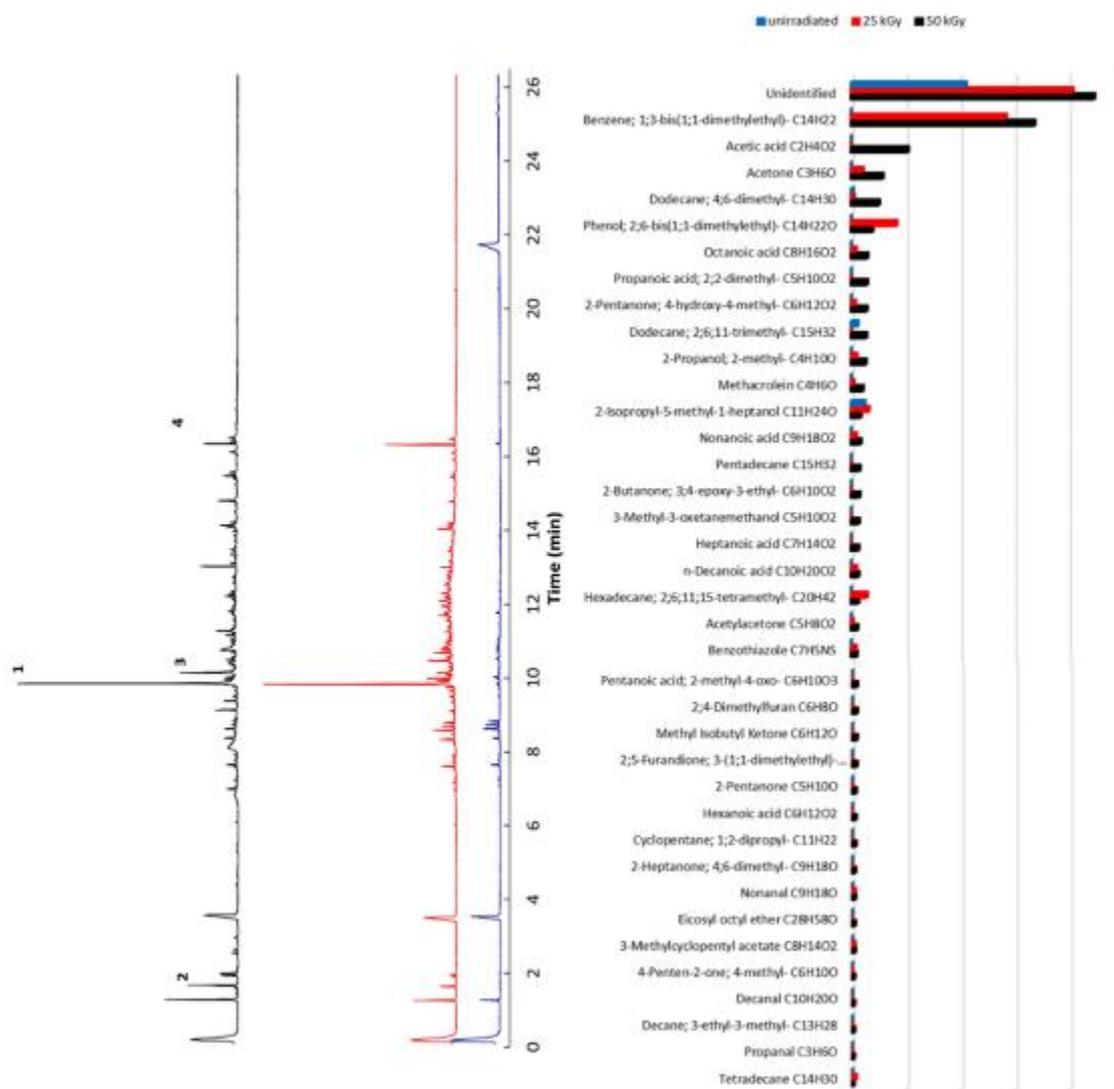


FIG. 4.4. Chromatogram of the surgery external face (peaks numbered: 1 \Rightarrow 1,3-bis(1,1-dimethylethyl)-benzene; 2 \Rightarrow acetone; 3 \Rightarrow acetic acid; 4 \Rightarrow 2,6-bis(1,1-dimethylethyl)-phenol) and diagram of identified molecules sorted by peak area (peak areas of all the unidentified products have been summed). Pictures arranged from [4].

4.2.2. FFP2 masks

Characterization have been achieved with e-beam and gamma rays, under vacuum and under air, at doses ranges from 10 to 60 kGy (batches L48, L49, L78, L302, L303, L305, L307, Valmy masks). Results are compiled in reference [6].

FTIR-ATR revealed no perceptible modifications at the molecular level when processed under vacuum, neither with gamma rays nor with e-beam.

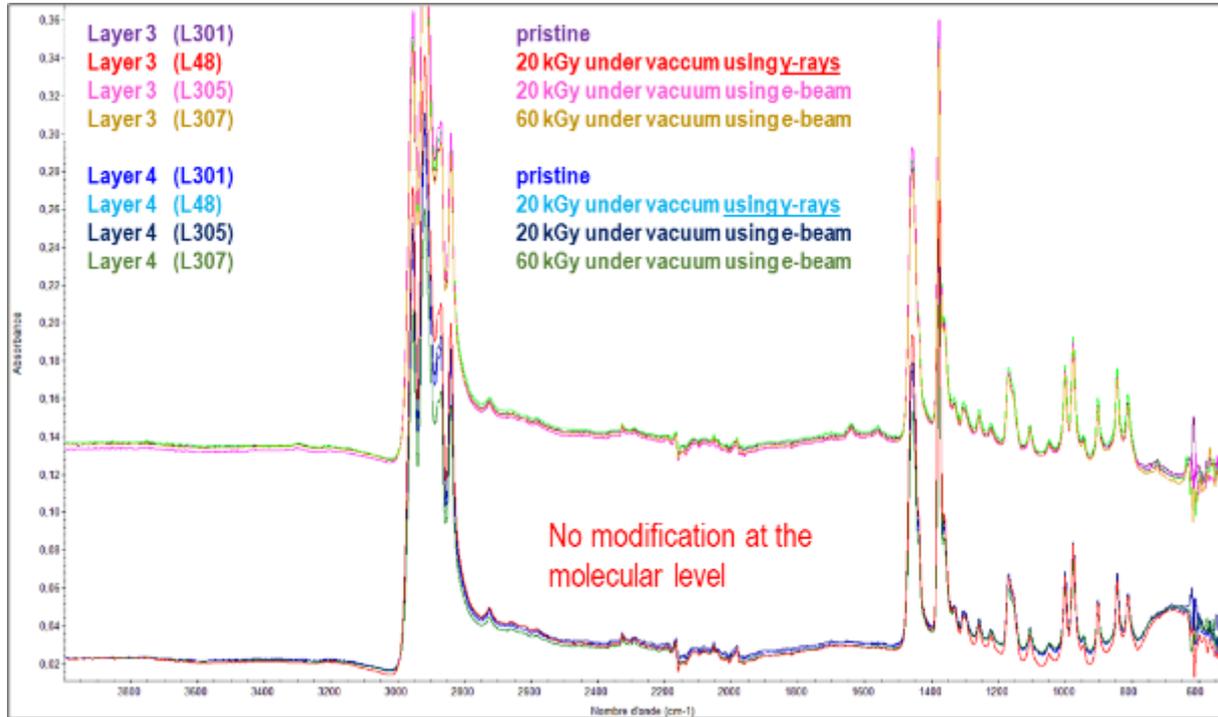


FIG. 4.5. FTIR spectra of meltblown (layer 3) and spunbond (layer 4) when irradiated under vacuum. Pictures from [6].

When processed in air, a small carbonyl bond peak appeared in meltblown layer with gamma irradiation, giving evidence of a beginning of oxidation, but not with e-beam, or when gamma processed under confined air.

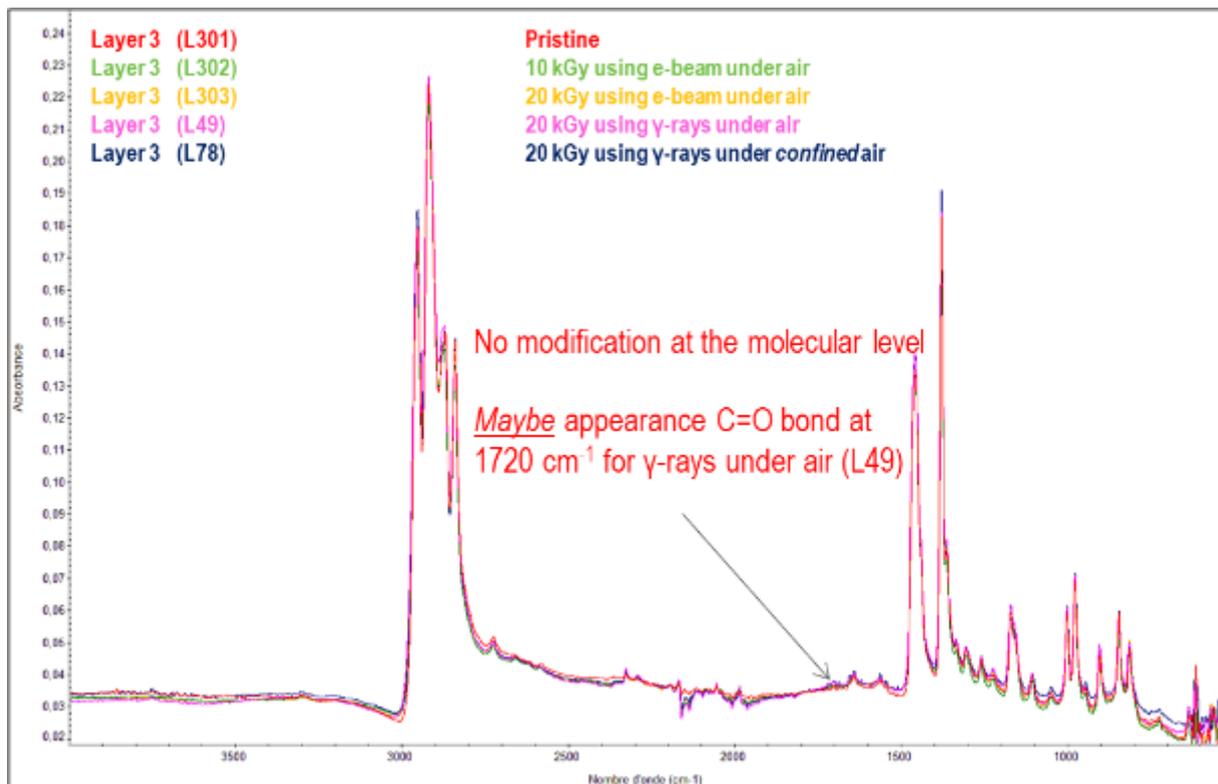


FIG. FIG. 4.6. FTIR spectra of meltblown (layer 3) when irradiated in air. Pictures from [6].

As for surgical masks, OIT measured using DSC revealed a complete consumption of antioxidant after irradiation, and TD-GC/MS showed degradation products coming from the degradation of phenolic primary antioxidants in low quantities.

Elastic strap shows also some S-containing degradation product molecules evidenced by TD-GC/MS, the more when gamma irradiation was conducted in air. These S-containing molecules are believed to come from a vulcanization process of the elastic strap.

4.3. Filtering tests

4.3.1. Surgical masks

First tests were made in IMT Nantes using particular flow with already worn and 50 kGy irradiated masks (L01). In the measured particle diameter range, from 1 to 2 μm , results show a low decrease of the performance with regards of untreated controlled new masks. It is interesting to see that some masks worn and irradiated at 50 kGy are still best than others new.

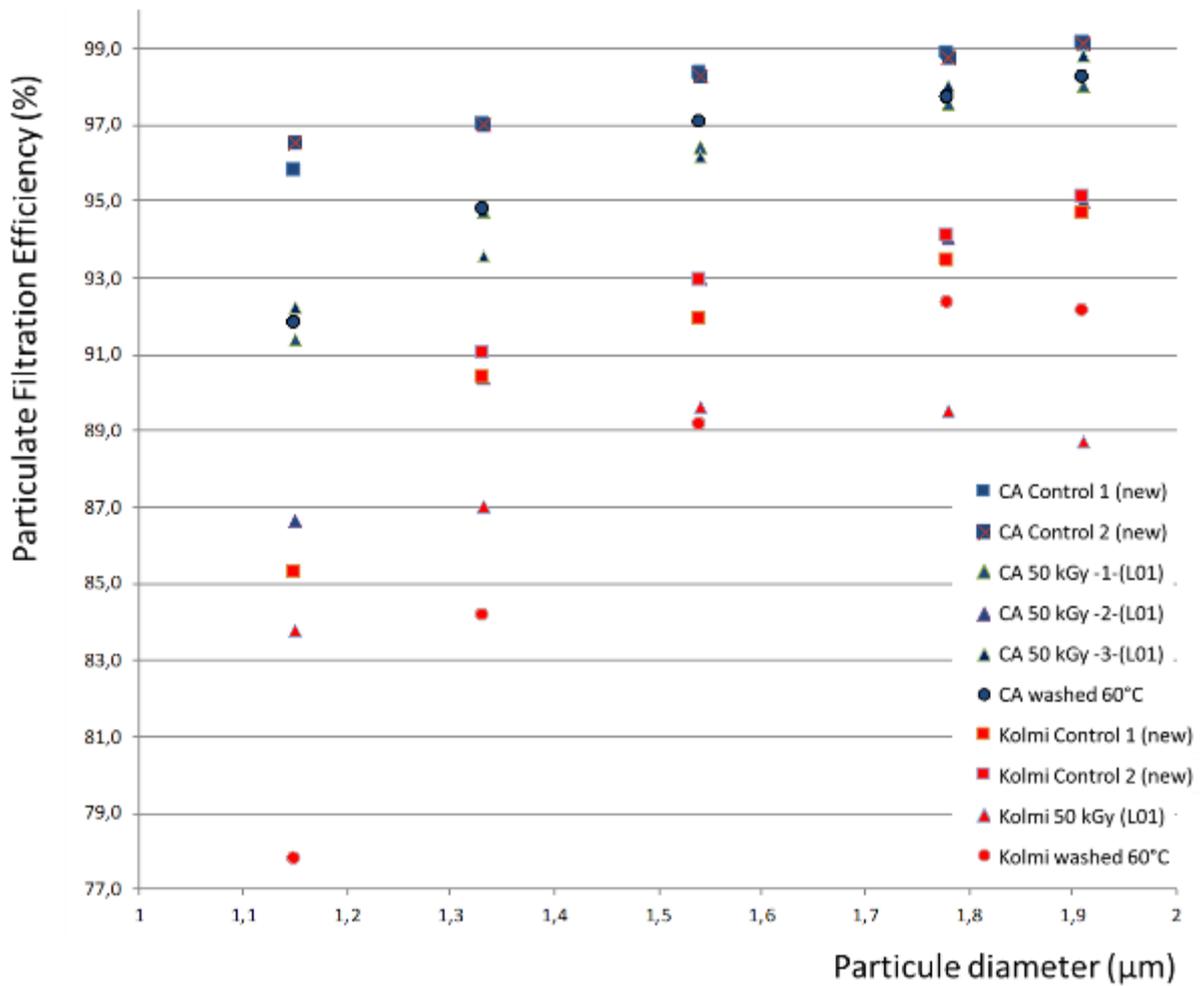


FIG. 4.7. Particulate Filtration Efficiency of worn and 50 kGy irradiated surgical masks measured on the bench of IMT Nantes.

Standard measurements made by Centexbel (bacterial filtration efficiency at 3 µm [7]) show lower value, from 84 to 88 % according the condition of irradiation.

On the other hand, the only test made on unworn mask was on L215, 3 cycles of washing + 20 kGy gamma irradiation, therefore cumulating 60 kGy, show no loss of efficiency.

Results of IMT Nantes and Centexbel are presented in TABLE 4.5.

TABLE 4.5. IMT NANTES AND CENTEXBEL RESULTS OF MICRONIC FILTRATION EFFICIENCY

Batch	Technique	Dose	Particular filtration efficiency (2 μm) IMT Nantes	Bacterial filtration efficiency (3 μm) Centexbel	Remarks
Control CA Diffusion	-	-	99,1%		
L01 CA Diffusion	Gamma	50 kGy	97,3%		Worn and irradiated
Control Kolmi	-	-	94,6%		
L01 Kolmi	Gamma	50 kGy	89,6%		Worn and irradiated
L07	Gamma	50 kGy		85,9%	Worn and irradiated
L08	Gamma	25 kGy		84,6%	Worn, washed and irradiated
L03	Gamma	48 kGy		86,4%	Worn and irradiated
L04	E-Beam	48 kGy		88,0%	Worn and irradiated
L215	Gamma	60 kGy	99,7 %		Unworn, 3 cycles washing + 20 kGy

4.3.2 FFP2 masks

APAVE official standard results of FFP2 masks are still missing, and we have until now just some incomplete results transmitted for information. They are expressed in the following TABLE 4.6.

TABLE 4.6. TRANSMITTED APAVE PENETRATION RESULTS ACCORDING EN 149

Batch	Technique	Dose	NaCl Penetration	Paraffin Penetration	Remarks
L01	Gamma	50 kGy	$\geq 50\%$	-	Worn and irradiated
L10-7	Gamma	25 kGy	$\geq 50\%$	-	Worn, washed and irradiated
L301 (Control)	-	-	0.2%	1.7%	
L302	E-Beam	10 kGy	17.7%	41.80%	under air
L303	E-Beam	20 kGy	22.0%	43.0%	under air
L305	E-Beam	20 kGy	20.0%	39.0%	vacuum sealed
L307	E-Beam	60 kGy	31.5%	38.0%	vacuum sealed

We are also expecting results of L44 batch (gamma 20 kGy + thermal annealing).

Results from IRSN give more indication [7], including spectral filtration efficiency. They confirm a significant loss of efficiency in the range of 50 to 500 nm, whatever the type of irradiation is.

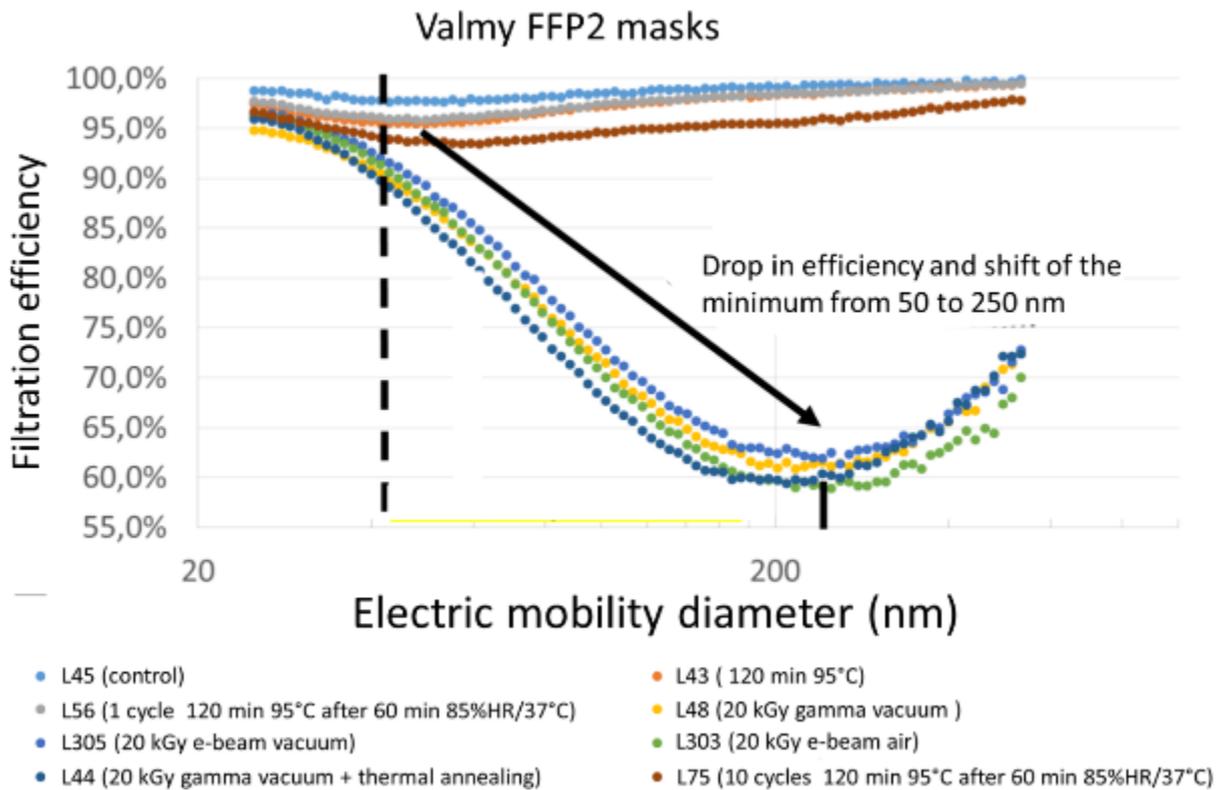


FIG. 4.8. Spectral Particulate Filtration Efficiency of different batches of FFP2.
Picture adapted from [8]

The total penetration, as defined in the EN 149 European standard, and the spectral penetration at 100 nm are given in the following TABLE 4.7.

TABLE 4.7. IRSN PENETRATION RESULTS.

Batch	Technique	Dose	Total NaCl Penetration	Spectral NaCl Penetration (101.8 nm)	Remarks
L44	Gamma	20 kGy	25.7%	31.4%	vacuum sealed + thermal annealing
L45 (Control)	-	-	0.3%	1.7%	
L48	Gamma	20 kGy	25.2%	29.5%	vacuum sealed
L303	E-Beam	20 kGy	28.3%	31.0%	air
L305	E-Beam	20 kGy	23.8%	28.8%	vacuum sealed

5. DISCUSSION AND CONCLUSION

The work undertaken sought to assess the feasibility of using radiation processing to decontaminate single-use medical masks after first use, aiming recycling them in the event of a possible shortage. After some first runs with high doses, “just to see”, 2 kGy was retained as the D_{10} value for surrogate of SARS-CoV-2 [9-10] so that 10 kGy could decontaminate at a -5 log level. To take into account a mass processing, for instance with a Dose Uniformity Ratio (DUR) of 2, 20 kGy was used as a reference in the study. However, this dose was not chosen according a complete risk analyses as it should be done if such solution is nominated.

Even if no morphological and very few chemical changes have been observed in the filtering PP material, FFP2 filtration performance in submicronic range is seriously affected by radiation processing, whatever the dose and the irradiation conditions are. This confirms works undertaken in Havard-MIT and Massachusetts General Hospital [11] on N95 masks that use the same technology. This effect has to be linked with the electrostatic filtration provided by the electric charge of the meltblown (“electret”) used in that type of masks. Indeed, high density of ionization induces the polymer discharge. It now appears clear that the decontamination radiation processing of FFP2, N95 or equivalent respiratory protection masks have to be avoided if one wants to preserve the submicronic filtration efficiency of such masks. Gamma and e-beam irradiation, under vacuum or in air, with or without thermal annealing after irradiation, cannot be recommended for treatment for re-using such masks with the present technology. However, some try are launched to assess the feasibility of recharging the electret for instance with corona effect.

Considering surgical masks, submicronic filtration is not required and indeed not effective as there is no such “electret” filter. The filtration is slightly affected in the micronic range after irradiation, depending on the dose, but all the results are not in very good agreement. A tentative for an intercomparison of the different bench used in these studies is underway in France, including both particular and bacterial efficiency. There is no significant evidence that irradiation condition such as use of very high dose rate like in e-beam processing, or processing in sealed vacuum bags, have benefit effect on the filtration performance after irradiation. However, processing with gamma rays in air must be avoided as this study indicates a beginning of oxidation of PP that could lead to important delayed post-effect degradation. Surprisingly, such beginning of oxidation was not confirmed when processing with gamma rays in closed airtight box, even though a high presence of O_3 . This result might be explained by oxygen concentration depletion in the closed container, but this hypothesis has to be confirmed. The other concern is the presence and increasing of compounds due to consumption of antioxidant. Even if in low quantities, as coming from the degradation of antioxidant that are already in low quantities, the potential risk of these compounds in such quantities have to be checked if this type of treatment is selected.

Generally speaking, the choice of a method in the frame of reuse of surgical masks during crisis must pass through a complete risk analysis. In this case, it must include the evaluation of the proper dose and operative condition with regards of the benefit in terms of virucide reliability for instance and the potential drawback such as loss of efficiency or amount of unwanted compounds.

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