IAEA Technical Report

STERILIZATION AND REPROCESSING OF PERSONAL PROTECTIVE EQUIPMENT (PPE), INCLUDING RESPIRATORY MASKS, BY IONIZING RADIATION

IAEA

FOREWORD

The use of ionizing radiation for sterilizing healthcare products has been steadily increasing since its introduction in 1950s. Presently radiation treatment is an essential part of the manufacturing processes for nearly half of all single-use medical devices, such as bandages, gloves, lab ware, syringes, procedural kits, and many other equipment. Radiation is an instrumental tool to produce ionization for the sterilization of medical devices. At the same time radiation can be powerful in the modification of the physical-chemical properties of protective materials to enable changes in their performance.

The IAEA promotes the industrial application of radiation such as sterilizing healthcare products to its Member States by helping countries through training, expert advice and research projects. As numbers of COVID-19 infections increase, shortages in personal protective equipment (PPE) for staff on the frontline of the pandemic continue to pose a problem in many countries. Upon request from several Member States (MS), the IAEA reviewed findings from five institutions that tested the use of ionizing radiation – gamma ray and/or electron beam – to sterilize used respiratory masks, such as models N95 and FFP2 commonly worn by medical personnel.[1]

The objective of the technical report is to provide scientific and technical information on feasibility of sterilization for reprocessing of disposable medical equipment by ionizing radiation and their acceptability for re-use. IAEA is working with MS to advance the studies on sterilization of PPE, with emphasis on knowledge gaps through performing tests of irradiation parameters, post-irradiation effects and components performance, as well as the microbiological validation.

The IAEA wishes to thank all contributors for their valuable contributions. The IAEA officers responsible for this publication were BumSoo Han and Celina Horak of the Division of Physical and Chemical Sciences.

[1] A new press release from IAEA related to the sterilization of masks with radiation. https://www.iaea.org/newscenter/pressreleases/radiation-effective-in-sterilizing-personal-protective-equipment-except-for-respiratory-masks-iaea

CONTENTS

1. INTRODUCTION

1.1 Background

Radiation sterilization is exposure of product to high energy electromagnetic radiation (gamma ray or X ray) or high energy particles (electrons) in a controlled and safe manner. Particle accelerators are used as a source of high energy electrons, and the same accelerators can be used to generate X ray in the form of Bremsstrahlung radiation. Radioisotope of Cobalt (Co-60) is the principal source of gamma ray for efficacious methods of sterilization.

The lethal effect of radiation on microbes is well understood and extensively documented.[2] High energy electron, X rays, and gamma rays interact with microorganisms through ionizing events that lead to scission of bonds in the biologically active macromolecules of the microbe. The DNA and RNA are particularly sensitive to these effects and depolymerization of them and subsequent changes in its chemistry effectively destroy its reproductive capacity. Ionizing radiation do not destroy the microorganism; they simply exclude its ability to reproduce. This method of sterilization has proven to be highly effective.

In light of the worldwide shortage of single-use personal protective equipment (PPE) to deal with the COVID-19 pandemic, many international and governmental organizations are taking steps to expand the availability of PPE. The World Health Organization (WHO) is addressing the urgent public health concerns caused by shortages of such products by taking a risk-based approach and giving strategies to optimize the availability of PPE. [3] The strategies for increasing the emergency supply of the PPE include the accessibility to effective sterilization methods to treat big number of products, reprocessing, extended use and/or limited reuse of these devices, and release of stockpiled devices, that have passed their shelf life. The decision to implement policies that permit extended use or limited reuse of PPE is being discussed and some temporary release guidelines are already available.

Among these PPE, face masks and respirators masks are some of the most demanding items worldwide. Face masks are mostly the surgical masks (protecting environment and near people from the wearer's respiratory emissions, and providing the wearer protection against large droplets, splashes, or sprays of bodily or other hazardous fluids) and the respiratory masks (N95, FFP2 and equivalents, reduces wearer's exposure to particles including small particle aerosols and large droplets). Even if mainly made of same kind of material, they use different technology. They are important to reduce the risk to healthcare workers around the world, but also are been fostered by governments to protect healthy people in community against infectious. In this regard, WHO also gives Advice on the use of face masks in the context of COVID-19. [4] Because of the promotion in the use of this masks, there is a need in understanding how radiation processing can contribute in the strategies for increasing the emergency supply of these PPE through the well-known application - sterilisation process- and the efficacy in the reuse, where some lack of information among the member States were stated.

[2] IAEA publication 'Trends in Radiation Sterilization of Health Care Products'.
https://www.iaea.org/publications/7691/trends-in-radiation-sterilization-of-health-care-products

[3] WHO announcement
https://www.who.int/news-room/detail/03-03-2020-shortage-of-personal-protective-equipment-endangering-health-workers-worldwide

[4] WHO Interim guidance
https://apps.who.int/iris/bitstream/handle/10665/331693/WHO-2019-nCov-IPC_Masks-2020.3-eng.pdf?sequence=1&isAllowed=y

1.2 Irradiation experiments on PPE

Five contributing expert groups shared their test result with the use of ionizing radiation – gamma ray and/or electron beam – in sterilization of PPE including used respiratory masks, such as models N95 and FFP2 commonly worn by medical personnel. The contributing institutions (countries in alphabetic orders) are:

- Nuclear and Energy Research Institute -IPEN/CNEN, Technological Research Institute – IPT, University of São Paulo, and Santa Catarina Hospital - HSC, Sao Paulo, Brazil;
- ARC-Nucléart, CEA, Université Grenoble Alpes, CNRS, TIMC-IMAG, Grenoble, CERMAV, CNRS, Grenoble, Université Paris Saclay, CEA, DES-SECR, Gif-sur-Yvette, IONISOS, Dagneux, Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SCA, Gif-Sur-Yvette, IMT Atlantique, GEPEA, Nantes, France;
- Soreq Nuclear Research Center (SNRC), Sor-Van Radiation Ltd., Yavne, Israeli Ministry of Defense, Israel;
- Advanced Radiation Technology Institute (ARTI), Korea Atomic Energy Research Institute (KAERI), Jeongeup-si, Republic of Korea;
- Institute of Applied Radiation Chemistry and Department of Material and Commodity Sciences and Textile Metrology, Faculty of Material Technologies and Textile Design, Lodz University of Technology, Lodz, Poland.

In Brazil, the multipurpose gamma irradiation facility (400 kCi) were used for irradiation. Irradiated with gamma rays at different absorbed doses (5 kGy, 10 kGy, 15 kGy, 25 kGy and 50 kGy) with 5-6 $kGy.h^{-1}$. Samples were sealed using vacuum to avoid oxidation. Dosimetry was performed using PMMA Harwell System. The cloth/textile masks were irradiated only with 10 kGy.

Most of gamma irradiation tests in France were performed in the ARC-Nucléart Grenoble irradiator, with dose rate of 1 $kGy.h^{-1}$. Dosimetry was done using routine Perspex dosimeters, Red and Amber. Masks were usually packaged in a vacuum envelope (vacuum sealing). Some gamma irradiations were also achieved in Ionisos Co-60 industrial plant, in routine conditions. Mean dose rate is 2 $kGy.h^{-1}$. Alanine dosimeters were used for those experiments. 10 MeV industrial electron accelerator (Ionisos) was used for electron irradiation, in routine conditions. Dose rate reaches several hundred kGy per minute.

All irradiations in Israel were performed at Sor-Van irradiation facility (up to 61 kGy), which operates a Nordion's JS-6500 cobalt irradiator. Sor-Van is a private company located at Soreq NRC (SNRC) area. Sor-Van provides sterilization services to the medical field, research institutions, hospitals and the food manufacturing plants.

Electron beam irradiation in Korea was performed using 2.5 MeV electron accelerator in ARTI, KAERI at different absorbed doses (9 kGy, 18 kGy, and 24 kGy) with 18 $kGy.s^{-1}$. The mask samples were sealed in vacuum pack to avoid the effect of oxygen.

Samples in Poland irradiated at RT by linear electron accelerator in Lodz University of Technology at 12.5 kGy, 25 kGy, and 50 kGy. Electron energy was 6 MeV and the dose per single pass was 12.5 kGy as determined by calorimetry.

2. STERILIZATION OF HEALTHCARE PRODUCTS

2.1 Sterility assurance level

Radiation sterilization of healthcare product means destruction of all viable organisms present on that product (mainly microorganisms) by using ionizing radiation. The destruction of microorganisms by physical or chemical agents follows an exponential law. Accordingly, one can calculate a finite probability of a surviving organism regardless of the magnitude of the delivered sterilization dose or treatment. The probability of survival is a function of the number and types (species) of microorganisms present on the product (bioburden), the sterilization process lethality and, in some instances, the environment in which the organisms exist during treatment. It follows that the sterility of an individual item in a population of products sterilized cannot be ensured in the absolute sense. A sterility assurance level (SAL) is derived mathematically and it defines the probability of a viable microorganism being present on an individual product unit after sterilization. SAL is normally expressed as 10^{-n}. Estimation of the minimum required radiation dose for sterilization (to achieving a SAL 10^{-6}) and for decontamination (reducing 5 to 6 orders of magnitude) is established using as reference a representative virus family member. For radiation sterilization of microorganisms other than viruses, the ISO 11137 (part 1 and 2) should be followed.

When a suspension of a microorganism is irradiated at incremental doses, the number of surviving cells forming colonies after each incremental dose may be used to construct a dose survival curve. The radiation resistance of a microorganism is measured by the so-called decimal reduction dose (D_{10} value), which is defined as the radiation dose (kGy) required to reduce the number of that microorganism by 10-fold (one log cycle) or required to kill 90% of the total number. The D_{10} value can be measured graphically from the survival curve; the slope of the curve (mostly a straight line on logarithmic scale) is related to the D_{10} value.

2.2 D_{10} Value for viruses

The radio-sensitivity of the agent depends on several factors, such as the physiological state of the organisms, the environmental conditions and even the strain of the agent of concern. Many products can protect microorganisms from the effect of irradiation while others may sensitise organisms to ionising irradiation. Organic material present in the products being irradiated will affect negatively to the efficacy of the irradiation treatment.
Therefore, the selection of the proper D_{10} value is essential. Using a representative family or surrogate, the environmental conditions should be similar to the real product.

The D_{10} value of 2 kGy should be selected as reference, as reported in the articles from Kumar et al. and Feldmann et al., who worked with viruses similar to the agent of concern and in a condition less sensitive (frozen). This is the most representative situation to a dry condition of the listed agents (the indirect effect is limited). Irradiation under vacuum conditions would also affect the efficacy of the process, reducing the oxidative species but also protecting the material.

TABLE 1. D_{10} VALUES OF SOME REPRESENTATIVE VIRUSES

Virus	Irradiation conditions	D_{10}	Dose (9 log_{10} reduction)	Reference / Remarks from authors
Coronavirus (transmissible gastreoenteritis)	Cell culture medium Cell culture media Liquid manure	2 kGy <3.1 kGy <3,6 kGy	18-32.4 kGy	Gamma irradiation as a treatment to address pathogens of animal biosecurity concern (agriculture.gov.au/ba)
MERS-CoV	Frozen (dry ice)	<2 kGy	< 18 kGy	*Kumar et al.* (The use of gamma irradiation was shown to render 10 log10 MERS-CoV undetectable by plaque assay following a dose of 2Mrad)
SARS-CoV	Wet and dry ice (not defined)	<2 kGy	< 18 kGy	*Feldmann et al.* (SARS-CoV, harboring the largest genome of all studied viruses here, was already completely inactivated by a dose of 1 Mrad)
Other RNA viruses	Frozen (dry ice)	2.5-2.7 kGy	~ 25 kGy	*Hume et al.* (D_{10} value calculated for rVSV-EBOVgp-GFP was 0.271 Mrad, the D10 value for LACV was 0.261 Mrad, and the one for rMVKSEGFP(3) was 0.253 Mrad)

2.3 Sterilization vs disinfection dose approaches

For radiation sterilization of virus, the required sterilisation dose (SD) depends on the initial contamination (bioburden; N), the radio-sensitivity of microorganism (D_{10}) and the Sterility Assurance Level required (SAL), which according to the equation is as follows:

$$SD = D_{10} (\log_{10}N - \log_{10}SAL)$$

In cases where radiation decontamination is required, the disinfection dose (DD) will depend on the level required. High level disinfection (those required for Semi-critical devices that come into contact with intact mucous membranes or non-intact skin), represents a 6 log reduction of a representative infectious agent, and low-level disinfection a 3 log reduction. In the case of face masks, a high-level disinfection would be enough to reduce 99,999% (-5 log) to 99,9999% (-6 log) of the infectious agent.

Under the current condition, we can assume that the possible variability in viral load in used masks, is randomly distributed among products.
The microbial (bacteria and fungi) contamination found in surgical masks (article) show that in an actual situation, the standard deviation of the bioburden is higher than the mean N: 47 ± 56 cfu/ml/piece for inside mask area and 166 ± 199 cfu/ml/piece from mask outside area. This is due the

variability in the mask use, environment, etc. Therefore, preprocessing the mask before irradiation should be recommended; however, some of the mask functional properties would be lost from preprocessing. Considering this, and that a reprocessing is not convenient, the assumption for the viral load can be calculated according to the results of this study, a maximum of 1000 microorganisms should be present in the product.

- Sterilization dose:

Considering a SAL 10^{-6}, an average viral load of 1000 IU, and a D_{10} value of 2 kGy:
DS = D_{10} ($\log_{10}N$ – $\log_{10}SAL$)
SD = 2 kGy [3 – (-6)]
SD = 18 kGy. This should be the minimum dose required to achieve a SAL 10^{-6}, under the assumptions mentioned.

- Decontamination dose (DD):
A 5 or 6 order of magnitude reduction, applied on the bioburden, yields the range of dose needed:
DD = $\text{Log}_{10}N$ x 5 - 6 D_{10}
DD (-5log) = 10 kGy
DD (-6log) = 12 kGy

Note: The ISO 11137 does not use a biological indicator, such as the other sterilization methods, but uses the natural contaminated bioburden of the product to determine the dose. In this approach, we are following the same approach.

2.4 Sterilization of PPE in special cases

2.4.1 Sterilization of handmade PPE

A special case are masks made in with cloth/textile and polypropylene nonwoven fabrics (surgical) produced by several social inclusion Brazilian projects that promote the fabrication by seamstresses and prisoners of the country penitentiary system. Because production conditions related to cleaning are unknown, the use of ionizing radiation is a good alternative to disinfect if it does not affect the mechanical properties or the efficiency of filtering.
With the physical and chemical examination after the irradiation sterilization of cloth /textile masks in Brazil, they remained structurally intact, the elastic band continued to be functional, fit test was satisfactory and no presented smell was present after irradiation. In Brazil, the free distribution of these PPE by different NGOs is making a big difference to mitigate the spread of the COVID-19.

2.4.2 Medical protective clothing

COVID-19 pandemic caused the worldwide shortage of single-use PPE, not only in respiratory masks, also the medical protective clothing, such as medical dressings and surgical gowns.
The results of the irradiation of medical protective clothing in Israel seem to be promising for reuse after sterilization. No visual changes, no coloration, no changes on touch and pull, no changes in chemical structure and water-repellent properties were observed for all tested samples after both low and high irradiation doses (30 - 60 kGy). The only detected effects of irradiation were the smell, similar to that observed from irradiated masks, and the reduction of the mechanical properties (UTS and corresponding tensile strain).

3. REPROCESSING OF RESPIRATORY MASKS

3.1 Respiratory masks

Currently there are basically two types of masks. The surgical masks, which are mainly used by professionals in operating rooms, which filter the air that is exhaled and therefore contain the agents, particles, bacteria or viruses that can be transmitted through breathing to other people. On the other hand, respiratory protection masks filter the air inhaled from the outside. These masks retain agents, particles, bacteria or viruses that come from the ambient environment. They are approved for different filtering capacities.
The most common respiratory protection masks are divided according to the filter protection:

- FFP1: 80% minimum filtration efficiency, maximum 22% of internal leak rate. Protects from non-toxic and non-fibrogenic residues from dust or aerosols. It prevents inhaling these and annoying odours.
- FFP2: 94% minimum filtration efficiency on submicronic particles (including bacteria, viruses and fungal spores), maximum 8% of internal leak rate. Like the previous one, it offers protection against non-toxic residues, but also against fibrogenic elements and biologic pathogen. In this way, it prevents inhaling toxic dust, aerosols and fumes.
- N95 has a particulate filtering efficiency of 95% of particle sizes 0.3-micron.
- FFP3: 99% minimum filtration efficiency, maximum 2% of internal leak rate. It acts against different poisonous and toxic types of dust, smoke and aerosols. It is effective against bacteria, viruses and fungal spores.

According to WHO, FFP2, FFP3 and N95 are recommended for coronavirus. The equivalent filtration grades to N95 are FFP2 (European Union), KN95 (China), and KF94 (Republic of Korea).

Such masks are composed of multiple layers of polypropylene nonwoven fabrics which two layers spun-bond polypropylene (PP) have been combined with one layer melt-blown[5] nonwovens PP inside, conforming them into a layered products, called SMS nonwoven fabric (spun-melt-spun), if combined with two layers melt-blown nonwoven PP inside, it's called SMMS nonwoven fabric (spun-melt-melt-spun). To improve the filtration efficiency, a persistent electric charge is introduced into melt-blown fibres during the melt-blowing process through corona discharge and/or other means into quasi-permanent dipoles called electrets. When these charged fibres are incorporated into fibrous webs, they provide unique properties, including improved filtering properties in the submicronic domain. [6]

3.2 Physical and chemical changes

The effect of irradiation on materials is strongly dependent on the type of material being irradiated, radiation environment, and absorbed doses. Isotactic PP is a semi-crystalline polymer that is widely used in syringes and other single-use medical supplies. Post-irradiation degradation may be observed due to slow migration of radicals formed in the crystalline regions of the irradiated polymer to the crystal surface, where they react with oxygen. However, the characteristics and the effect of irradiation on melt-blown PP, which was used for filter material, are not well understood yet.

Characterizations of masks after irradiation were performed by contributors with optical and scanning electron microscopy (SEM), 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).

---

[5] Melt blowing is a conventional fabrication method of micro- and nanofibers where a polymer melt is extruded through small nozzles surrounded by high speed blowing gas. The randomly deposited fibers form a nonwoven sheet product applicable for filtration, sorbents, apparels and drug delivery systems. The substantial benefits of melt blowing are simplicity, high specific productivity and solvent-free operation.

[6] US4215682A, 1980 ‘Melt-blown fibrous electrets’

3.2.1 Observation of morphological changes by SEM

No significant changes in morphological structures of filter materials found either in gamma irradiation (up to 61 kGy) and electron beam irradiation (up to 50 kGy). The SEM analysis of samples irradiated in air and in vacuum did not reveal any significant visible changes in the studied structure of the fabric or fibres. Similar results were reported in all observation.

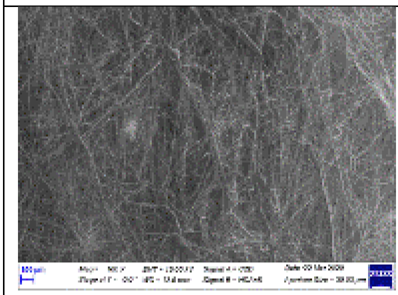
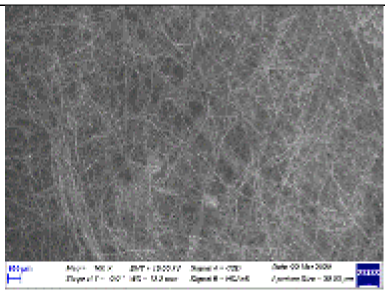
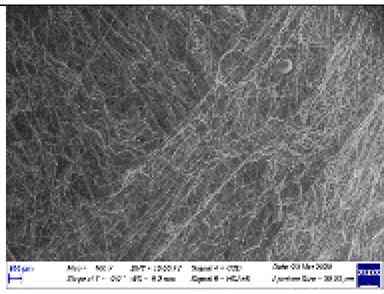
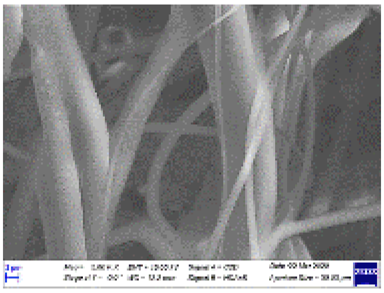
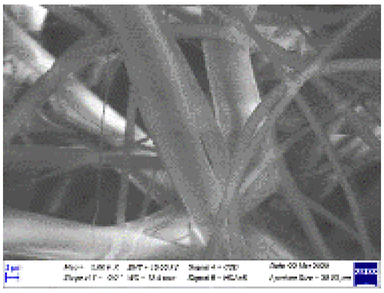
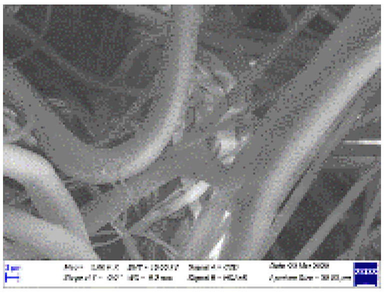
Reference	30 kGy	61 kGy
		
Low magnification		
		
High magnification		

FIG. 1. SEM images of the inner layer of the FFP3 Mask before and after irradiation. (Report from Israel)

3.2.2 Chemical structure change

In order to check if irradiation have caused significant changes in the chemical structure of the melt-blown PP, samples of the middle layer of the mask have been analysed before and after irradiation by FT-IR in the transmission mode.

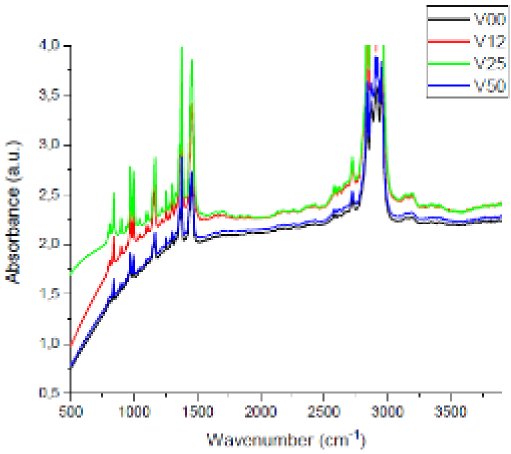


FIG. 2. Transmission-mode FT-IR spectra of the inner layer of the mask (25 g/m^2 melt-blown PP) non-irradiated and EB-irradiated in vacuum. Dose (kGy) in the legend. (Report from Poland)

The spectra show typical spectral features of polypropylene, with characteristic absorption bands as $–CH_3$ (2949 and 1454 cm^{-1}), $–(CH_2)n–$ (2838, 1454 and 840 cm^{-1}). Irradiation hasn't caused any significant changes in the spectra. Similar results on irradiated samples were reported in other observations.
To further check the possibility for crosslinking or decomposition reaction of respiratory mask filter in details, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) were conducted after electron beam irradiation.

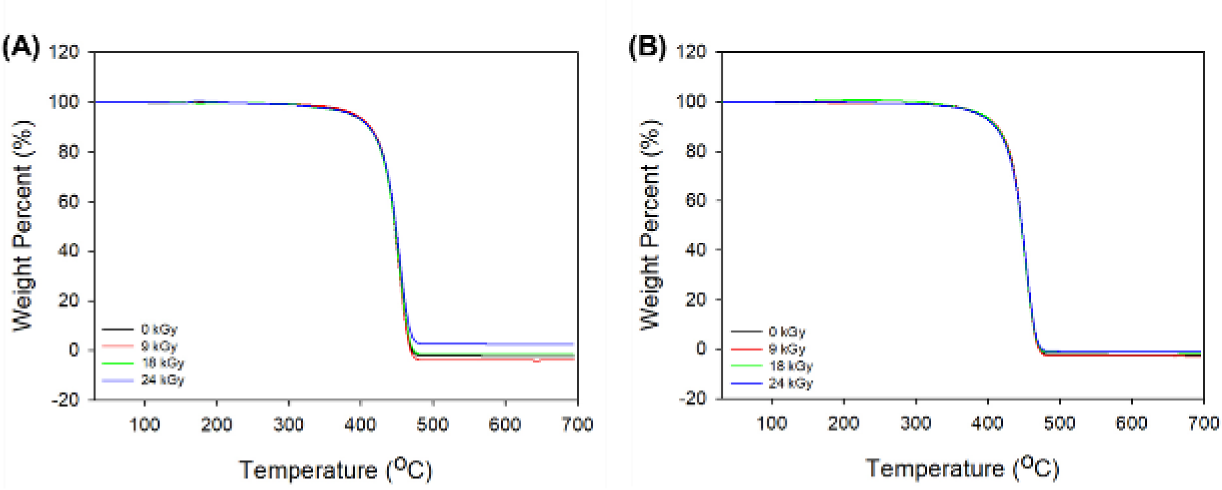


FIG. 3. TGA results of electron beam irradiated electrostatic filter under (A)air and (B)vacuum condition (report from republic of Korea)

Thermal decomposition (Tg) temperature of each sample electron beam irradiated is identical to that of pristine case irrespective of irradiation conditions. This result indicates that irradiation does not induce a measurable chemical reaction such as crosslinking or chain scission and crystallinity.

3.3 Performance test after irradiation

3.3.1 Fitting and reusability

Irradiated masks were inspected firstly for visual changes on the main structure of the mask. Slight coloration and smell were reported at high dose irradiation, which might be a result of radiation-induced oxidation of the filter material and/or additives. Face-seal leakage test of Masks before and after irradiation was performed using TSI PortaCount® Pro+ Respirator Fit Tester 8038 in Israel. The TSI Portacount is an ambient particle counting device which is used to conduct Fit Testing by providing a quantitative assessment of face-seal leakage. Test results indicate that the fit factor does not change significantly even after high dose irradiation of 30-50 kGy.

3.3.2 Mechanical Testing

The mechanical properties of mask materials and medical protective clothing were tested, before and after gamma-irradiated, using a universal testing machine. The mechanical properties of thin inner layers taken from surgical masks were tested before and after high-dose irradiation (61 kGy). Tensile test results of the reference and irradiated samples indicate that irradiation did not have any apparent negative effect on the mechanical properties of inner material.

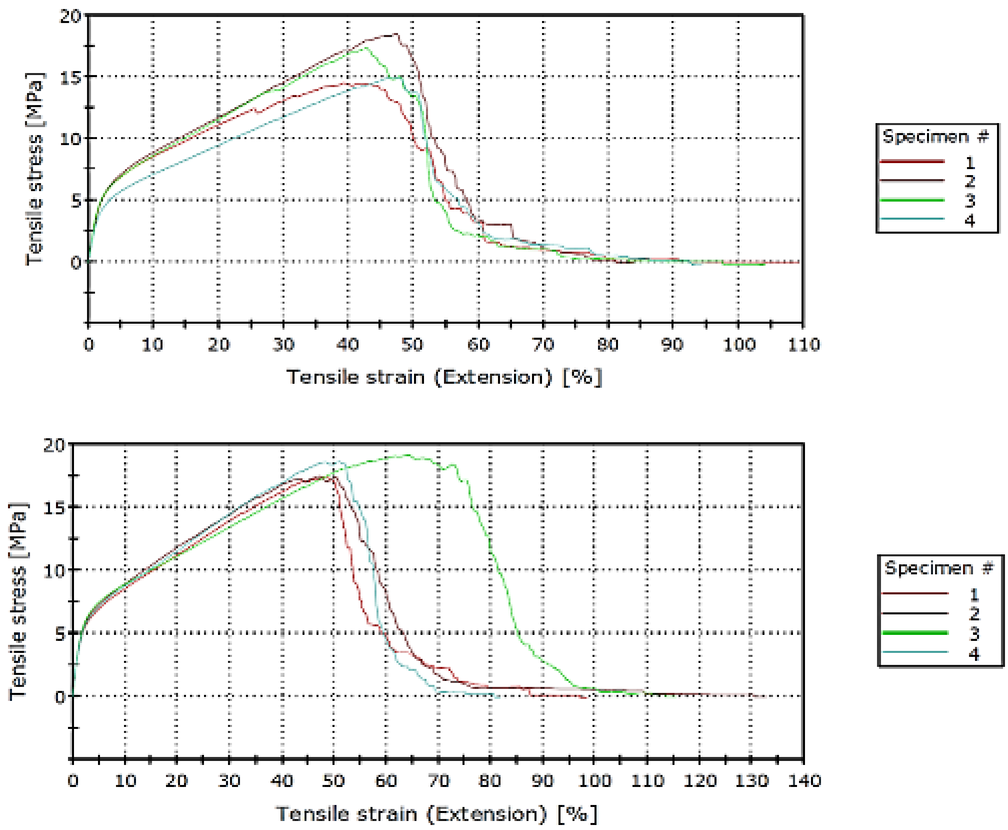


FIG. 4. Tensile test results of thin inner layer of masks, before (upper) and irradiated (lower) (Report from Israel)

3.3.3 Filtration test

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

However, unfortunately, the filtration efficiency in most all the irradiated samples from 5 to 60 kGy showed significant decrease. It is observed in France a significant loss of efficiency in the range of 50 to 500 nm, whatever the type of irradiation is. The total penetration, as defined in the EN 149 European standard, and the spectral penetration at 100 nm are given in the following table:

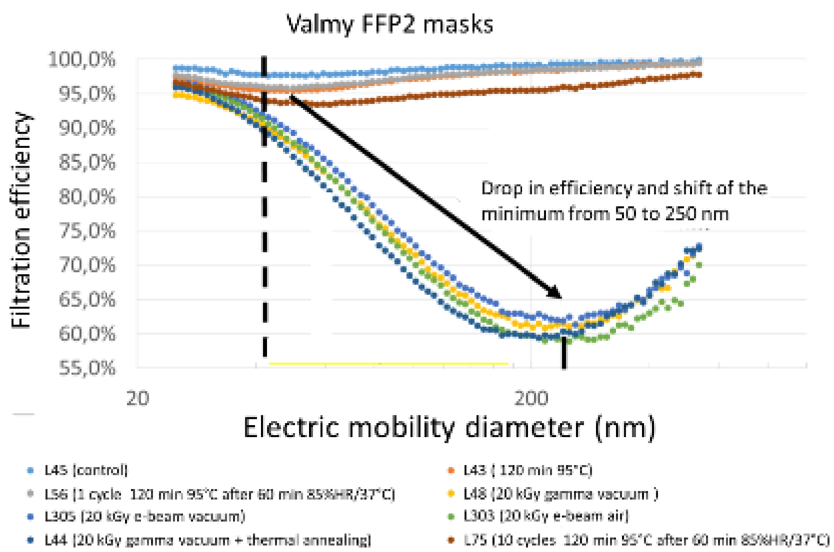


FIG. 5. Spectral Particulate Filtration Efficiency of different batches of FFP2. (Report from France)

The FFP2 / N95 mask is composed of multiple layers of, typically, nonwoven PP fabrics. Among these layers, the most critical is that which is produced by the melt-blown PP. Typically the melt-blown layer is 100−1000 μm in thickness and composed of microfibers with diameters in the range of ～1−10 μm, as seen in the SEM images in FIG.1., which produces a three-dimensional network that has a porosity of 90%, leading to high air permeability. Since the fibre diameters are relatively small and the porous space is large, the filtration efficiencies of melt-blown fabrics by themselves should not be adequate for fine particle filtration. To improve the filtration efficiency while keeping the same high air permeability, these fibres are charged through corona discharge and/or other means into quasi-permanent dipoles called electrets. The irradiation may destroy such electrets and may lower the filtration efficiency.
The decrease in filtration efficiency in irradiated masks are observed in both gamma irradiation and electron beam irradiation and in whatever atmospheric condition (in air or in vacuum).

TABLE 2. PENETRATION TEST RESULTS (REPORT FROM FRANCE)

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

TABLE 3. FFP2-N95 FILTRATION EFFICIENCY AFTER GAMMA RAY IRRADIATION (REPORT FROM BRAZIL)

Sample set name	Dose [kGy]	% retention average value
	0	89.8
sp1	5	58.2
sp2	10	48.8
sp3	15	45.3
sp4	25	43.6
sp5	50	42.5

TABLE 4. NACL AEROSOL-BASED FILTRATION EFFICIENCY OF KF94 MASKS BEFORE AND AFTER ELECTRON BEAM IRRADIATION IN AIR CONDITION (REPORT FROM KOREA REP. OF)

	0 kGy	9 kGy	18 kGy	24 kGy
#1	99.2%	56.6%	61.9%	68.4%
#2	99.4%	57.5%	64.2%	67.9%
#3	99.4%	59.8%	66.1%	66.4%
Average	99.3%	57.9%	64.1%	67.6%

TABLE 5. KN95-N95 FILTRATION EFFICIENCY AFTER GAMMA RAY IRRADIATION (REPORT FROM ISRAEL)

Sample name	Dose [kGy]	Filtration Efficiency (%)	Remarks
Z1	0	95.3	
X1	30	34.3	
Y1	60	36.4	
F3	6	56.3	
F5	32	64.0	
G1	0	99.9	
G6	32	64.8	
G4	32	65.1	vacuum sealed
G8	60	64.6	vacuum sealed

3.4 Summary of reprocessing test

Comparison with other methods of sterilization method (e.g., heat steam, ethylene oxide) shows that radiation sterilization of PPE has a number of advantages. Radiation sterilization is more energy-efficient and can be used with products that are not thermally stable when compared with sterilization by heat. It has the advantages over ethylene oxide sterilization of leaving no toxic residues (ethylene oxide is a potential carcinogen and mutagen) and of allowing sterilization of sealed packages. Furthermore, radiation sterilization depends only on the absorbed doses, and control is relatively easy compared with other means of sterilization that depend on a variety of factors such as temperature, pressure, moisture, and gas composition. Radiation sterilization is also rapid compared with steam and ethylene oxide sterilization. A further benefit arises from this since radiation sterilization can be carried out as a continuous rather than a batch process, simplifying automation of the operation.

Even if no morphological and very few chemical changes have been observed in the nonwoven melt-blow PP material, FFP2 filtration performance in submicronic range is seriously affected by radiation processing, whatever the dose (beyond 5 kGy) and the irradiation conditions are. This effect can probably be linked with the electrostatic filtration provided by the electric charge (electret) to the melt-blown used in that type of masks. 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.

Radiation sterilization is recommended to surgical masks, home-made masks with cloth/textile and medical protective clothing, those which submicronic filtration is not required and indeed not effective as there is no such electrostatic charge. The results of the irradiation of medical protective clothing seem to be promising for reuse after sterilization. No visual changes, no coloration, no changes on touch and pull, no changes in chemical structure and water-repellent properties were observed for all tested samples after both low and high irradiation doses (30 - 60 kGy).

4. CONCLUSIONS

The contributors of technical report concluded that the ionizing radiation is an effective and established tool to sterilize personal protective equipment (PPE) that is in high demand during the COVID-19 pandemic, except for respiratory face masks (N95, FFP2 and equivalent) as it decreases the filtration efficiency, probably by damaging the electret in their filters. It was also concluded that:

(1) Radiation sterilization has the advantage that arises from its ability to destroy contaminating microorganisms with an insignificant rise in the temperature of the irradiated materials, thereby preserving their properties and characteristics of PPE.

(2) The high penetrating power of radiation allows a large number of materials for use in the manufacture and packaging of medical devices and pharmaceuticals with reliability and safety.

(3) The experiments on reprocessing of used surgical and respiratory masks demonstrated the efficacy of radiation inactivation of the viral load.

(4) Irradiation on respiratory masks (N95, FPP2 and equivalent with melt-blown nonwoven PP filter) caused no significant changes in morphology and thermal properties, however irradiated masks showed significant decrease in filtration efficiency in the submicronic domain. Therefore, it is not recommended to use ionizing radiation for sterilization and reprocessing of this kind of respiratory masks. The decrease in filtration efficiency may arise from the changes in electrostatic properties of melt-blown PP filter which was charged with electrets.

(5) Simple surgical-type masks and handmade masks with cloth/textile and polypropylene nonwoven fabrics, which are not intended to fulfil the FFP2, N95 specifications are not much affected by irradiation with respect to their structure and functional properties. Such masks could be sterilized by ionizing radiation with classical doses for decontamination.

(6) Irradiation of medical protective clothing seem to be promising for reuse after sterilization. No significant visual changes, coloration, changes on touch and pull, changes in chemical structure and water-repellent properties were observed even in high irradiation doses.

(7) However, if radiation sterilization is considered for particular PPE including simple face masks and medical protective clothing at particular conditions, further tests should be performed to verify the suitability of this technique in a given specific case.

INDIVIDUAL REPORTS FROM CONTRIBUTORS

DEVELOPMENT OF METHODOLOGIES FOR DECONTAMINATION, REUSE AND IMPROVEMENT OF THE PROPERTIES OF RESPIRATORY PROTECTIVE EQUIPMENT USING IONIZING RADIATION – PRELIMINARY RESULTS

P.A.S. VASQUEZ[1], F. MORAS[3], F.S. LIMA[2], P. S. SANTOS[1], O. MORAES[4], P. ARTAXO[3], V.M. JOHN[3], M.L.E. NAGAI[3], M.J.A. OLIVEIRA[1], L.H. CATALANI[3], Y. KODAMA[1], L. OTUBO[1]

[1] Nuclear and Energy Research Institute -IPEN/CNEN, Sao Paulo, Brazil
[2] Technological Research Institute – IPT, Sao Paulo, Brazil
[3] University of São Paulo – USP, Sao Paulo, Brazil
[4] Santa Catarina Hospital - HSC, Sao Paulo, Brazil

Abstract

The pandemic generated by the new coronavirus (SARS-CoV-2) increased the demand for personal protective equipment (PPE), specifically respiratory protective equipment (RPE) or masks causing a shortage of stock of these materials worldwide. The WHO (World Health Organization) promotes and defends the use of this equipment, in this context cloths/textile masks, surgical masks and the filtering facepiece respirators (FFP) type N95 have a fundamental role in preventing the contagion of health professionals who deal with daily care for infected people. According to WHO, it is known until now that the spread of SARS-CoV-2 occurs through droplets (expelled during speech, coughing or sneezing), through direct contact with infected people, and by indirect contact, through the hands, with contaminated objects or surfaces. Its transmission is similar to that of other respiratory pathogens, however its spread has generated mass contamination, with significant impacts on health and funeral services. Considering this scenario, WHO has raised the need to seek alternatives that make it possible to guarantee the use of surgical masks and the N95 type in healthcare environments, reinforcing the need to research possibilities for reuse. The goal of this work is proposed to develop methodologies for decontamination and reuse of cloth/textile masks, surgical masks and FFP-2 masks (type N95) as well as the improvement of filtering properties using ionizing radiation (gamma rays or electron beam), aiming to contribute to the demand for masks caused by the pandemic, in addition to aiming at reducing waste.

1. OBJECTIVES OF THE RESEARCH

Develop methodologies for decontamination and reuse of cloth/textile masks, surgical masks and FFP-2 masks (type N95) and improving properties using ionizing radiation, aiming to supply the mask demand caused by Covid-19 and the reduction of residues.

2. INTRODUCTION

Researchers around the world are committed to finding a technique that is efficient for disinfecting / sterilizing N95 and surgical type masks. However, it is observed that the techniques studied so far have some type of deficiency that jeopardizes the efficiency (filtering) for the reuse of these masks. Some researchers studied techniques for washing surgical masks and FFP-2 in an autoclave and in a solution at pH 13, temperature at 100 °C for 30 minutes and ionizing radiation with doses of 25 kGy and 50kGy. Results showed degradation of the material of the filters of the FFP-2 masks, compromising their reuse. However, gamma radiation from cobalt-60 can be explored more using combinations of techniques and materials. The irradiation dose (kGy) and the dose rate (kGy.h-1) and its combination can be also studied, associated with the form of sample preparation (inert atmosphere) and conventional treatments (temperature, chemical agents, quarantine time, etc.). In this research, it is proposed to carry out a methodological study to decontaminate surgical masks and FFP (N95) respirators, combining processing conditions with ionizing radiation (gamma rays and electron beam). Selected samples are been irradiated in vacuum conditions and in an atmosphere of nitrogen (N_2), to control the possible degradation caused by oxygen present in the environment. With the practical tests of the filtration efficiency, it will be possible to define the limit radiation dose that does not generate the degradation of the masking materials, but still efficient in the elimination of viruses and bacteria, enabling safe reuse or decontamination. In addition, with the results obtained, it is intended

to generate a reuse protocol for the N95 masks studied in this research. The use of sterilization with ionizing radiation offers less manipulation of contaminated masks and thus a decrease in the probability of contagion in this process when compared to the use of gases and others. Contaminated materials are treated directly in the collection or transport packaging. It is also intended to impregnate the masks with cross-linkable polymeric solutions rich in silver nanoparticles (AgNp) and other polymers that can create grafting after the irradiation process and thus increase the filtering properties and provide these materials with antiviral and antibacterial properties [1][2][7].
A special case are masks made in with cloth/textile and polypropylene nonwoven fabrics (surgical) produced by several social inclusion Brazilian projects that promote the fabrication by seamstresses and prisoners of the country penitentiary system. Because production conditions related to cleaning are unknown, the use of ionizing radiation is a good alternative to disinfect if it does not affect the mechanical properties or the efficiency of filtering.

3. MATERIALS AND METHODS

3.1 Personal respiratory protective equipment (masks)

3.1.1 Surgical masks and polypropylene nonwoven fabric

Three kind of polypropylene nonwoven fabric samples, Polar FIX (green), FITESA (white), and FUNAP (white) were selected to be irradiated. Samples were provided by the social inclusion projects, who make surgical mask for hospitals and essential workers (*FIG. 3*). Material properties are shown in **Error! Reference source not found.**, FIG. 1, TABLE 2 and FIG. 2.

TABLE 1. POLAR FIX INDÚSTRIA E COMÉRCIO DE PRODUTOS HOSPITALARES LTDA AND FUNAP – PP NONWOVEN FABRIC

Properties	Method	Unit	Average value
Grammage	NWSP130.1	g/m²	40

FIG. 1 – Polar FIX nonwoven PP samples

TABLE 1 - FITESA® DEFENDER SURGICAL FACE MASK PP – PP NONWOVEN FABRIC

Properties	Method	Unit	Minimum value	Average value	Maximum value
Grammage	NWSP130.1	g/m^2	38	40	42
Resistance MD	NBR13041	N	90	120	-
Resistance CD	NBR13041	N	55	70	-
Water Column	NWSP080.6	cmH20	40	48	-
Air permeability	NWSP070.1	$l/min/cm^2$	1	2	5
Differential pressure	NBR15052	mmH2O	-	-	4
Delamination	NBR14621	N/in^2	38	45	-

FIG. 2 – FITESA nonwoven PP samples

FIG. 3 – FUNAP surgical masks production by prisoners

3.1.2 Filtering facepiece respirators (FFP2) - N95

FFP samples were select in function of the type used in the hospitals as shown in FIG. 4.

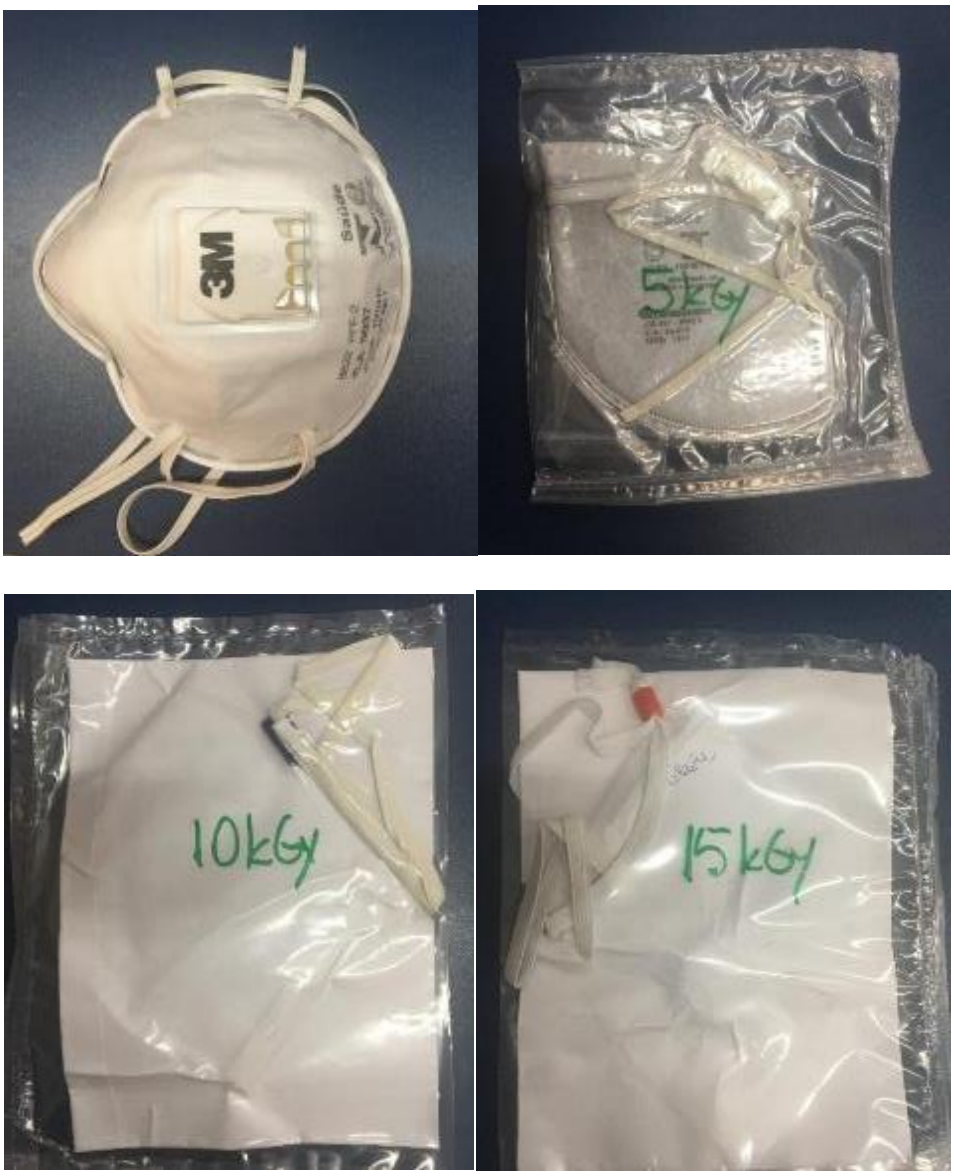


FIG. 4 – FFP2 – N95 sample respirators

3.1.3 Cloth/textile masks

The cloth/textile (cotton) masks were provided by the Paraisopolis community as shown in FIG. 5

FIG. 5 –Seamstresses cotton masks fabrication

3.2 Irradiation facilities at the IPEN

The IPEN has the Multipurpose Gamma Irradiation Facility and the Electron Beam Accelerator Facilities as the most representatives. In addition, another equipment area available as a Gammacell and a Panoramic Irradiator with low installed activities. A mobile Electron Beam unit for environmental applications is already under construction.

a. Multipurpose Gamma Irradiation Facility

This is Brazilian technology facility started in 2004. This facility is a panoramic wet source storage compact irradiator (IAEA - Category IV); the radioactive sources are stored and fully shielded in a pool of 7m. depth deionized water. The facility uses standard cobalt-60 source pencils. The source pencils are distributed into 16 source modules and these modules are distributed over two source racks. The installed activity is 400kCi (2019) related to 64 pencils (total capacity 500 pencils). The Multipurpose Gamma Irradiation Facility can be operated in dynamic or stationary modes. In the dynamic, mode a container overlap system is used to transport the products around the radioactive sources. Nevertheless, research materials or very delicate objects (e.g. cultural heritage or human tissues) need to be loaded by hand and the stationary method is the more suitable to take care mainly parameters related to the distribution dose (DUR). Then the stationary operations can be described in the following methods in function of the DUR (*FIG. 6*).

FIG. 6 – Multipurpose Gamma Irradiation Facility, IPEN - Brazil

b. Electron Beam Accelerator Facility

This facility has 02 electron beam accelerators under the same building/shielding. Each accelerator has an independent control system. One accelerator is dedicated to research applications and the other one works with cable and wire cross-linking applications (*FIG. 7*).

a) Electron Beam Accelerator JOB 307 (Dynamitron®) energy 1.5 MeV, beam current 65mA, scan 60 to 120 cm , beam power 97.5 kW

b) Electron Beam Accelerator JOB 188 (Dynamitron®) energy 1.5 MeV, beam current 25mA scan 60 to 120 cm, beam power 37.5 kW.

FIG. 7 – Electron Beam Accelerators, IPEN - Brazil

3.3 Radiation processing conditions

In this first part of the research, samples were irradiated with gamma rays at different absorbed doses (5kGy, 10kGy, 15kGy, 25kGy and 50kGy) using 5-6 $kGy.h^{-1}$. Samples were sealed using vacuum to avoid oxidation. Dosimetry was performed using PMMA Harwell System. The cloth/textile masks were irradiated only with 10 kGy.

3.4 Filtration efficiency and mechanical tests

The filtration efficiency was measured as the aerosol filtration retention capacity was measured at Atmospheric Physics Laboratory of the University of Sao Paulo - USP, according to the methodology, before and after the fabric has been folded and kneaded manually. An aerosol generator releases particles of 20 and 800 nm that are captured by an air flow produced by a pump with a flow rate of $1L.min^{-1}$ in a support with 42 mm internal diameter. The flow is transported to a SMPS (Scanning

Mobility Particle Sizer), coupled to a CPC (Condensation Particle Counter) nanoparticle counter. For each sample, (a) counting of the amount of particles generated is performed (b) 3 tests of counting of particles that pass through the filter material, and (c) counting of particles generated, each counting lasts 1 minute calculated as average (b * ((a + c) * 0.5) -1).

The Technological Research Institute - IPT performed the mechanical test as breathability (differential pressure), air permeability and bursting strength at the Textile Laboratory.

3.5 Field-emission Gun Scanning Electron Microscopy (FEGSEM) and Energy Dispersive Spectroscopy (EDS)

Scanning electron microscopy was used to analyze and characterize the non-irradiated (0 kGy) and the effective disinfected samples. Surface topography and elemental analysis of the films were analyzed by scanning electron microscopy (FEGSEM), using a Jeol JSM-6701F electron microscope with a field emission gun operating at 1 kV and 6 kV with a coupled Thermo EDS detector. A piece of each sample was cut and fixed with a double-sided conducting carbon tape. The images were taken with the “raw” samples at an accelerating voltage of 1 kV, but for EDS analysis, the samples were previously coated with carbon to avoid damage using 6 kV of accelerating voltage. For semi-quantification of elements, it was chosen a general scan for the elements distributions of the samples and a single point individual analyses, which means selecting many points to reach the composition of a selected region of the micrographs. The results will be presented in due course.

3.6 Nanostructured cross-linked polymeric hydrogels obtained by ionizing radiation (Ag-Np)

Samples are already been irradiated after polymer impregnation (PVP) with Ag-Np; however, the results will be presented in due course.

4. RESULTS AND DISCUSSION

4.1 Surgical masks and polypropylene nonwoven fabric

Irradiated samples were analysed to perform measurements of the filtration efficiency and mechanical tests. As shown in FIG. 8 and TABLE 3, TABLE 3 and TABLE 4, the nonwoven samples analysed maintain their properties after irradiation [3].

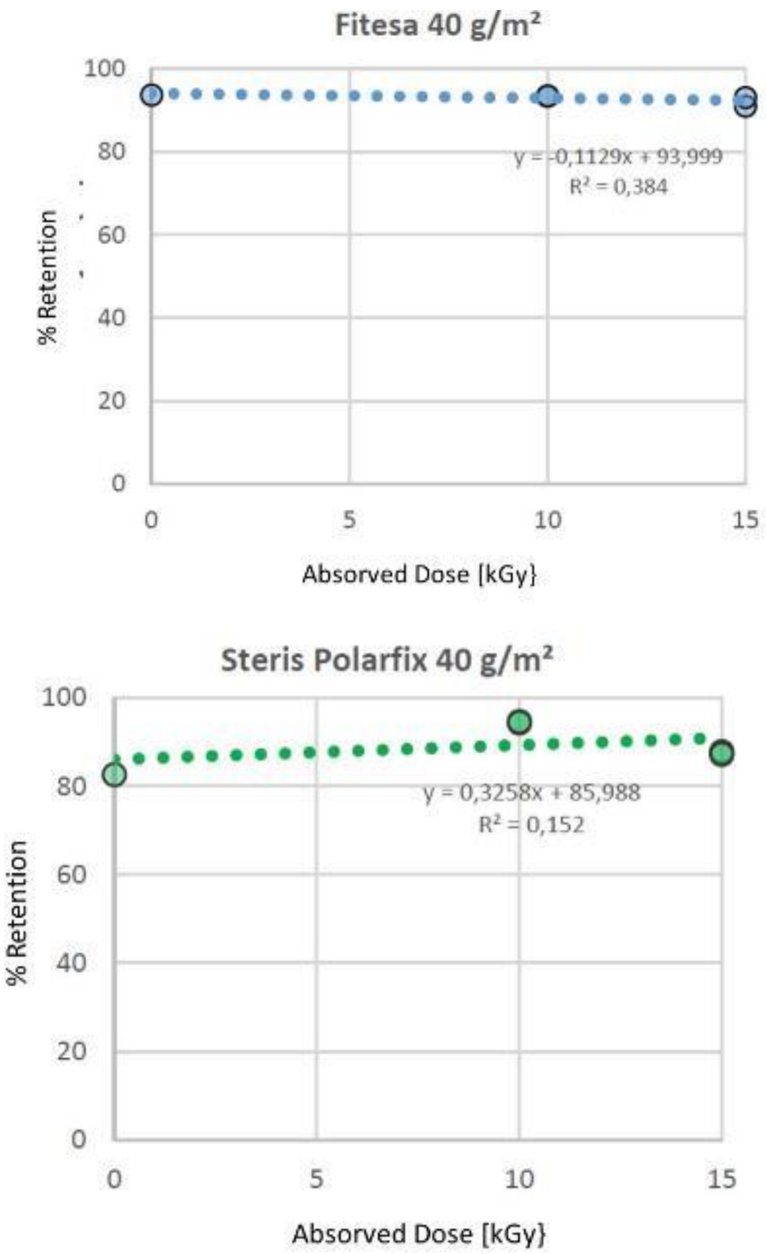


FIG. 8 – Filtration efficiency for nonwoven PP

TABLE 2 BREATHABILITY (DIFFERENTIAL PRESSURE) RESULTS – SP = SAMPLE NAME

Breathability (differential pressure) (mmH_2O/cm^2) Q=8 L/min --- Test area: 4.9 cm²			
Approved: < 4 mmH2O/cm²			
Sample	Result	Sample	Result
Fitesa 0 kGy		Polar 0 kGy	
sp1	2.94	sp1	2.91
sp2	3.31	sp2	2.82
sp3	3.12	sp3	2.89
sp4	3.39	sp4	2.98
Fitesa 10 kGy		Polar 10 kGy	
sp1	3.25	sp1	2.72
sp2	2.99	sp2	3.15
sp3	3.70	sp3	3.01
sp4	3.37	sp4	2.99
Fitesa 15 kGy		Polar 15 kGy	
sp1	3.39	sp1	3.50
sp2	3.29	sp2	2.71
sp3	3.62	sp3	2.78
sp4	3.49	sp4	3.02

TABLE 3 - AIR PERMEABILITY

Air Permeability (L/m²/s)			
Test for comparative performance evaluation - There is no limit references			
Sample	Result	Sample	Result
Fitesa 0 kGy		Polar 0 kGy	
sp1	143	sp1	145.00
sp2	131	sp2	135.00
sp3	120	sp3	140.00
Fitesa 10 kGy		Polar 10 kGy	
sp1	125.00	sp1	144.00
sp2	135.00	sp2	162.00
sp3	136.00	sp3	157.00
Fitesa 15 kGy		Polar 15 kGy	
sp1	127.00	sp1	161.00
sp2	135.00	sp2	145.00
sp3	134.00	sp3	158.00

TABLE 4 - BURSTING STRENGTH RESULTS – SP = SAMPLE NAME

Bursting strength (Bar)			
Comparative: higher results = higher strength material			
Sample	Result	Sample	Result
Fitesa 0 kGy		Polar 0 kGy	
sp1	2.33	sp1	1.81
sp2	2.52	sp2	2.12
sp3	2.18	sp3	2.15
Fitesa 10 kGy		Polar 10 kGy	
sp1	1.95	sp1	2.01
sp2	1.99	sp2	1.95
sp3	2.04	sp3	1.76
Fitesa 15 kGy		Polar 15 kGy	
sp1	2.01	sp1	1.90
sp2	1.80	sp2	1.88
sp3	1.93	sp3	1.85

4.2. Filtering facepiece respirators (FFP2) - N95

In this report, for the N95 respirators studied are presented only the filtering efficiency results. Other tests are already done. The respirators maintained the structure and the elastic band intact and the fit test was satisfactory, however the filtering efficiency was compromised as shown in **Error! Reference source not found.** and *FIG. 9* [4].

TABLE 5 - FFP2-N95 FILTRATION EFFICIENCY

Sample set name	Dose [kGy]	% retention average value
	0	89.8
sp1	5	58.2
sp2	10	48.8
sp3	15	45.3
sp4	25	43.6
sp5	50	42.5

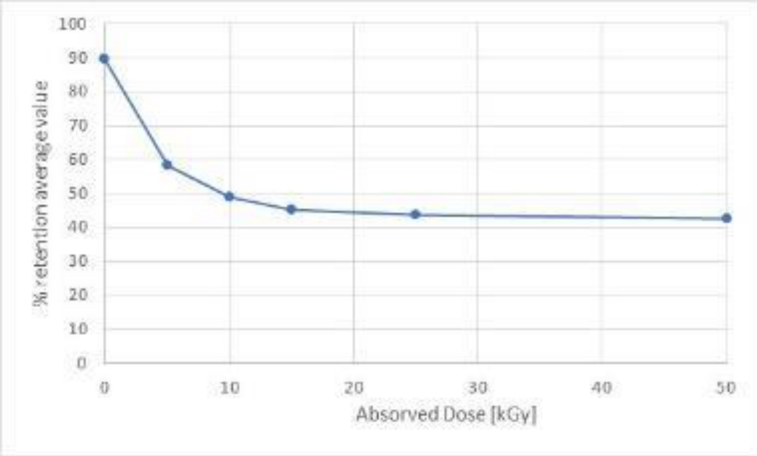


FIG. 9 – Filtration efficiency for FFP2-N95 respirators

4.3 Cloth/textile masks

Cloth /textile masks remained structurally intact, the elastic band continued functional, fit test was satisfactory and no presented smell after irradiation. In Brazil, the free distribution of these PPE by different NGOs is making a big difference to mitigate the spread of the virus as shown in FIG. 10.

FIG. 10 – Gamma radiation disinfected cloth masks distribution

5. PRELIMINARY CONCLUSIONS

According preliminary results, disinfection / sterilization using ionizing radiation can be applied safely for surgical masks (polypropylene nonwoven) and for cloth / textile masks with no morphologic modifications on fibres with filtration efficiency preserved. However, FFP2 (N95) respirators cannot be sterilized directly using ionizing radiation because the filtration efficiency is compromised even when the morphological properties are preserved. Apparently, the filtration process of small particles is governed by an electrostatic process, rather than mechanical processes, then ionizing radiation discharges the respirators filter [4].
Likewise, it is important to encourage the study of mixed sterilization techniques and the possibility of incorporating polymers and nanoparticles into the filtering system where ionizing radiation could in addition to improve properties, incorporate biocidal nanoparticles[1][7].

ACKNOWLEDGMENTS

The authors would like to thank the support provided by the IAEA.

REFERENCES

[1] ROBERT J. FISCHER. R.F., MORRIS. D.H., VAN DOREMALEN, N. Assessment of N95 respirator decontamination and re-use for SARS-CoV-2. medRxiv preprint doi: https://doi.org/10.1101/2020.04.11.20062018.this version posted April 15, 2020.
[2] FELDMANN. F., SHUPERT W.L., HADDOCK. E., Gamma irradiation is an effective method for inactivation of emerging viral pathogens Am. J. Trop. Med. Hyg., 100(5), 2019, pp. 1275–1277 doi:10.4269/ajtmh.18-093
[3] KEENE. B., BOURHAM. M., VISWANATH. V. Characterization of Degradation of Polypropylene Nonwovens Irradiated by gamma-Ray. J. APPL. POLYM. SCI. 2014, DOI: 10.1002/APP.39917
[4] CRAMER A., TIAN E., YU S., SHORT, M. Disposable N95 Masks Pass Qualitative Fit-Test But Have Decreased Filtration Efficiency After Cobalt-60 Gamma Irradiation. medRxiv preprint doi: https://doi.org/10.1101/2020.03.28.20043471
[5] IAEA, International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources, IAEA SAFETY STANDARDS for protecting people and the environment, Draft 3.0 January 2010.
[6] IAEA SAFETY STANDARDS SERIES No. SSG-8, RADIATION SAFETY OF GAMMA, ELECTRON AND X RAY IRRADIATION FACILITIES, INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA, 2010
[7] J. J LOWE, K. D PALADINO, J. D FARKE, K. BOULTER, K. CAWCUTT, M. EMODI, S. GIBBS, R. HANKINS, L. HINKLE, T. MICHEELS, S. SCHWEDHELM, A. VASA, M. WADMAN, S. WATSON, AND M. E RUPP, N95 Filtering Facepiece Respirator Ultraviolet Germicidal Irradiation (UVGI) Process for Decontamination and Reuse, Nebraska Medicine (2020).

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

L. CORTELLA, C. ALBINO, K. FROMENT
ARC-Nucléart, CEA, Grenoble, France

P. CINQUIN, J.-P. ALCARAZ
Université Grenoble Alpes, CNRS, TIMC-IMAG, Grenoble, France

L. HEUX, C. LANCELON-PIN
CNRS, UPR 530, CERMAV, Grenoble, France

M. FERRY, S. ESNOUF
Université Paris Saclay, CEA, DES-SECR, Gif-sur-Yvette, France

S. ROUIF
IONISOS, Dagneux, France

F.-X. OUF, S. BOURROUS, V.M. MOCHO
Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SCA, Gif-Sur-Yvette, France

L. LE COQ, A. JOUBERT, Y. ANDRES
IMT Atlantique, GEPEA, CNRS UMR 6144, Nantes, France

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'Energie Atomique et aux Energies 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-Nucleart 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.

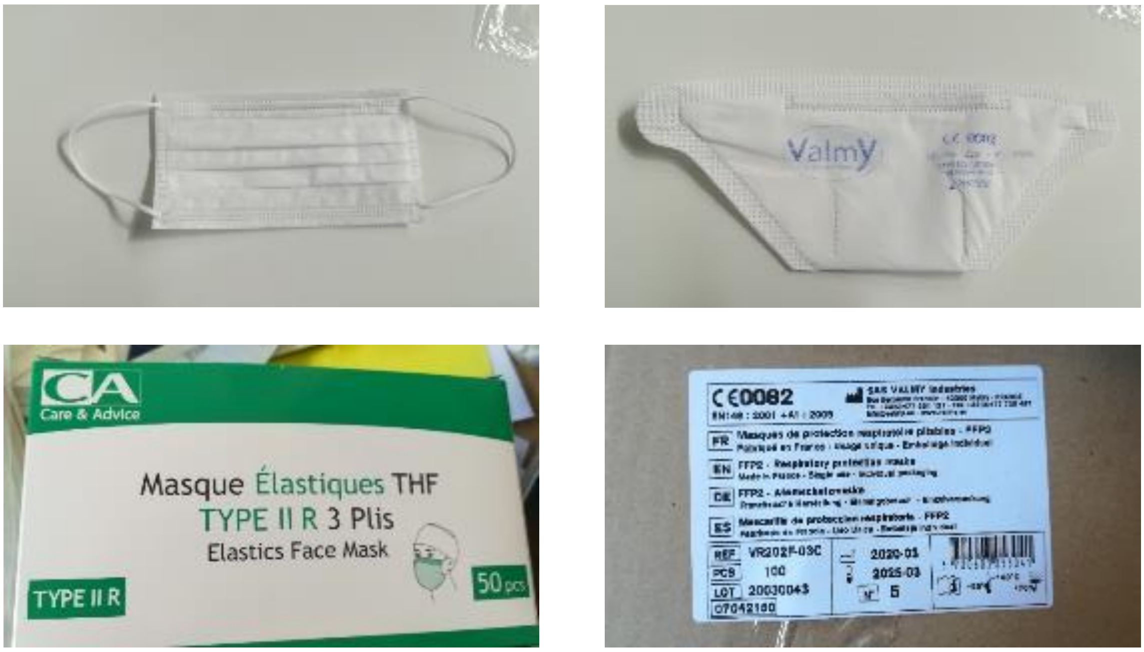
FFP2 masks must meet the European standard EN 149, a Personal protective equipment (PPE) qualification. They must be able to filter more than 94% of submicronic particles in the range of hundred nanometers with side leaks less than 8%. They are very near N95 American standard masks. The tested masks 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 O_3 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 ^{60}Co 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 kGy.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 µm mean size (aerosol size ranges from 0.65 to 7 µm). 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 µm to 5 µm (instead of a bacterial aerosol). This set-up allows determining the particulate filtration efficiency at 3 µm.

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 express 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 µm in number and around 0.600 µm 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 radiosensibility 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
L??	Surgical	Worm	CHUGA laundry washed	Gamma irradiation	25 kGy	Vacuum sealed
L??	FFP2	Worn	none	Gamma irradiation	25 kGy	Vacuum sealed
L??	FFP2	Worn	none	Gamma irradiation	50 kGy	Vacuum sealed
L??	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 chirurgical 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
L??	FFP2	Worn	none	Gamma irradiation	48 kGy	Vacuum sealed
L??	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	Conditionning
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 ± 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 ± 10%	53.1 kGy ± 20% *	1.8 $kGy.h^{-1}$
L02	25 kGy	27.7 kGy ± 10%	29.8 kGy ± 10%	1.1 $kGy.h^{-1}$
L06 to L09	50 kGy	48.6 kGy ± 10%	60.3 kGy ± 20% *	2.2 $kGy.h^{-1}$
L10-6 and L10-7	25 kGy	29.5 kGy ± 10%	32.3 kGy ± 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 (± 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 ⇨ 1 kGy -0%/+20%
- L46 – L47 – L60 – L62 – L77 ⇨ 2 kGy -0%/+20%
- L66 ⇨ 5 kGy -0%/+20%
- L67 ⇨ 10 kGy -0%/+20%
- L44 – L48 – L49 – L72 – L73 – L78 – L213 ⇨ 20 kGy -0%/+20%
- L214 ⇨ 40 kGy -0%/+20%
- L63 ⇨ 50 kGy -0%/+20%
- L215 ⇨ 60 kGy -0%/+20%
- L64 ⇨ 100 kGy -0%/+20%

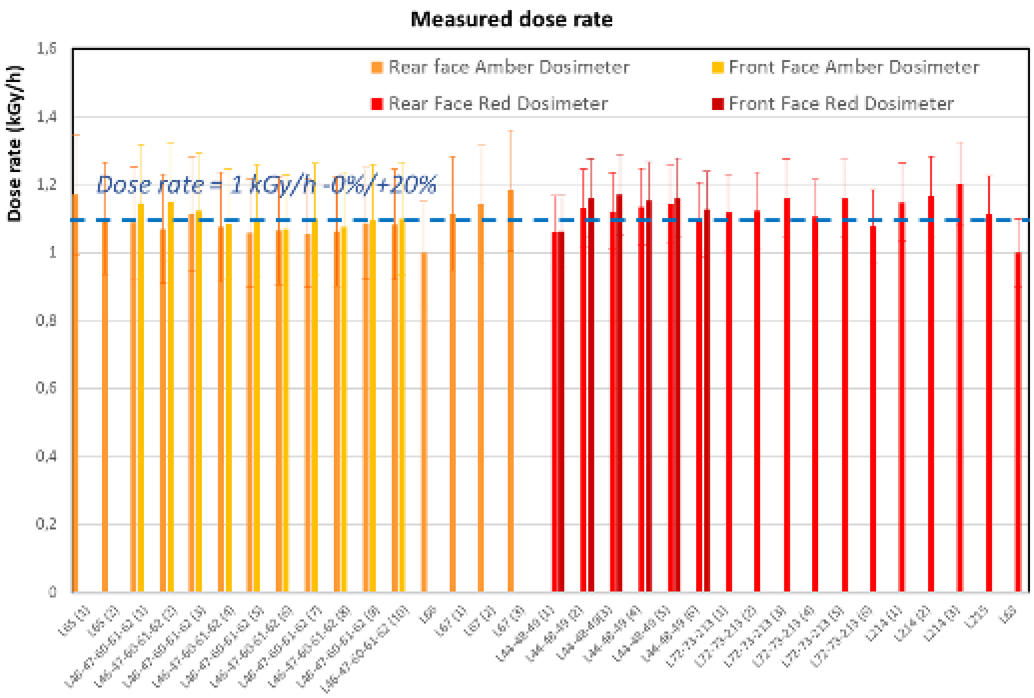


FIG. 4.1. Control measurement of the dose rate. Average dose rate, 1.1 $kGy.h^{-1}$, gave reference value of 1.0 $kGy.h^{-1}$ -0%/+20% taking into account the uncertainty.

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 wass 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

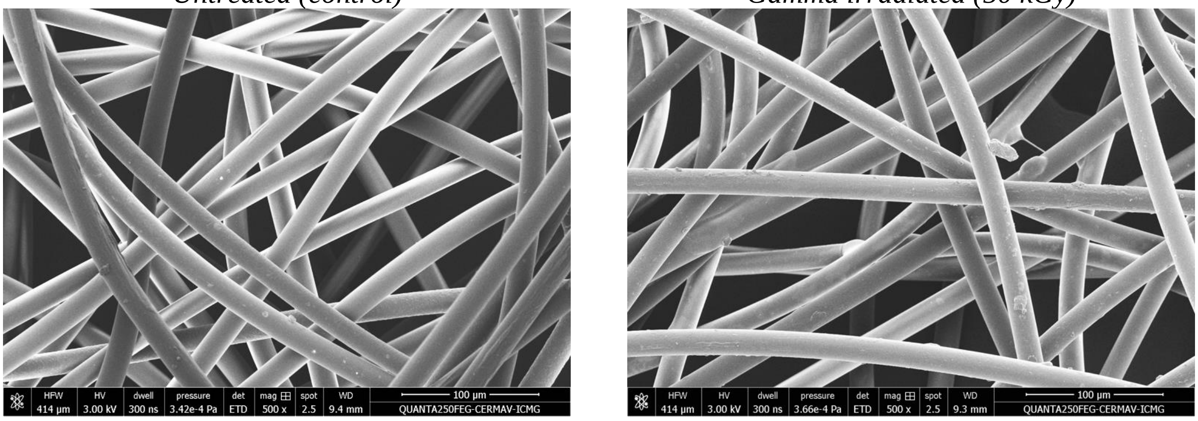
Batch	Dose target	Controlled Dose	Dosimetric method	Dosimetric uncertainty
L302	10 kGy	10,4 kGy	calorimeter	4,6%
L303	20 kGy	20,2 kGy	calorimeter	4,6%
L304	10 kGy	10,4 kGy	calorimeter	4,6%
L305	20 kGy	20,2 kGy	calorimeter	4,6%
L306	40 kGy	40,4 kGy	calorimeter	4,6%
L307	60 kGy	59,1 kGy	calorimeter	4,6%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

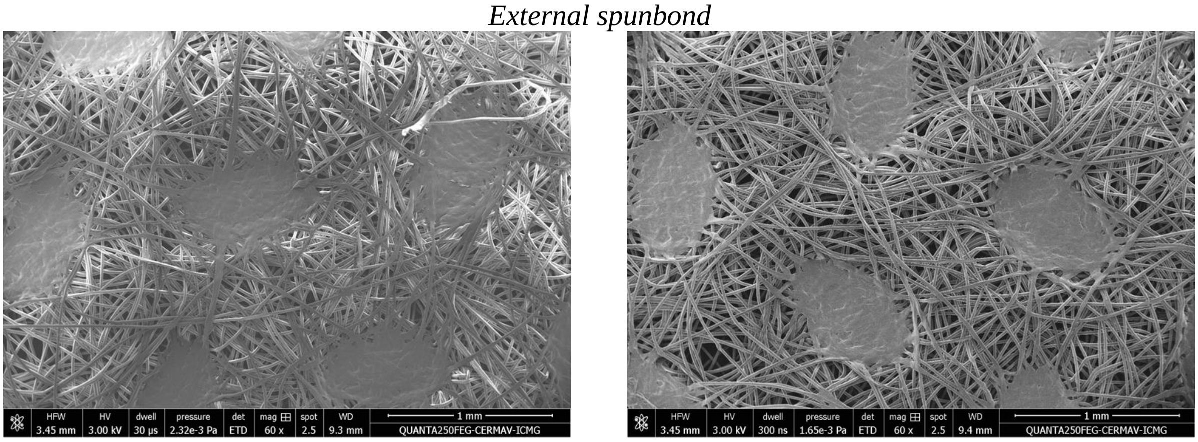
4.2.1. Surgical masks

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.

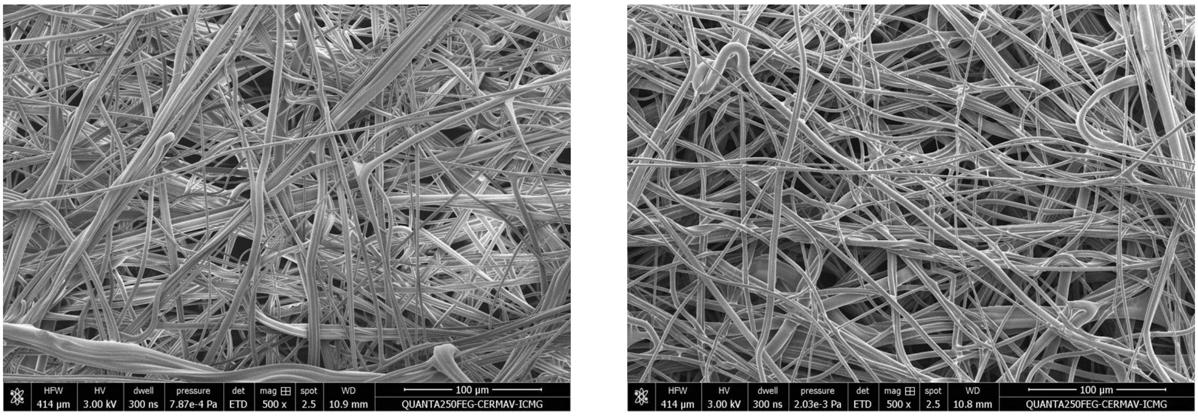
Untreated (control) *Gamma irradiated (50 kGy)*



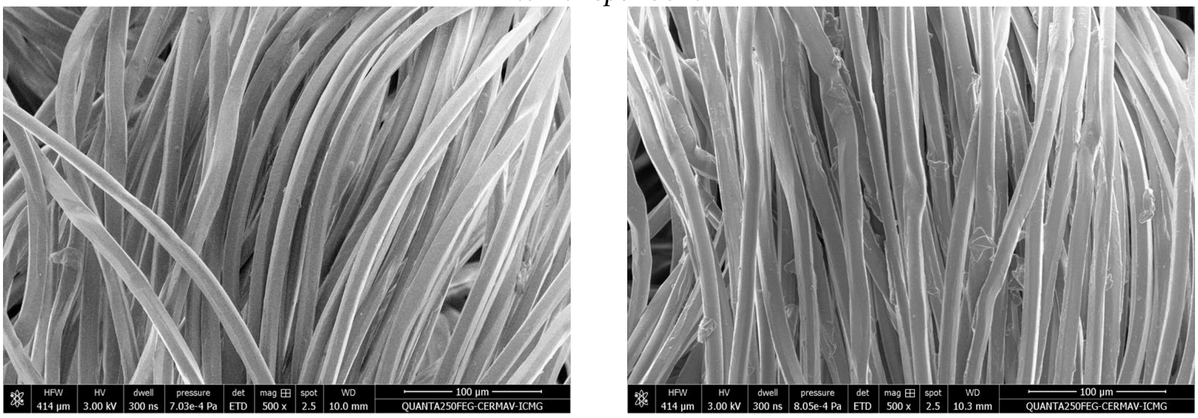
External spunbond



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].

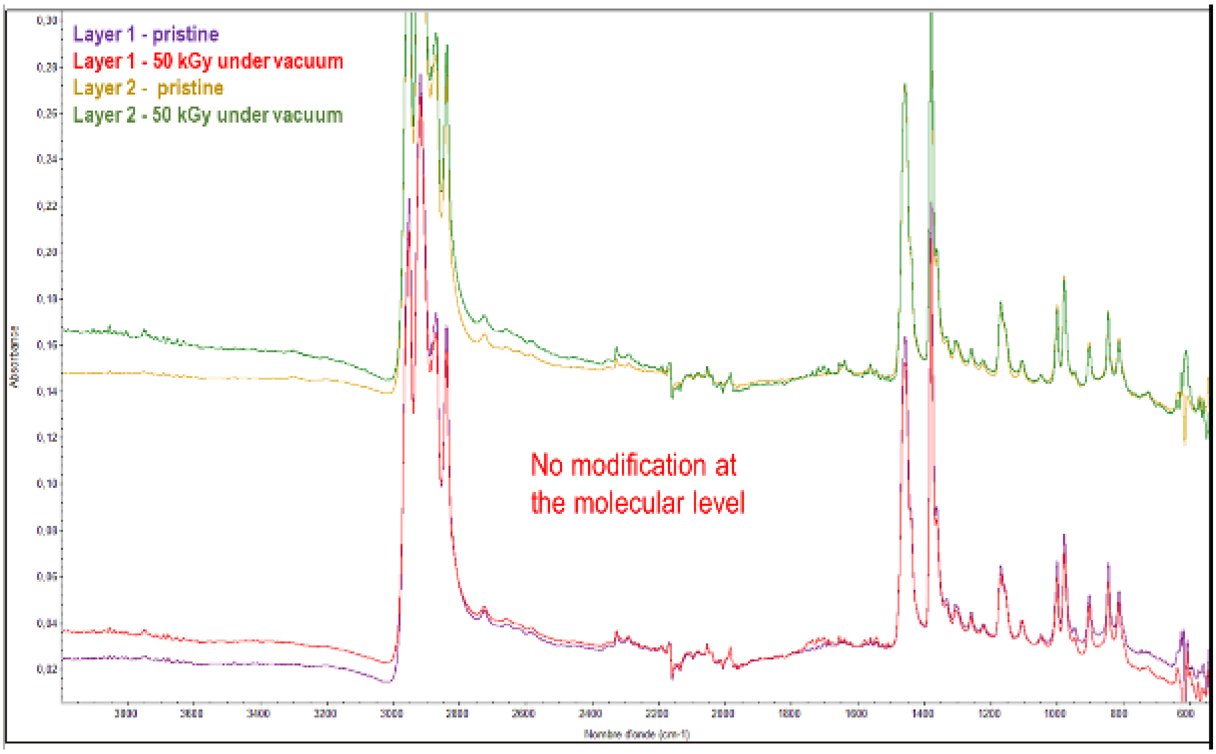


FIG. 4.3. FTIR-ATR spectra of the internal and of the meltblown layer before and after irradiation. Pictures from [5].

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.

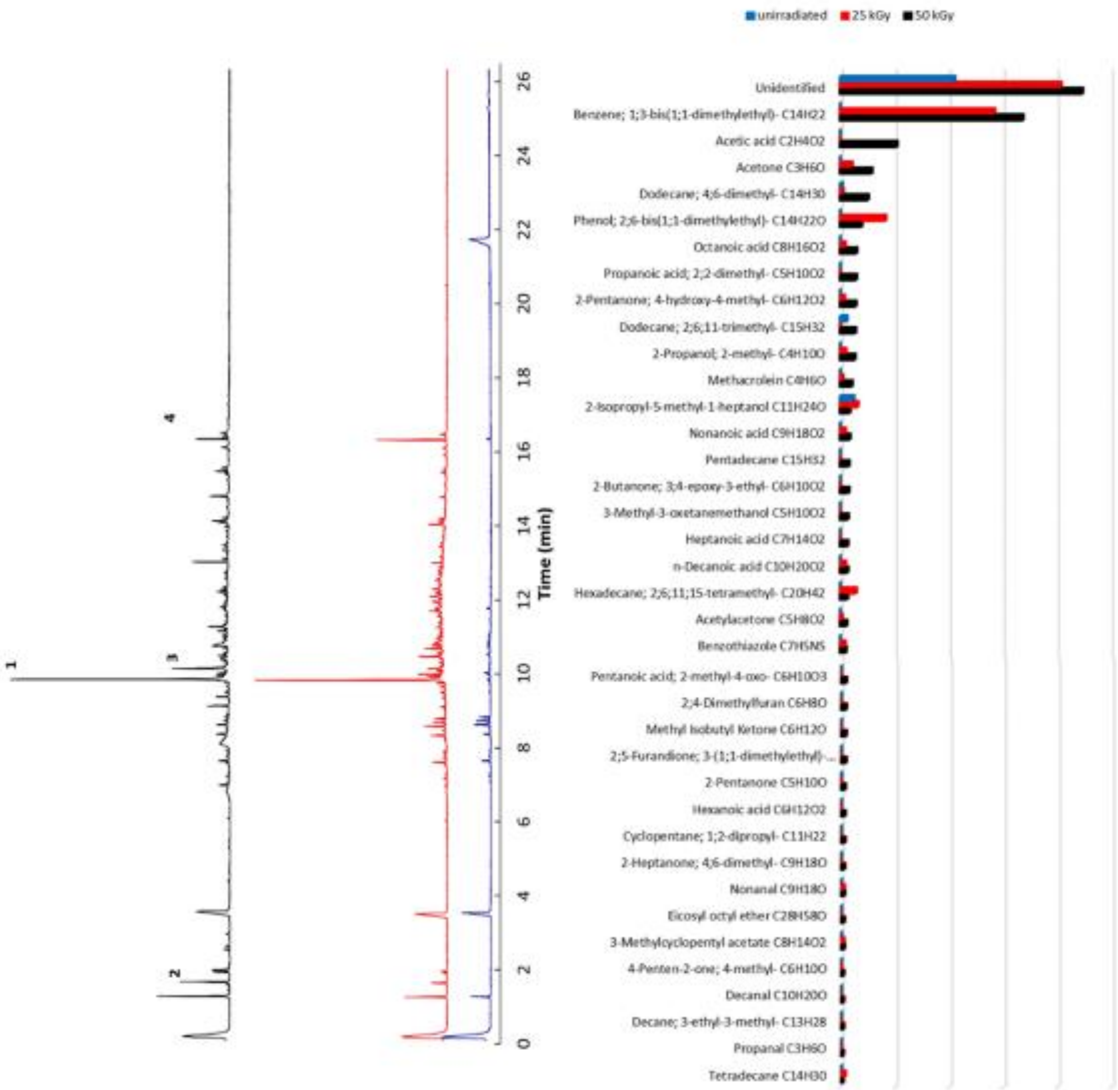


FIG. 4.4. Chromatogram of the surgery external face (peaks numbered: 1⇨ 1,3-bis(1,1-dimethylethyl)-benzene; 2⇨ acetone; 3⇨ acetic acid; 4⇨ 2,6-bis(1,1-dimethylethyl)-phenol) and diagram of identified molecules sorted by peak area (peak areas of all the unidentified products have been summed). Pictures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

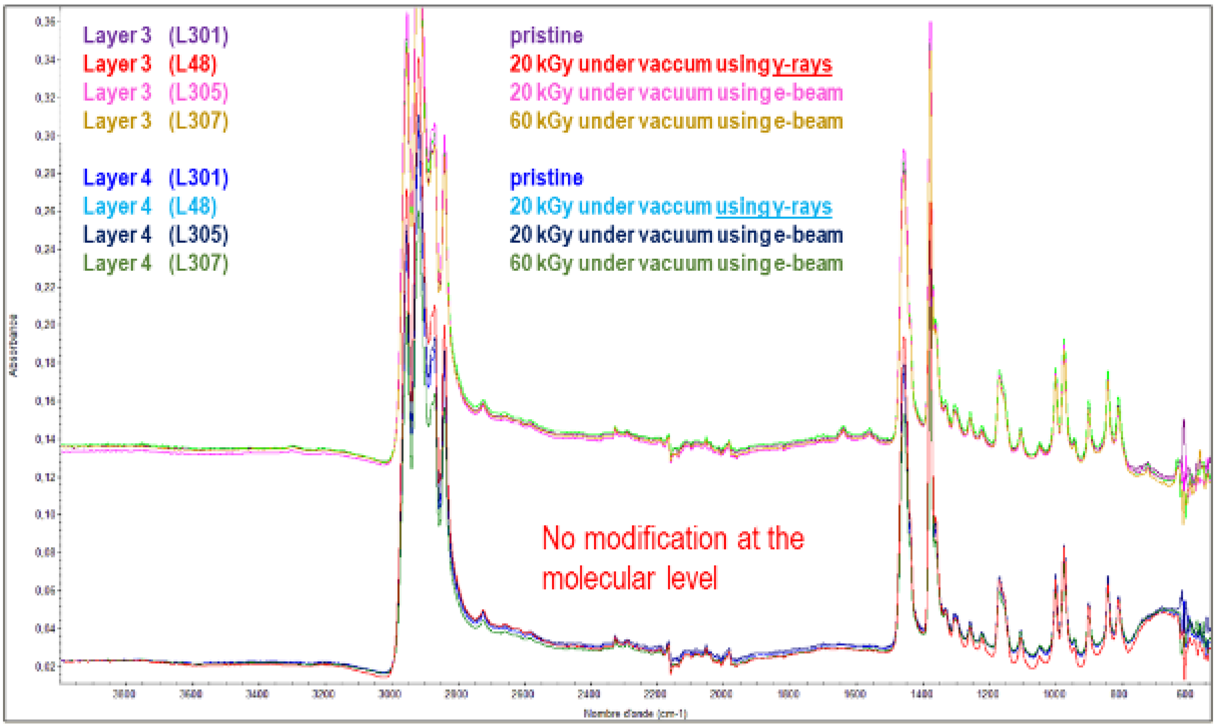


FIG. 4.5. FTIR spectra of meltblown (layer 3) and spunbond (layer 4) when irradiated under vacuum. Pictures from [6].

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.

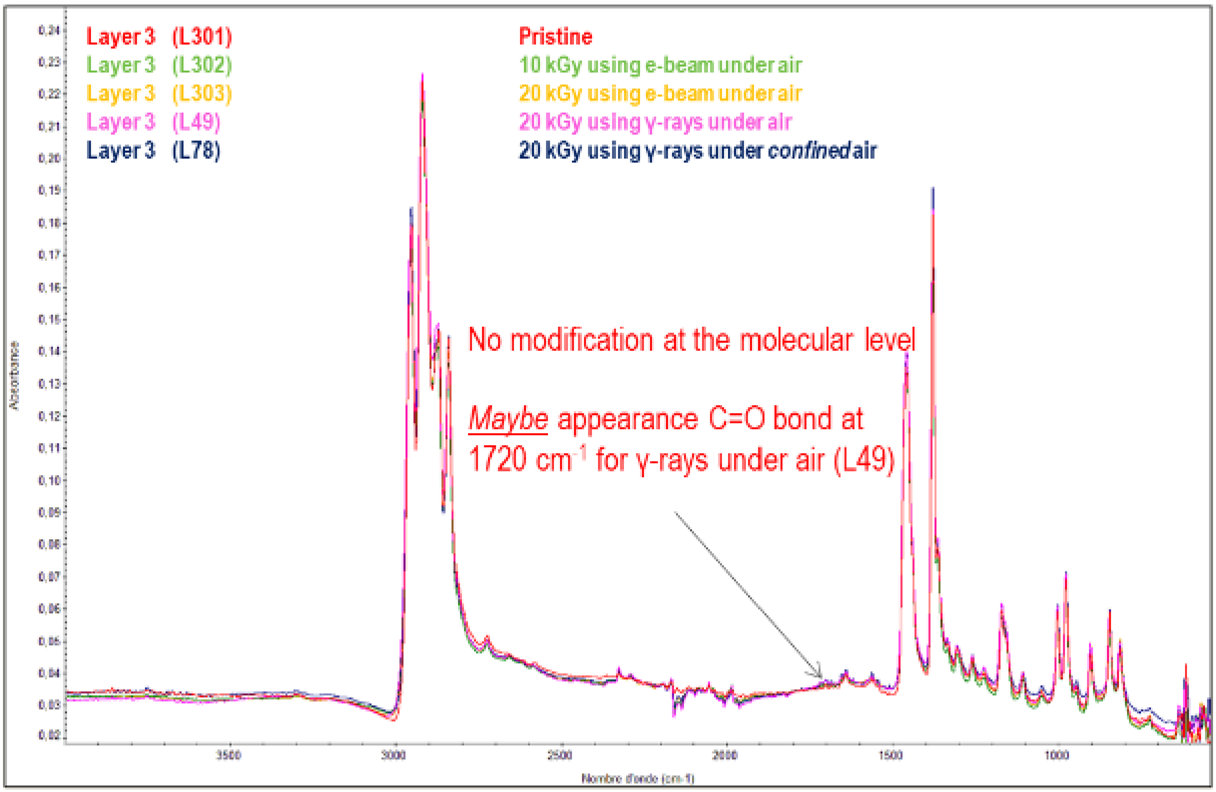


FIG. FIG. 4.6. FTIR spectra of meltblown (layer 3) when irradiated in air. Pictures from [6].

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.

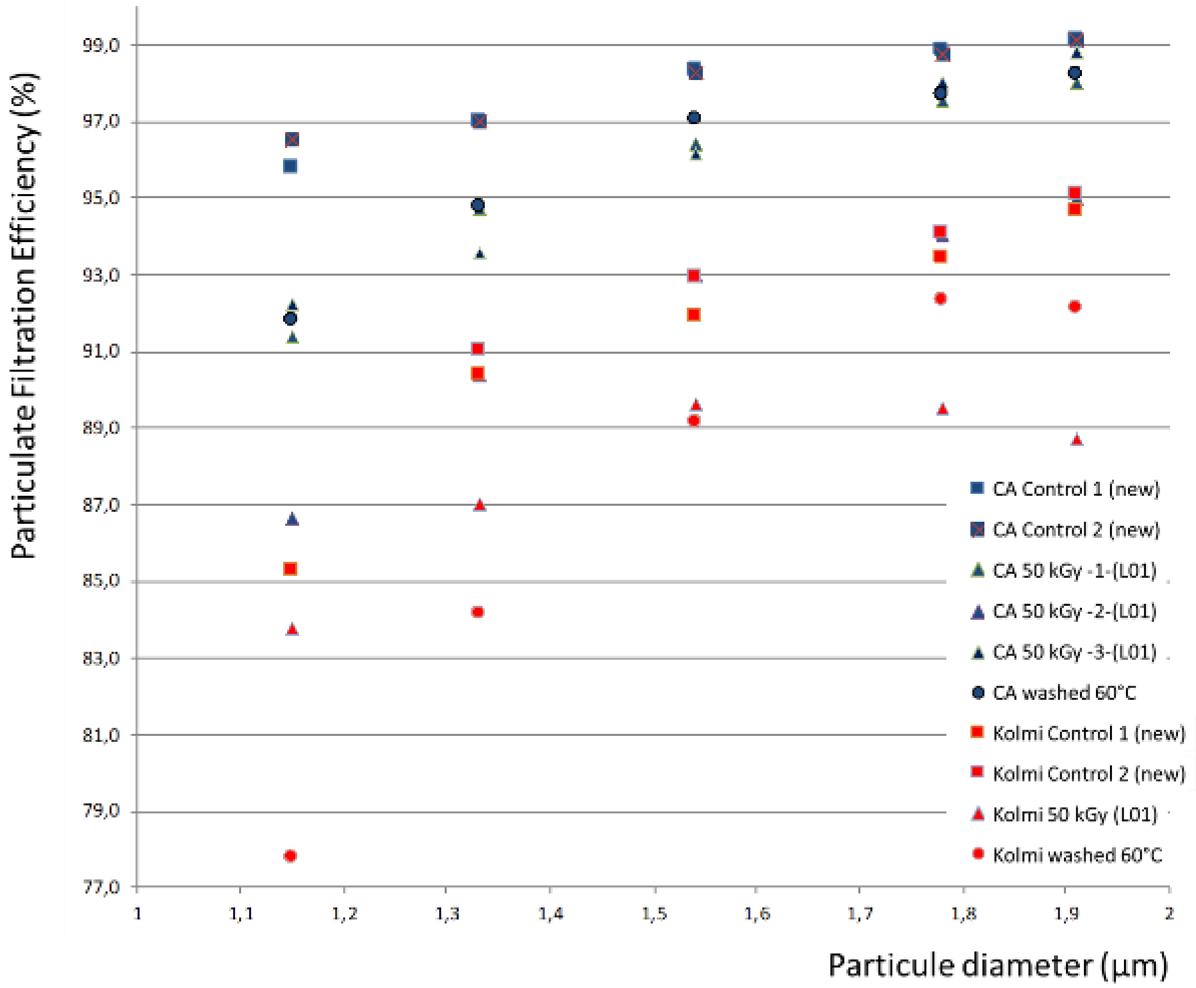


FIG. 4.7. Particulate Filtration Efficiency of worn and 50 kGy irradiated surgical masks measured on the bench of IMT Nantes.

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
L??	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
L??	Gamma	50 kGy	≥ 50%	-	Worn and irradiated
L??	Gamma	25 kGy	≥ 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.

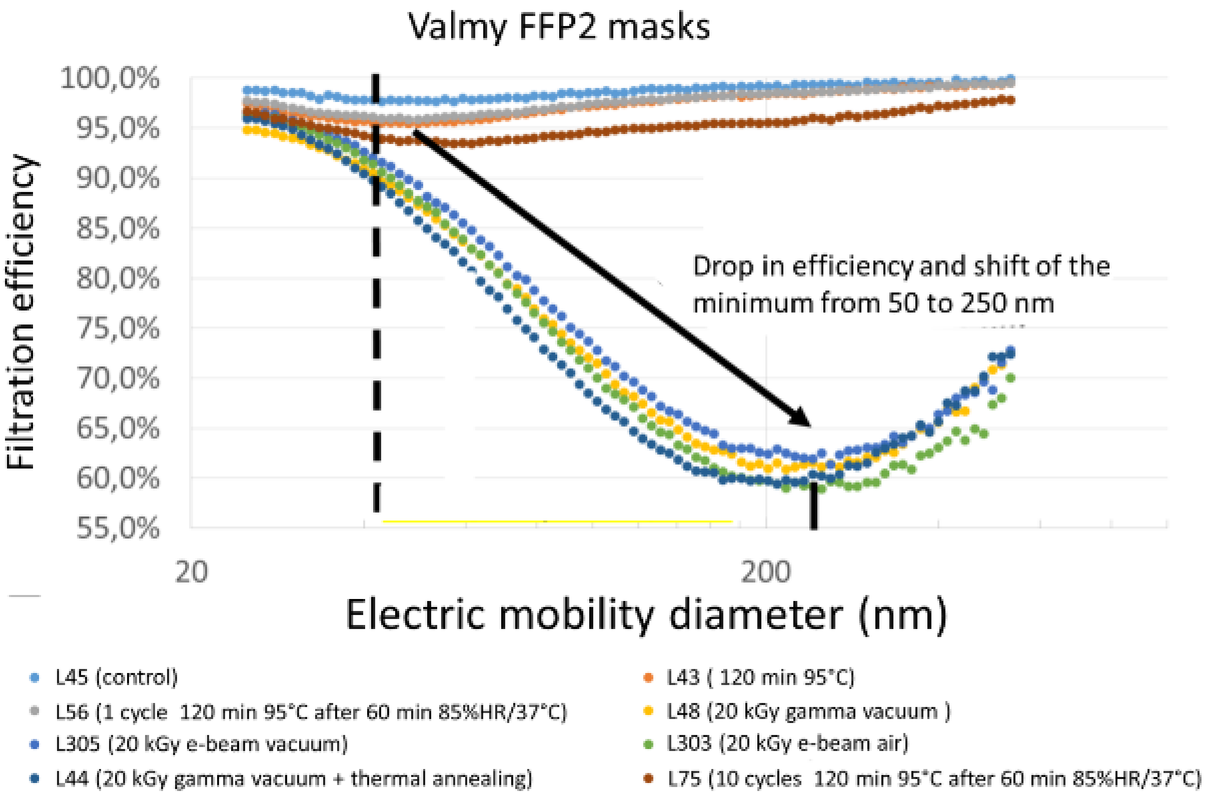


FIG. 4.8. Spectral Particulate Filtration Efficiency of different batches of FFP2. Picture adapted from [8]

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.

REFERENCES

[1] L. CORTELLA, Irradiation of batches of medical masks to assess the feasibility of a treatment for reuse after a first use. Informative progress report. ARC-Nucleart, CEA Grenoble, March 24, 2020, Update on March 30, 2020.
[2] G. DROBNY, in Ionizing Radiation and Polymers: Principles, Technology, and Applications, Plastic Design Library Series, Elsevier, Oxford, 2013, p 231
[3] L. HEUX, Etude de masque chirurgicaux après irradiation par RMN du solide, CERMAV, Grenoble, 2020_03_19_rapport_SSNMR.
[4] L. HEUX, Observations en microscopie électronique à balayage de masques chirurgicaux, CERMAV, Grenoble, 2020_03_19_observation_MEB.
[5] S. ESNOUF, M. FERRY, S. LE CAER, E. RICHAUD, Chemical modification of surgery masks after irradiation under vacuum using γ-rays, Report CEA-ENSAM, Saclay-Paris, March 2020.
[6] S. ESNOUF, M. FERRY, RUM (Re-Use Masks) : Chemical modification of medical masks after different sterilization protocols – Surgical mask, CEA Saclay, version 3 of 04/27/2020.
[7] S. ESNOUF, M. FERRY, RUM (Re-Use Masks): Chemical modification of medical masks after different sterilization protocols – FFP2 mask (Valmy), CEA Saclay, version 3 of 05/06/2020.
[8] CENTEXBEL, Rapport d'analyse 20.017882.00 – Preview, 04/30/2020, Grâce-Hollogne, Belgium.
[9] F.-X. OUF, M. BARRAULT, S. BOURROUS, V. MOCHO, S. POIRIER, Mesure d'efficacités de filtration de médias composant les masques FFP2 après différents traitements : avancement des travaux de l'IRSN 30/04/20, Saclay, 04/30/2020.
[10] F. FELDMANN, W.L. SHUPERT, E. HADDOCK, B. TWARDOSKI, H. FELDMANN, Gamma Irradiation as an Effective Method for Inactivation of Emerging Viral Pathogens, Am J Trop Med Hyg. 2019 May;100(5):1275-1277. doi: 10.4269/ajtmh.18-0937.
[11] M. KUMAR, S. MAZUR, B.L. ORK, E. POSTNIKOVA, L.E. HENSLEY, P.B. JAHRLING, R. JOHNSON, M.R.HOLBROOK, Inactivation and safety testing of Middle East Respiratory Syndrome Coronavirus, J Virol Methods. 2015 Oct; 223:13-8. doi: 10.1016/j.jviromet.2015.07.002. Epub 2015 Jul 17.
[12] A. CRAMER, E. TIAN, S.H. YU, M. GALANEK, E. LAMERE, J. LI, R. GUPTA, M.P. SHORT, Disposable N95 Masks Pass Qualitative Fit-Test But Have Decreased Filtration Efficiency After Cobalt-60 Gamma Irradiation, medRxiv preprint (which was not peer reviewed), https://doi.org/10.1101/2020.03.28.20043471.

THE FEASIBILITY OF STERILIZATION FOR REUSE OF DISPOSABLE MEDICAL EQUIPMENT: GAMMA IRRADIATION OF MEDICAL MASKS AND MEDICAL PROTECTIVE CLOTHING

I. GOUZMAN, H. DATZ, R. VERKER, A. BOLKER, L. EPSTEIN, L. BUCHBINDER, Y. FRIED and E. SARID
Soreq Nuclear Research Center (SNRC), Yavne, Israel

E. ZUCKERMAN
Sor-Van Radiation Ltd., Yavne, Israel

G. BOAZ
Israeli Ministry of Defence

Abstract

Soreq Nuclear Research Center (SNRC) has geared up for the national effort facing the challenges of the COVID-19 virus epidemic (the coronavirus). One of the problems was the risk of shortage of medical protective equipment, especially for medical staff. SNRC responded to the challenge by examining the feasibility of sterilization using gamma radiation in order to enable the reuse of disposable medical protective equipment.
This report describes our test results and analysis of preliminary findings. These tests refer to the possible change of properties after the irradiation. No biological tests were done for the effectiveness of the irradiation, reasonable and acceptable dose values, 6-60 kGy, were used in the tests. Due to the limited availability of the testing equipment, a small number of tests was performed. Nevertheless, the results of the irradiation of medical protective clothing with high radiation doses seem to be promising for reuse after sterilization. For all tested samples, no visual changes, no coloration, no changes on touch and pull, no changes in chemical structure and water-repellant properties were observed.
For the tested N95 and surgical masks, no visual, morphological, and chemical changes of the masks' materials were observed. However, we found that the irradiation has significantly impaired the filtration efficiency of N95\FFP2 masks, a finding that raises the question of the benefit and the feasibility of gamma irradiation sterilization for reuse of such masks.

1. Scientific Background

Sterilization using gamma radiation has been in use since the late 1950's. Gamma radiation causes DNA and RNA strand breaks and inactivate microorganisms. ISO standard 11137-1 deals with sterilization of health care products. According to the standard the required doses range between 25-40 kGy [1]. The standard also mentions that most health care products are irradiated to a dose of 25 kGy. The standard defines a Sterility Assurance Level (SAL) as the probability of a single viable microorganism occurring on an item after sterilization. Generally, a value of 10^{-6} is used for new health care products. This standard does not specify the requirements for used products.
Irradiation of health care products reduces the number of microorganisms exponentially according to their sensitivity to radiation [2]. The required dose for the inactivation of 90% of a population of the microorganism (D10) ranges between 0.3 kGy for Salmonella typhimurim and 8.4 kGy for HIV. It was found that the D10 value can reach up to 10 kGy for certain viruses [3].
According to the above mentioned D10 Values, a dose of 25 kGy will result in a reduction of 10^{-3} to a population of HIV virus, as opposed to a 10^{-24} reduction in a Salmonella typhimurim population [4]. If the COVID-19 virus has similar sensitivity as the HIV virus, we expect that a 25 kGy dose will result in a 10^{-3} reduction of the population. If we double the dose, we can reach sterility level of 10^{-6}. Viruses are less susceptible to radiation than bacteria. However, it is likely that single strand viruses such as the COVID-19 virus is more susceptible to radiation compared to the double strand viruses [5].

2. Irradiation Facility

All irradiations described in this report were performed at Sor-Van irradiation facility, which operates a Nordion's JS-6500 cobalt irradiator. Sor-Van is a private company located at Soreq NRC (SNRC) area. Sor-Van provides sterilization services to the medical field, research institutions, hospitals and the food manufacturing plants.
During the irradiation process, while the radiation proceeds through the object its intensity decreases, resulting in the decrease of dose with depth. The rate of decrease depends on the composition and density of the irradiated object. One method of describing the non-uniformity of dose is the concept of dose uniformity ratio (DUR), which is the ratio of the maximum dose in a product container to the minimum dose in the container (also called TOT). This ratio increases with the density of the product as well as with the size of the container. Before the irradiations were carried out at Sor-Van facility, DUR measurements were performed for two densities: 0.05 gr/cm^3 and 0.32 gr/cm^3.

For each DUR measurement, a full container of equipment was irradiated at the tested density. The dose was measured using 36 dedicated dosimeters (Harwell Red 4034 Perspex Dosimeter) located in the container volume. When exposed to gamma rays, the sealed dosimeters darken. After the end of the irradiation process, we remove the seals and perform a spectrophotometer readout. For each density, 3 repetitions were made for 2 doses: 31.8 kGy (0.05 gr/cm^3 test) and 17.8 kGy (0.32 gr/cm^3 test).

Figure 1 shows the dose at the different positions in the containers, normalized to the dosimeters at the middle-top-front location marked by *
TABLE 1 summarizes the results of the DUR measurements. The results obtained are similar to the values measured for similar cobalt irradiation facilities.

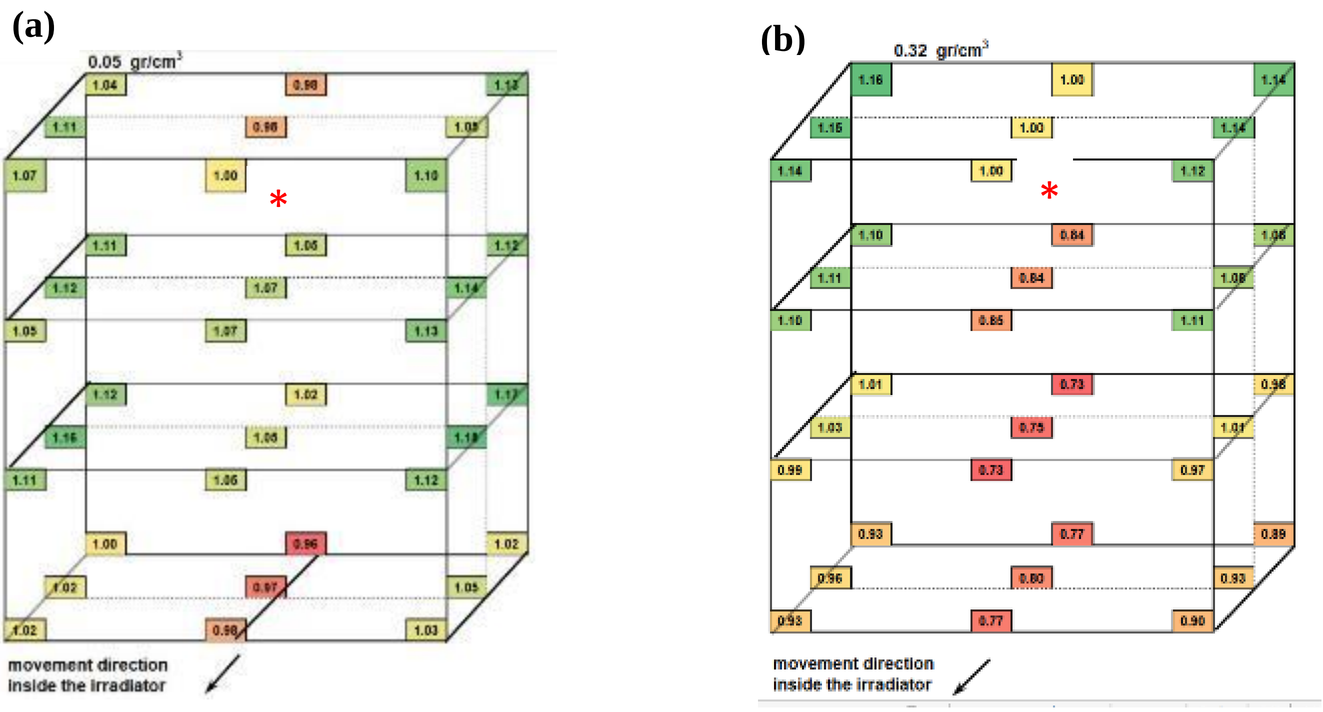


FIG. 1 Normalized dose for each dosimeter located in the container volume. Each point represents the average dose of 3 measurements and the percentage standard deviation.
(a) Target dose 31.8 kGy for 0.05 gr/cm^3 test. (b) Target dose 17.8 kGy for 0.32 gr/cm^3 test.

TABLE 1. SOR-VAN IRRADIATION FACILITY DUR MEASUREMENTS

Density gr/cm^3	Target Dose kGy	Normalized Target dose	Normalized Minimum Dose	Normalized Maximum Dose	DUR Max./Min. Dose
0.05	31.8	1	0.96	1.18	1.23
0.32	17.8	1	0.73	1.16	1.60

3. Analytical techniques

All irradiated samples were visually studied before and after irradiation. Some materials were analyzed before and after irradiation using scanning electron microscopy (SEM) using SIGMA 300 VP HR SEM from Zeiss. The materials were studied in the variable pressure mode, which allows working with non-conductive samples without any coating.

The mechanical properties of mask materials and medical protective clothing were measured under tension, before and after they were gamma-irradiated, using a universal testing machine (Instron model 3365), equipped with pneumatic grips. The tests were performed at a rate of 20 mm/min using a 100 N load cell. The thickness of the samples was measured using a Mitutoyo Absolute indicator.

Chemical structure of the mask materials was studied using FTIR. FTIR measurements were carried out using a NICOLET iS10 FTIR, in iD5 ATR-Diamond mode.

Water repellent properties of the medical protective clothing were assessed by measuring water contact angle before and after irradiation. The measurements were carried out using 200-FI Rame-Hart Goniometer with DropImage software.

Face-seal leakage test before and after irradiation was performed using TSI PortaCount® Pro+ Respirator Fit Tester 8038. Filtration tests for various mask samples are described below.

4. Results

4.1 Medical Masks

4.1.1 List of studied masks

For initial evaluation of the effect of gamma irradiation on medical masks various samples were used, as listed in TABLE 2. As shown in TABLE 2, Samples A to K were exposed to different irradiation doses according to ISO 11137 recommendation for sterilization dose of 25-30 kGy and for double doses of 50-60 kGy [1].

TABLE 2. LIST OF TESTED MASKS.

SNRC Sample Name	Mask Type	Appearance	Irradiation dose
A	3M 8710E Unvalved Cup-Shaped (FFP1)		0 (Ref) 30 kGy
B	M3 KIMBERLY CLARK 62465		0 (Ref) 30 kGy 61 kGy
C	3M aura 9332+ (FFP3)		0 (Ref) 30 kGy 61 kGy
D	Cotton Respiratory Venus V-430 SLV (FFP3 NR)		0 (Ref) 30 kGy
E	HP3 1102 (FFP2 NR D)		0 (Ref) 25 kGy 50 kGy
F	3M 9501+ KN95 Mask Particulate Respirator		0 (Ref) 32 kGy 60 kGy
G	Makrite Niosh N95 Cone Mask 9500		0 (Ref) 32 kGy 60 kGy (both in air and in sealed vacuum bag)
K	BI WEI KANG KN95 - 9600 Folding Dust Respirator		0 (Ref) 32 kGy 60 kGy

4.1.2 Masks visual inspection after irradiation

Sample A:

(I) 30 kGy: No visual changes on the main structure of the mask were observed. However, the soft over-the-nose stripe inside the mask was detached (see Fig. 2).

Non-irradiated Irradiated

FIG. 2. Mask A before and after irradiation.

Sample B:

(I) 30 kGy: No visual changes after irradiation, however slight smell has appeared.
(II) 61 kGy: Higher dose resulted in rupture of the ear loop.

Sample C:

(I) 30 kGy: Slight coloration and smell.
(II) 61 kGy: Slight coloration and smell. The edges of the mask and the inner fabric seemed to become more fragile compared to the non-irradiated sample.

FIG. 3. Mask C before and after irradiation.

Note, that the coloration observed for the higher irradiation dose was less pronounced compared to that obtained after the lower dose. This effect is not clear at the current stage of the study.

Sample E:

(I) 25 kGy: Very slight coloration, less pronounced than in sample C. The same smell, as in sample C.
(II) 50 kGy: Very slight coloration, less pronounced than in sample C. The same smell, as in sample C. The edges of the mask seemed more fragile compared to the non-irradiated sample and could be easily deformed.

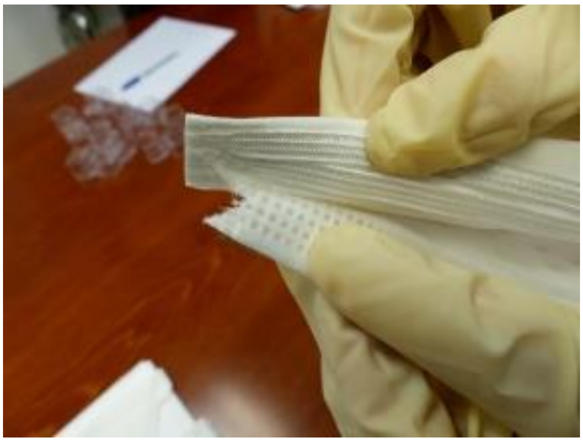


FIG. 4. Mask E after irradiation (50 kGy).

Sample G

No visual changes were observed after low and high irradiation doses. However, the same smell, as in samples C and E, was sensed.
Regarding polypropylene (PP), it is known that the radiation degradation can be attributed mainly to the oxidation of polymer. It was suggested that if the irradiation would be carried out when the masks are sealed in a vacuum bag, the appearance of smell may be reduced. In order to check this hypothesis, different samples of masks G were irradiated concurrently under an ambient air environment and in a sealed vacuum bag. The available household vacuum sealer (see Fig. 5) reduces the pressure and seals the package automatically. The residual pressure in the sealed bag estimated to be about 50 - 200 mbar. Unfortunately, a similar smell was detected after irradiation of masks under ambient air and in a sealed vacuum bag. Perhaps, higher vacuum is required to prevent the oxidation of masks materials under irradiation. The other possibility is that the trapped radical originated from additives and/or impurities in the processed PP are responsible for the observed oxidation and resulting smell.

FIG. 5. Household vacuum sealer (left). Sealed vacuum bag mask sample G after irradiation (right).

4.1.3 Morphological changes (SEM analysis)

Internal layers of the samples C and E were analysed before and after irradiation using HR SEM. Fig. 6 shows SEM images of Mask C morphology before and after irradiation.

No changes in fibres morphology or micro-cracks of the inner filter were observed for both Masks, C and E, after 30 kGy and 61 kGy irradiation.

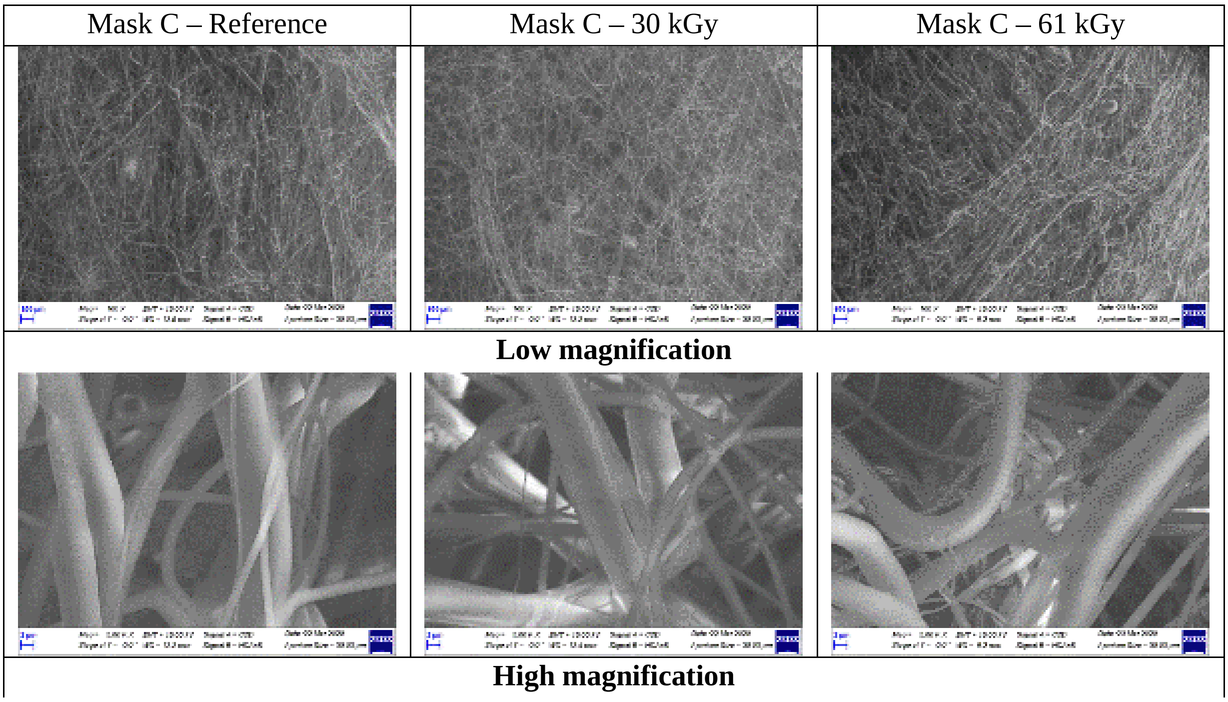


FIG. 6. SEM images of the inner layer of the Mask C before and after irradiation.

4.1.4 Chemical structure: FTIR measurements

Chemical structure of the mask materials was examined for masks B, C, E and G and for Flat Sheet N95 Filter Media (Hepworth air filtration). FTIR measurements indicate that at least one of the layers in all masks is made of Polypropylene (PP). Typical spectrum of the filter material is shown in Fig. 7. All the observed dominant bands are the characteristic vibration bands of the isotactic PP [7-9]. The FTIR spectrum also presents a shoulder at 2875 cm^{-1}, the asymmetric and symmetric in-plane C–H (– CH_3) vibrations at 1455 and a shoulder at 1356 cm^{-1} which are typical for PP. The peak at 1375 cm^{-1} is assigned to –CH_3 group. The presence of the same main bands in the irradiated PP indicates that the isotactic nature of PP is not destroyed by a gamma irradiation, even at a high dose of about 60 kGy [10].
Mask G was made of three layers, internal and external fabric layers, and the internal filter layer. The FTIR spectrum of the internal filter was identical to PP, while the internal and external fabric layers were characterized by a different FTIR spectrum, as shown in Fig. 8. This spectrum is characteristic of Polyester [11]. The main vibration band at 1713 cm^{-1} (-C=O), at 1095 cm^{-1} and 1242 cm^{-1} (C-O-C) confirm the presence of ester group. No changes in the main bands of Polyester fabric after high irradiation dose were obtained.

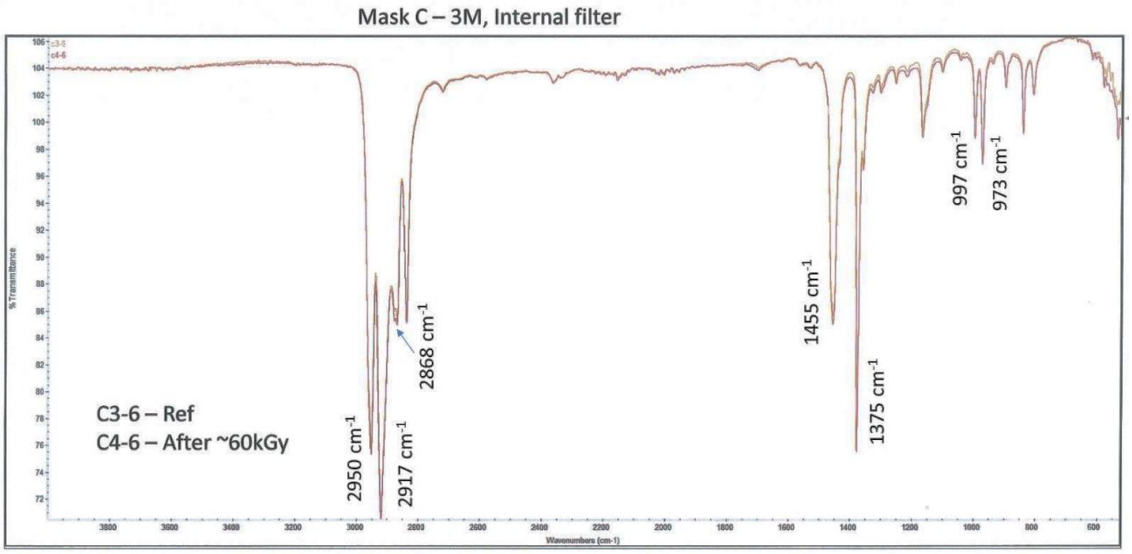


FIG. 7. FTIR measurements of the internal filter of Mask C before and after irradiation. The spectrum is characteristic for PP. Similar spectra were obtained for all layers of Mask E, internal filter of Mask G, and for the Flat Sheet N95 Filter Media.

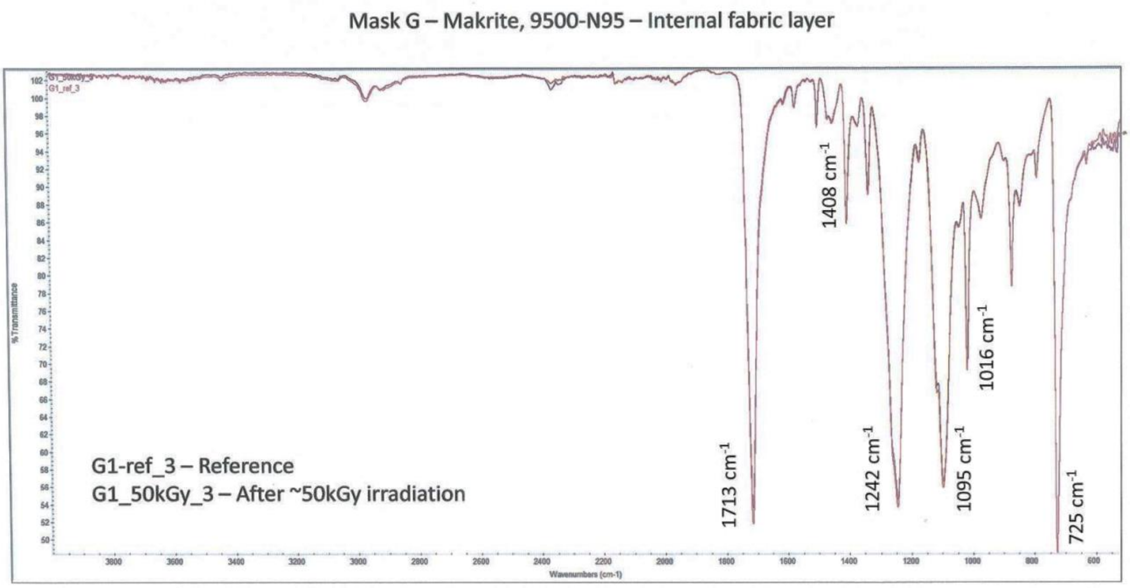


FIG. 8. FTIR measurements of the internal fabric of Mask G before and after irradiation.

Mask B also consists of three layers. The FTIR spectrum of the internal fabric layer is identical to that of PP, while the external layer and a thin filter show different FTIR spectra. The spectrum of the internal fabric is attributed to polyethylene (PE) (see Fig. 9), while the spectrum of the thin inner filter may be attributed to a blend of PE and Polyester (see Fig. 10). The main stretching vibrations for PE appear at 2915 and 2848 cm^{-1}. The main bending mode of the $–CH_2$ group is around 1470 cm^{-1} [12]. Note, that the FTIR spectra of non-irradiated and irradiated samples are similar, as in the cases of Mask C and G.

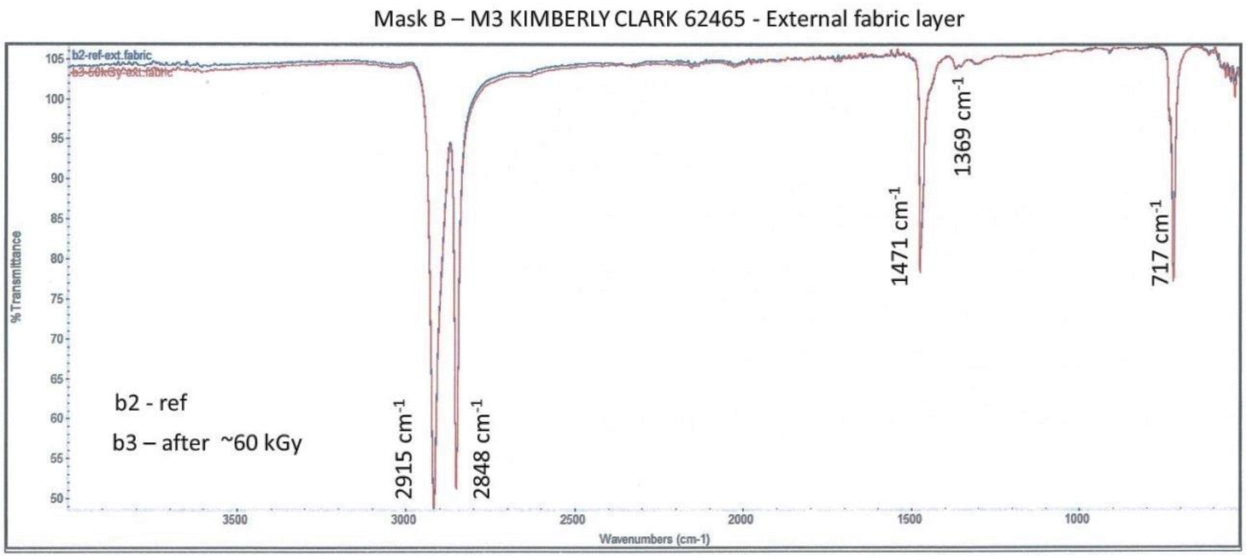


FIG. 9. FTIR measurements of the external fabric of Mask B before and after irradiation.

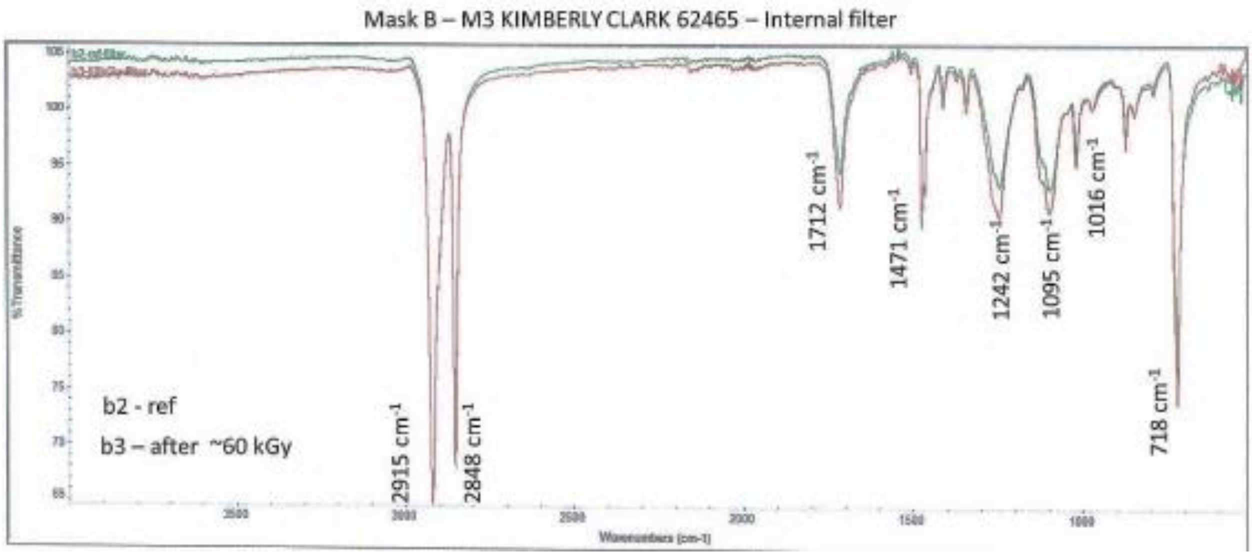


FIG. 10. FTIR measurements of the internal filter of Mask B before and after irradiation.

Chemical structure of the mask materials is unaffected by gamma irradiation.

4.1.5 Mechanical properties (initial Instron measurements)

Changes of the mechanical properties of the mask materials were examined only for mask B and mask E, because these mask types allowed preparation of the proper samples for tensile measurements. The mechanical properties of the reference mask or and a gamma-irradiated masks, were tested under tension using a universal testing machine (Instron model 3365), equipped with pneumatic grips. Mask B and mask E are composed from several layers. They are separated layer-by-layer, and different layers were cut into ~10 mm wide strips using a scalpel. The tests were performed at a rate of 20 mm/min using a 100 N load cell. The thickness of the samples was measured using a Mitutoyo Absolute indicator. Four measurements were performed for each type of sample.

Mask B:

The mechanical properties of thin inner layers taken from masks B were tested before and after high-dose irradiation (61 kGy). Fig. 11 and Fig. 12 present tensile test results of the reference and irradiated samples, respectively. For each type of sample four measurements were performed. The initial results indicate that irradiation did not have any apparent negative effect on the inner material mechanical properties.

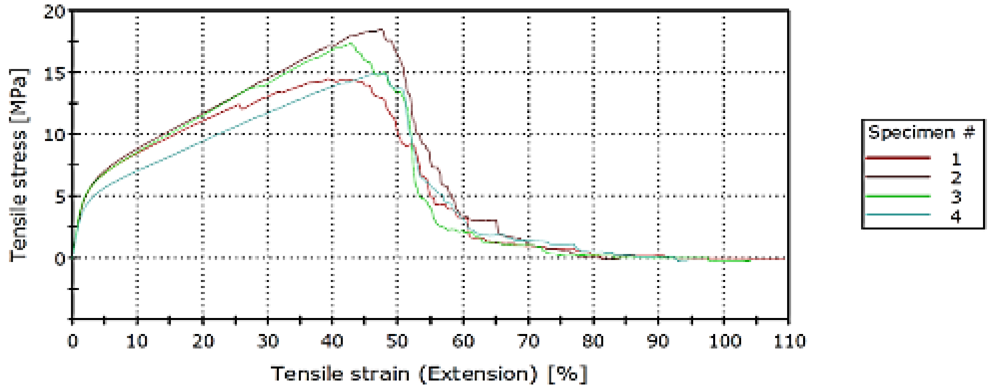


FIG. 11. Stress-strain tension results of thin inner layer samples, taken from non-irradiated Mask B.

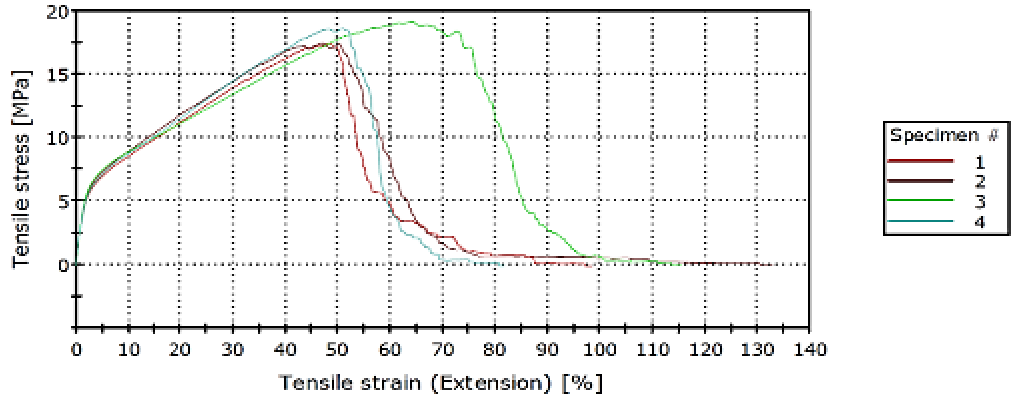


FIG. 12. Stress-strain tension results of thin inner layer samples, taken from irradiated (61 kGy) Mask B.

The tensile test of the thin layers can be divided into three major regions:
1. An elastic region, up to a strain of ~2.5%.
2. A plastics region, up to a strain of 45-50%, where the thin layer fabric collapses and the fibres become more aligned.
3. A failure region, where the layer slowly deteriorates and torn apart.

Mask E:

The E-type mask consists of three layers. The two outer layers are perforated while the in-between layer is continuous. The effect of gamma irradiation on the mechanical properties of the outer layer was tested under tension conditions. Two types of samples were measured: perforated layers taken from a reference mask, and from a mask after 50 kGy irradiation.
Fig. 13 shows the tensile test results for two tested samples. TABLE 3 summarizes the ultimate tensile stress and strain results of these measurements.

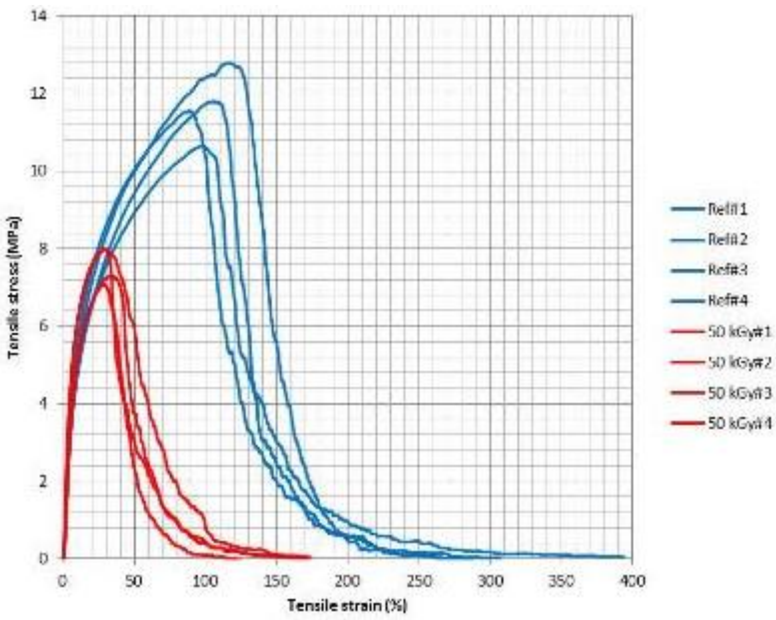


FIG. 13. Tensile test results the Mask E outer layer.

TABLE 3. ULTIMATE TENSILE STRESS AND STRAIN RESULTS.

Sample	Ultimate tensile stress (MPa)	Ultimate tensile strain (%)
E - Reference	11.7 ± 0.9	101.8 ± 12.4
E3 - 2	7.6 ± 0.5	29.8 ± 2.3

The three regions of the tensile test can be easily discerned (the elastic region, the plastics region, and the failure region). As shown in TABLE 3, the mechanical properties of the outer layer of the irradiated mask were severely deteriorated: the ultimate tensile stress was degraded by ~35% and the ultimate tensile strain was degraded by ~70%. Note, that at this stage, the continuous inner layer of the mask E has not been tested yet.

4.1.6 Face-seal Testing

Face-seal leakage test of Masks D and E before and after irradiation was performed using TSI PortaCount® Pro+ Respirator Fit Tester 8038. The TSI Portacount is an ambient particle counting device which is used to conduct Fit Testing by providing a quantitative assessment of face-seal leakage. Test results are summarized in TABLE 4.

The test was performed according to the system protocol for N95 masks, where the subject to be tested wore the mask on his face and follow the instructions defined by the system as follows:

- Talking
- Grimace
- Bending over
- Normal breathing
- Normal breathing
- Deep breath
- Moving head side to side
- Moving up and down

TABLE 4. FACE-SEAL TEST RESULTS.

Mask Type & Appearance	SNRC Sample Name	Irradiation Dose	Fit Factor	Ratio after irradiation / before irradiation
 HP3 1102 FFP2 NR 0	E1-2	0 (ref)	5.2 (4.7-6.4)	**0.85**
	E3-1	50 kGy	4.4 (3.7-5.1)	
 Venus V-430 SLV FFP3 NR	D2-1	0 (ref)	5.7 (5-20)	**0.86**
	D1-1	30 kGy	4.9 (2.1-19)	
 Makrite Niosh N95 Cone Mask 9500	G1-1	0 (ref)	2.0	**0.90**
	G3-1	32 kGy (in sealed vacuum bag)	1.8	
	G5-1	32 kGy	2.1	

Differences of 10-15% were found for 3 types of irradiated masks, for 3 different doses, compared with the same irradiated mask. Such differences can indicate that the fit factor does not change significantly even after high dose irradiation of 30-50 kGy. A similar level of variation was observed during several tests with the exact same mask by the same tester.

It is important to note that:
1. The results are based on tests of 3 masks only, and by only one tester.
2. The findings shown in TABLE 3 do not indicate retention / impairment of filtration efficiency and this topic requires further research.

4.1.7 Filtration Efficiency Test

Filter test was performed before and after irradiation of (i) FFP2 mask (SNRC sample Mask E) and (ii) Flat Sheet N95 Filter Media (Hepworth air filtration) using ATI 100X Automated Filter Tester and (iii) N95 mask (SNRC sample Mask G) using TSI Automated Filter Tester Model 8130, at SHALON Chemical Industries (Kiryat Gat, Israel).

The actual filter testing process using ATI Automated Filter Tester is illustrated in Fig. 14 (left to right) and the results of all measurements are summarized in TABLE 5.

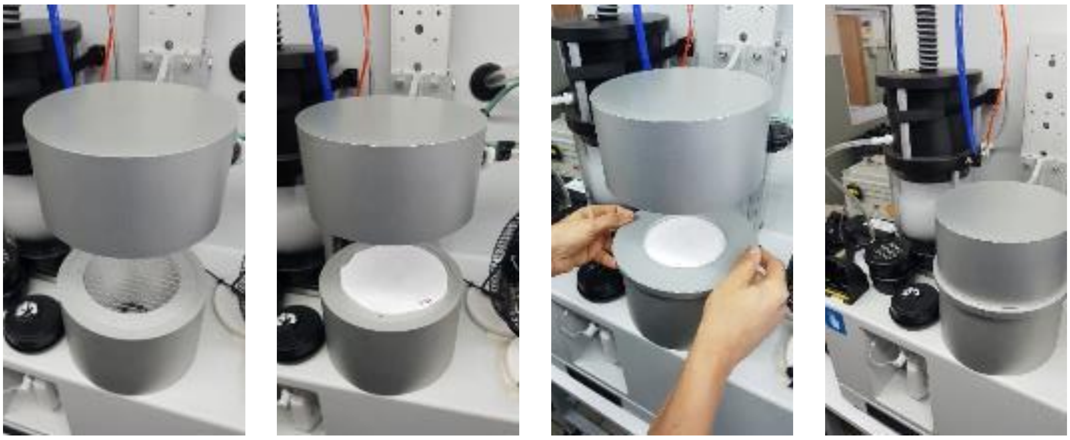


FIG. 14. Filter testing process using ATI 100X Automated Filter Tester

Flat sheet N95 filter media: as expected, the results of the test for un-irradiated filter showed more than 95% filtration efficiency. In contrast, the filtration efficiency was sharply decreased to about 34% and 38% for the same type of filter media, which was irradiated to 30 kGy and 60 kGy, respectively- compared with non-irradiated filters, the filtering efficiency for irradiated samples decreased by factor ~3.

Surgical Mask (mask B): For un-irradiated mask (Samples BH1 and B21) the filtration efficiency is ~80%. The irradiated masks (32 kGy) samples B41, BH3, BH5 and B61 showed a filtration efficiency of ~30%, reduction by factor ~2.6 in filtration efficiency compared with non-irradiated masks. It is important to note that no difference was found between masks irradiated in a sealed vacuum bag compared with those irradiated in air.

FFP2 mask (mask E): For the new non-irradiated mask (Sample E1-3) the filtration efficiency is ~38% and not as expected from the FFP2 masks to have a minimum of 94% filtration percentage. Sample E2-2, the irradiated mask (25 kGy) showed a filtration efficiency of 24%, reduction by factor ~1.5 in filtration efficiency compared to non-irradiated mask.

Regarding the results, it is suspected that the tested FFP2 mask is a malfunctioning mask. Therefore, our decision is not to establish a scientific position relating to the results obtained in this examination.

N95 mask (masks F and G): as expected, the results of the test for un-irradiated mask (samples G1 and G2) showed more than 95% filtration efficiency. Samples G3 and G6, the irradiated mask in air (32 kGy) showed a filtration efficiency of 50-65%, reduction by factor 1.5-2 in filtration efficiency compared with non-irradiated masks. Samples G4 and G5, the irradiated masks in sealed vacuum bag (32 kGy), showed a filtration efficiency of 65-86%, reduction by factor 1.16-1.5 in filtration efficiency comparing to non-irradiated masks.
Samples G7 and G7, the irradiated masks in sealed vacuum bag for double dose (60 kGy), showed a filtration efficiency of ~65%, a reduction by factor 1.5 compared with non-irradiated masks.
There is no difference in the filtration efficiency of the masks irradiated to 32 kGy and those irradiated to 60 kGy. Besides, similar to surgical mask B, there is no difference in the filtration efficiency decrease between the masks irradiated with and without a sealed vacuum bag.
Samples F3 and F5, were irradiated to 6 kGy and 32 kGy, respectively. Both samples showed a filtration efficiency of ~ 60%. i.e., there is no difference in filtration efficiency even after a low dose irradiation of 6 kGy compared to a high dose of 32 kGy.

Note, that according to our measurements, the filtration efficiency of the irradiated N95 masks (masks F and G) is lower than the filtration efficiency of the non-irradiated surgical mask (mask B).

With regard to the above findings, it is clear that <u>the irradiation has impaired the filters efficiency</u>, a finding that raises the question of the benefit and the feasibility of gamma irradiation sterilization of medical masks.

TABLE 5. FILTER TEST RESULTS. ALL MEASUREMENTS PERFORMED WITH TEST FLOW OF 30 LPM.

Type & Appearance	SNRC Sample Name	Irradiation Dose (kGy)	Filtration Efficiency (%)	Resistance (mmH_2O)
 Hepworth air filtration, Flat Sheet N95 Filter Media	Z1-1	0 (ref)	95.3	**4.5**
	Z1-2	0 (ref)	95.4	**4.4**
	Z1-2	0 (ref)	95.2	**4.5**
	X1-1	30	34.3	**4.3**
	X1-2	30	33.3	**3.7**
	Y1-1	60	38.3	**4.1**
	Y1-2	60	36.4	**3.7**
 M3 KIMBERLY CLARK 62465	B21	0 (ref)	82.6	**4.6**
	BH1	0 (ref)	79.6	**5.5**
	B41	32	31.4	**5.4**
	BH3	32	49.5	**4.5**
	BH5	32 in sealed vacuum bag	29.0	**4.8**
	B61	32 in sealed vacuum bag	29.9	**4.5**
 HP3 1102 FFP2 NR	E1-3	0 (ref)	37.5	**1.4**
	E2-2	25	24.4	**1.6**
	E4	32 in sealed vacuum bag	52.0	**4.2**
 3M 9501+ KN95	F3	6	56.3	**7.9**
	F5	32	64.0	**7.6**
 Makrite Niosh N95 Cone Mask 9500	G1	0 (ref)	99.9	**12.2**
	G2	0 (ref)	99.8	**7.1**
	G3	32	51.0	**11.0**
	G6	32	64.8	**6.2**
	G4	32 in sealed vacuum bag	65.1	**7.2**
	G5	32 in sealed vacuum bag	85.9	**12.9**
	G7	60 in sealed vacuum bag	60.8	**7.3**
	G8	60 in sealed vacuum bag	64.6	**7.3**

Soreq NRC group findings regarding the reduction of the filtration efficiency after mask irradiation are similar to those of other research groups, including MIT/USA (gamma irradiations) [13], CEA-ENSAM/France (gamma irradiations) and ARTI-KAERI/South Korea (gamma and electron beam irradiations). Similar results we observed for all irradiation doses, from the low dose of 6 kGy, up to high dose of 60 kGy, both under ambient air and in a sealed vacuum bag. We assume that the loss of filtration efficiency could be related to the change of electrostatic properties of the filtration media after irradiation, or changes in the material surface chemistry affecting the surface sticking coefficient.

There are two principal types of filtration: surface filtration and depth filtration. Depth filtration captures particles both from the surface and throughout the depth of the medium. The depth filtration is usually achieved by using non-woven fabrics. Polypropylene and Polyester fibers are mostly used for mask production [14, 15]. The main mechanisms that affect the aerosol particles penetration through the filters are shown schematically in Fig. 15. These mechanisms include (i) diffusion, (ii) interception, (iii) inertial impaction, (iv) gravitational settling and (v) electrostatic attraction [15]. Most of these processes work as mechanical capture mechanisms, except for electrostatic attraction, which is based on the attractive forces between the particles and the fibers.

From our group initial study, it is evident that the morphology and chemical structure of the fibers are unaffected by gamma irradiation. However, mechanical properties are degraded. It was reported in earlier works that the mechanical properties of the PP are affected by gamma irradiation in the 10^6 - 10^7 rad (10 kGy - 100 kGy) range [16]. The effect of the radiation depends on the fiber grade and stabilization or other special additives, which might differ from manufacturer to manufacturer [17]. At this stage of the study, it is not clear how mechanical properties correlate with the filtration efficiency of the PP. Another observed effect of irradiation is appearance of a smell, which might be a result of radiation-induced oxidation of the filter material and/or additives.
Based on these results, it may be suggested that the main filtration mechanism that is affected by ionizing radiation is electrostatic attraction.
Assuming that the filtration efficiency of the PP filters is strongly correlated with the electrostatic charging of the fibers, this parameter should be addressed as a function of initial use of the masks, as well as a function of gamma irradiation dose. However, for a strong science-based understanding of the PP fibers interaction with gamma radiation, more experiments with a wider range of relevant medical masks are necessary.

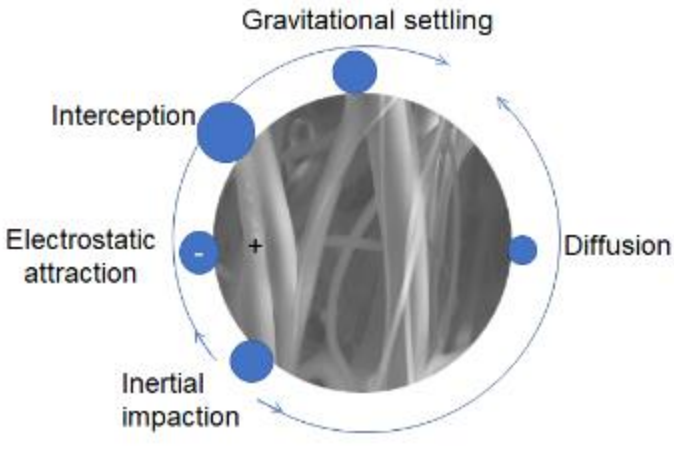


FIG. 15. Basic filtration mechanisms.

4.2 Medical protective clothing

4.2.1 List of studied medical protective clothing

For initial evaluation of the effect of gamma irradiation on medical protective clothing the various samples listed in TABLE 6 were used. As shown in TABLE 6, Samples R, S, and T were exposed to different irradiation doses according to ISO 11137 recommendation for dose sterilization of 30 kGy and double dose of 60 kGy [1].

TABLE 6. LIST OF PROTECTIVE CLOSING UNDER EVALUATION.

SNRC Sample Name	Protective Clothing Type	Appearance	Irradiation Dose
R	Tyvek Classic Plus CHA5a Protective Overall Cat. III Type 4B+5B+6B		0 (Ref) 30 kGy 60 kGy
S	Lakeland SafeGard 76 Disposable Type 5-6 Coverall		0 (Ref) 30 kGy 60 kGy
T	Medical dressing disposable surgical gown		0 (Ref) 30 kGy 60 kGy

4.2.2 Protective clothing visual inspection after irradiation

No visual changes, no coloration, no changes on touch and pull were observed for all tested samples after both low and high irradiation doses. The sole effect of irradiation was the smell, similar to that observed from irradiated masks.

Samples from the inner and outer side of the coverall “R” were analyzed before and after irradiation (samples R1, R2 and R3) using HR SEM. No changes in fibers morphology or micro-cracks of the inner and outer side of the coverall fabric were observed after 29 kGy and 50 kGy irradiation, as shown in Fig. 16.

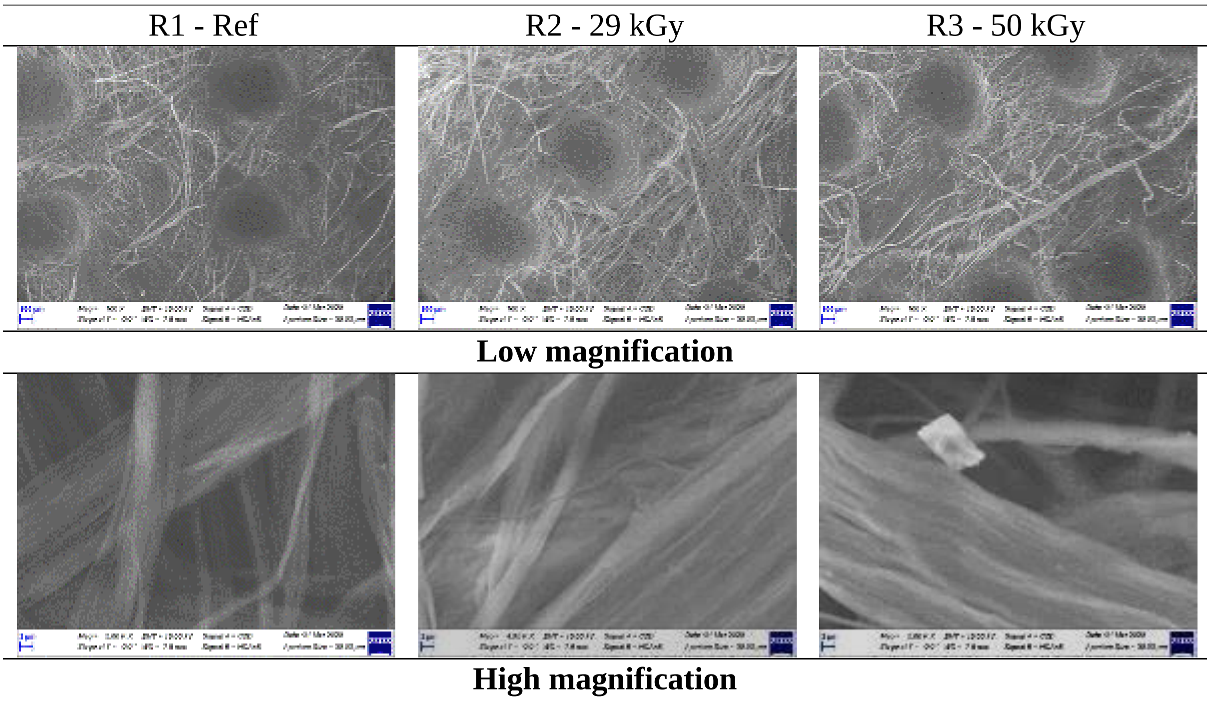


FIG. 16. SEM images of the inner layer of the Coverall "R" before and after irradiation.

4.2.3 Chemical structure

Chemical structure of the coverall R and coverall S was examined by FTIR measurements. Fig. 17 shows FTIR spectra of the coverall R samples before and after irradiation. The spectra are characteristic of polyethylene (PE) [12]. The main stretching vibrations for polyethylene appear at 2915 and 2848 cm^{-1}. The main bending mode of the $-CH_2$ group is located between 1471 cm^{-1} and 1462 cm^{-1}. It is difficult to differentiate between high-density PE (HDPE) and low-density PE (LDPE) based on these spectra. However, it is clear that the chemical structure of the material is not affected by both low and high gamma irradiation doses.

The inner side of the coverall S is composed of PP (identical to the spectrum on FIG. 7), while the FTIR spectrum of the outer side material indicates that it is made of a blend of PE and other materials which is difficult to identify by FTIR (see FIG. 18). No changes after irradiation were observed.

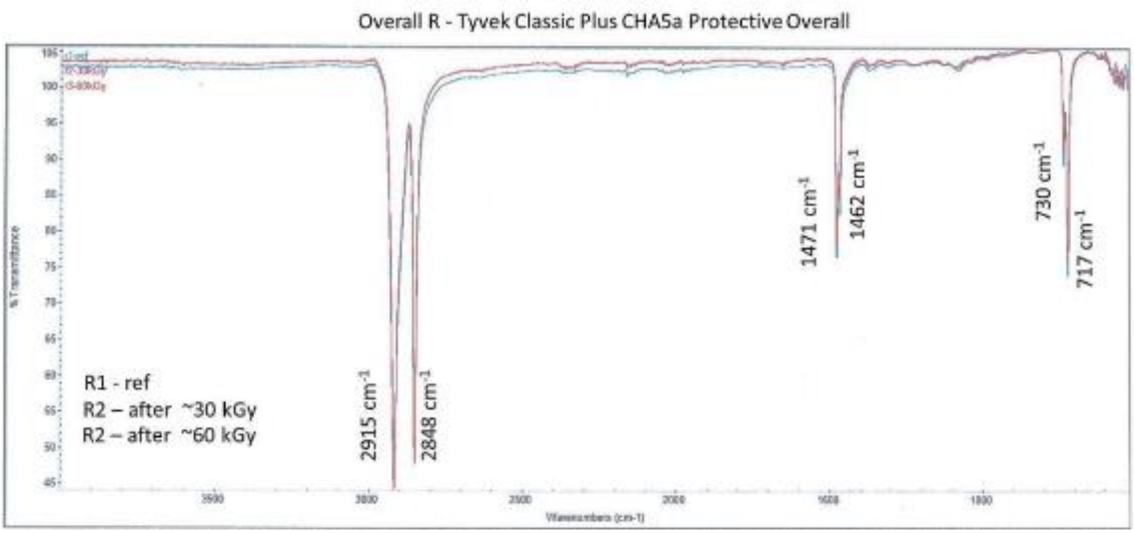


FIG. 17: FTIR measurements of the coverall R samples before and after irradiation.

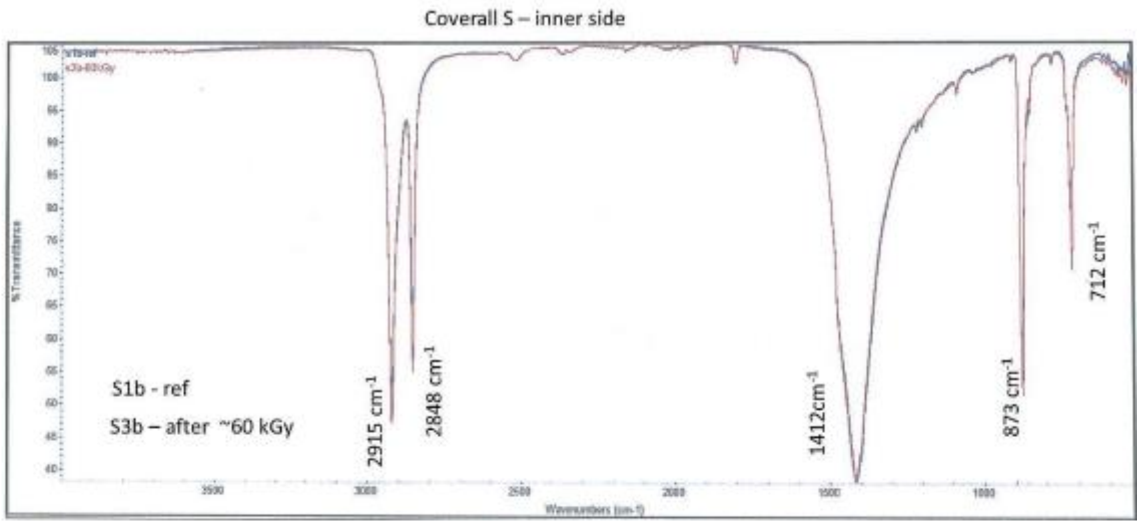


FIG. 18: FTIR measurements of the outer side of the coverall S samples before and after irradiation.

4.2.4 Water repellency

The protective coveralls samples R and S are characterized by their manufacturer as liquid repellant. This property should be critical for its reuse after sterilization. In order to study the effect of water repellency, the water contact angle and spray test were measured before and after irradiation to 30 kGy and 60 kGy.

Contact angle measurements:
The contact angle measurements were carried out using Rame-Hart Goniometer with DropImage software. For each sample at least 5 measurements were carried out on different surface areas. The typical drop images are shown in Fig. 19. The results of the contact angle measurement are summarized in TABLE 7. Within the accuracy of the contact angle measurement, there was no change in the water repellant properties of the tested samples.

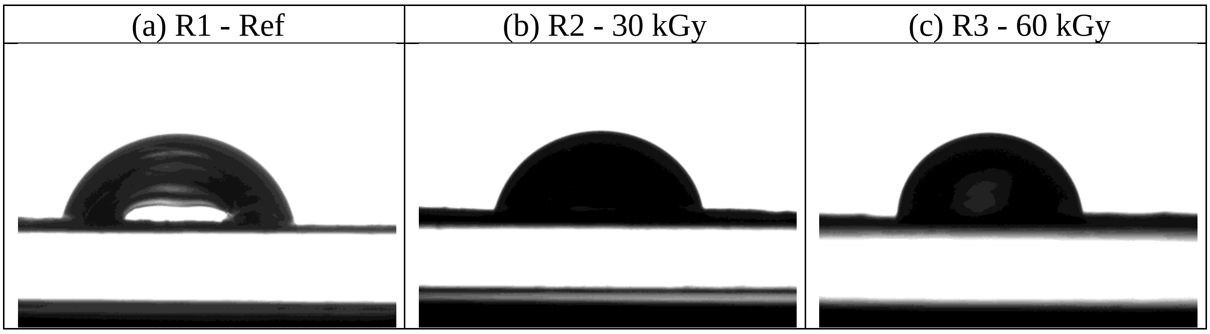


Fig. 19: Typical water drops images on the surface of protective coverall R samples before and after irradiation.

TABLE 7. CONTACT ANGLE MEASUREMENTS FOR COVERALL R AND S.

	R1 Ref (0)	R2 30 kGy	R3 60 kGy
	78.1	101.4	84.1
	77.7	101.3	97.7
	79	100.7	87.1
	86.4	95	87.8
	86.7	77.6	72
	86.7	77.3	92.3
Average	**82.6 ±4.8**	**92.1±11.7**	**86.8±8.7**
	S1 Ref (0)	S2 30 kGy	S3 60 kGy
	89.8	78.1	75.7
	82.5	87.1	79.1
	78.5	86.6	70
	85.2	84.1	82.3
	78.2	81.6	78.8
Average	**82.8 ± 4.3**	**83.5 ± 3.3**	**77.2 ± 4.2**

Spray test:

The spray test measurements were carried for the protective coverall sample R according to AATCC 22-2017 standard [18]. The test is to judge the pattern of water spray on the surface of a sample under controlled conditions using visual rating scale. The wettability index is evaluated according to descriptive (ISO) or photographic scales (AATCC). The ISO index ranges from 0 (wetting of the entire surface) to 5 (dry surface) as shown in Fig. 20. The results of the spray test measurement are summarized in TABLE 8.

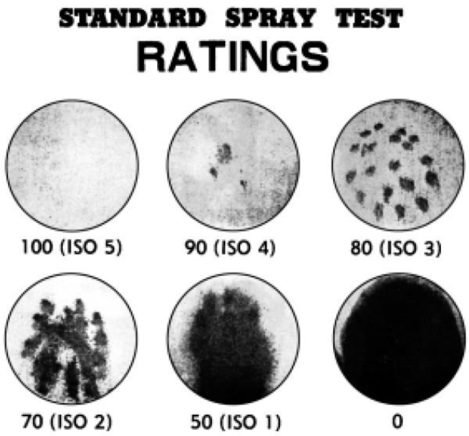


FIG. 20: Standard Spray test ratings according to AATCC 22-2017.

TABLE 8. SPRAY TEST RESULTS.

	Sample / Dose	Grade
	R1 / Ref (0) After Wash	90-100
	R2 / 30 kGy After Wash	90-100
	R3 / 60 kGy After Wash	90-100

No change was observed in the characteristics of protective coverall sample R to spray resistance after exposer to 30 kGy and 60 kGy.

4.2.5 Mechanical properties

The effect of gamma irradiation on the mechanical properties of an S-type, R-type coverall fabric and T-type medical dressing disposable surgical gown were tested under tension conditions. The mechanical properties of the samples before and after irradiation for 30 kGy and 60 kGy were tested under tension using a universal testing machine, Instron model 3365. The layers were cut into 20 mm wide strips using a scalpel. Five measurements were performed for each type of sample. Fig. 21 shows typical tensile test setup; Fig. 22, Fig. 23, and Fig. 24 show the obtained stress-strain curves for R-type, T-type, and S-type protective closing, respectively. TABLE 9 shows the tensile test results summary.

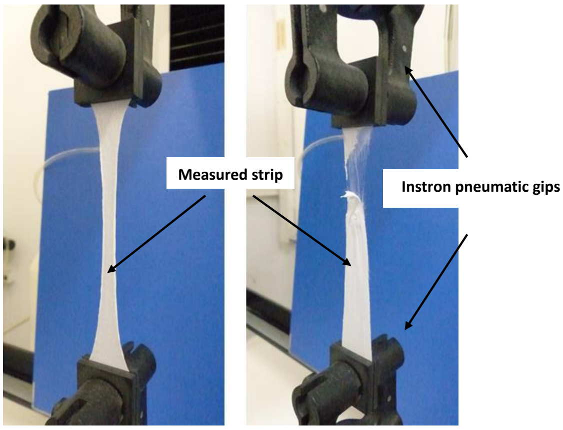


FIG. 21. Typical tensile test setup: sample of coverall S before (left) and after (right) failure of the inner layer.

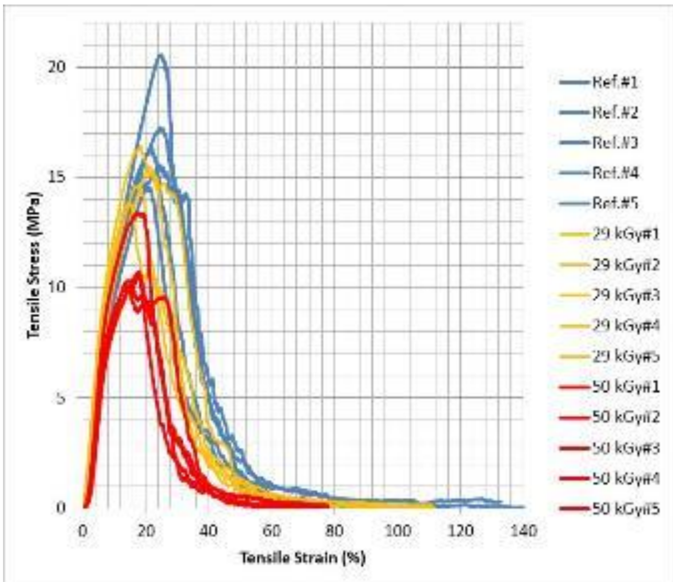


FIG. 22. R-type coverall fabric tensile tests results summary.

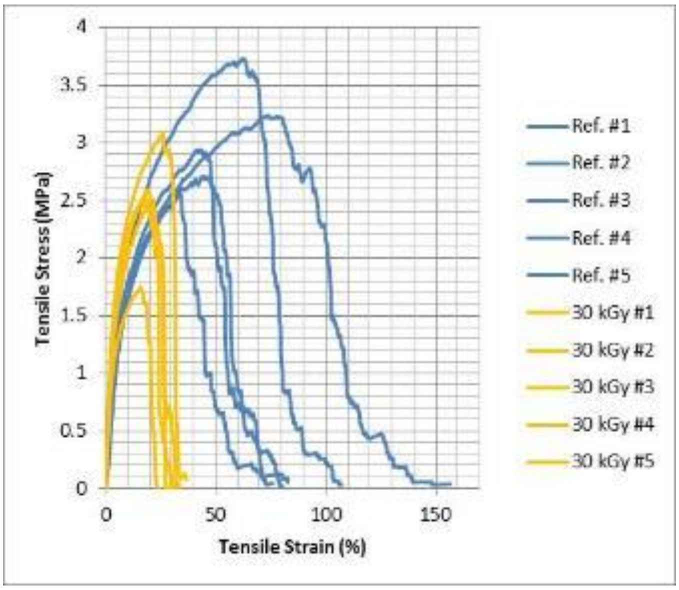


FIG. 23. T-type coverall fabric tensile tests results summary.

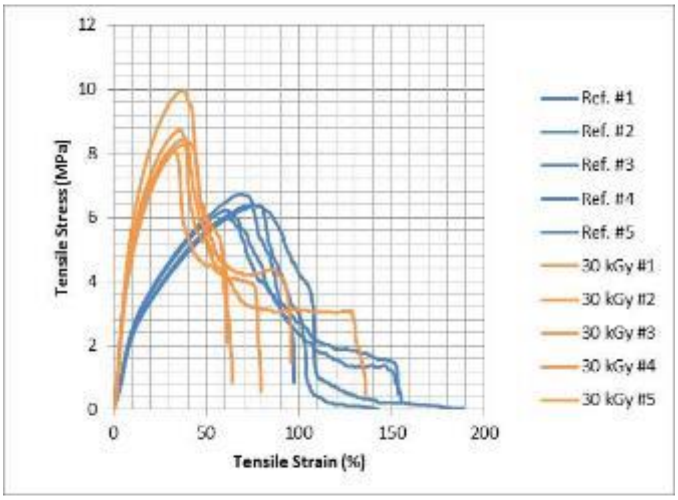


FIG. 24. S-type coverall fabric tensile tests results summary.

R-type coverall fabric:

Based on FTIR results, the R-type coverall is made of PE. As shown in TABLE 9, the ultimate tensile stress and strain of the irradiated fabric of R-type were degraded in comparison to the properties of the reference fabric. As a result of the irradiation, at a dose of 30 kGy, the ultimate tensile stress was decreased from and average value of 17.0 MPa to 14.2 MPa, a degradation of ~16%. The ultimate tensile strain was decreased from 22.8% to 18.7%, a degradation of ~18%. After higher irradiation dose of 60 kGy, the mechanical properties of the fibers continued to degrade. The ultimate tensile stress reached a value of 11 MPa, a degradation of 35% in comparison with the pristine samples. The ultimate tensile strain reached a value of 16 MPa, a degradation of 28% in comparison with the pristine samples.

T-type medical dressing disposable surgical gown:

As shown in TABLE 9, the tensile tests of the gamma irradiated T-type samples show different behavior- as a result of the irradiation the failure region during these tests is much shorter and the fail occurs abruptly. The mechanical properties of the irradiated samples were severely deteriorated. As a result of the gamma irradiation the ultimate tensile stress was degraded by 18.4% and the ultimate tensile strain was degraded by 62.2%.

S-type coverall:

The S-type coverall is comprised of a single fused material. Based on FTIR analysis this material consists of an inner non-woven PP layer and an outer layer, which may be attributed as PE-based water-repellent. The tensile behavior can be divided into four major regions: the elastic region, a plastics region, a failure region where the layer slowly deteriorate, and a failure region where a sudden drop in the tensile stress occurs and the waterproof coating is torn apart, see Fig. 24. In the case of the gamma-irradiated samples, the tensile tests show similar behavior, however, each stage is shorter in terms of the strain. Unlike previous measurements, the ultimate tensile stress increased after gamma irradiation, by 37%, probably due to radiation induced crosslinking. However, the ultimate tensile strain was severely deteriorated. As a result of the gamma irradiation it degraded by ~47 %.

TABLE 9. ULTIMATE TENSILE STRESS AND STRAIN RESULTS.

	Sample	Ultimate tensile stress (MPa)	Ultimate tensile strain (%)
	R1 - Reference	17.0 ± 2.1	22.8 ± 2.7
	R2 - 30 kGy	14.2 ± 2.3	18.7 ± 2.6
	R2 - 60kGy	11.0 ± 1.3	16.3 ± 1.9
	T1 - Reference	3.0 ± 0.5	51.3 ± 16.2
	T2 - 30 kGy	2.5 ± 0.5	19.4 ± 3.9
	S1 - Reference	6.4 ± 0.3	68.6±8.2
	S2 - 30 kGy	8.7 ± 0.8	36.4 ± 2.4

Intermediate conclusions

For all tested **medical masks**, no visual and morphological changes of the masks' materials were observed. FTIR indicated no changes in the chemical structure. However, mechanical properties, both ultimate tensile stress (UTS) and strain at UTS were diminished. Another observed effect of the irradiation was the appearance of a smell, which might be a result of radiation-induced oxidation of the filter material and/or additives. Moreover, for the tested N95 and surgical masks we found that the irradiation has significantly impaired the filtration efficiency for all irradiation doses, from the low dose of 6 kGy, up to high dose of 60 kGy. This finding raises the question of the benefit and the feasibility of gamma irradiation sterilization of medical masks.

The results of the irradiation of **medical protective clothing** seem to be promising for reuse after sterilization. No visual changes, no coloration, no changes on touch and pull, no changes in chemical structure and water-repellant properties were observed for all tested samples after both low and high irradiation doses (30 - 60 kGy). The only detected effects of irradiation were the smell, similar to that observed from irradiated masks, and the reduction of the mechanical properties (UTS and the corresponding tensile strain).

References

1. "Sterilization of health care products - Radiation - Part 1: Requirements for development, validation and routine control of a sterilization process for medical devices," *ISO Standard 11137-1*, 2006.
2. Feldmann, F., W.L. Shupert, E. Haddock, B. Twardoski, and H. Feldmann, "Gamma Irradiation as an Effective Method for Inactivation of Emerging Viral Pathogens", *American Journal of Tropical Medicine and Hygiene,* **100**(5), 1275-1277, 2019.
3. Nather, A., N. Yusof, and N. Hilmy, "Radiation in tissue banking: Basic science and clinical applications of irradiated tissue allografts". 2007. 1-561.
4. "Radiation Sterilization of Tissue Allografts: Requirements for Validation and Routine Control", *Vienna: International Atomic Energy Agency,* 2007.
5. Kumar, M., S. Mazur, B.L. Ork, E. Postnikova, L.E. Hensley, P.B. Jahrling, R. Johnson, and M.R. Holbrook, "Inactivation and safety testing of Middle East Respiratory Syndrome Coronavirus", *Journal of Virological Methods,* **223**, 13-18, 2015.
6. "Gamma irradiators for radiation processing", *International Atomic Energy Agency,* 2006.
7. Lanyi, F.J., N. Wenzke, J. Kaschta, and D.W. Schubert, "A method to reveal bulk and surface crystallinity of Polypropylene by FTIR spectroscopy - Suitable for fibers and nonwovens", *Polymer Testing,* **71**, 49-55, 2018.
8. Zhu, X., D. Yan, and Y. Fang, "In Situ FTIR Spectroscopic Study of the Conformational Change of Isotactic Polypropylene during the Crystallization Process", *The Journal of Physical Chemistry B,* **105**(50), 12461-12463, 2001.
9. Fang, J., L. Zhang, D. Sutton, X.G. Wang, and T. Lin, "Needleless Melt-Electrospinning of Polypropylene Nanofibres", *Journal of Nanomaterials*, 9, 2012.
10. Abdel-Hamid, H.M., "Effect of electron beam irradiation on polypropylene films—dielectric and FT-IR studies", *Solid-State Electronics,* **49**(7), 1163-1167, 2005.
11. Natarajan, S. and J.J. Moses, "Surface modification of polyester fabric using polyvinyl alcohol in alkaline medium", *Indian Journal of Fibre & Textile Research,* **37**(3), 287-291, 2012.

12. Jung, M.R., F.D. Horgen, S.V. Orski, V. Rodriguez C, K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.J. Royer, K.D. Hyrenbach, B.A. Jensen, and J.M. Lynch, "Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms", *Marine Pollution Bulletin,* **127**, 704-716, 2018.
13. *http://news.mit.edu/2020/gamma-radiation-found-ineffective-in-sterilizing-n95-masks-0410*, 2020.
14. Akalin, M., I. Usta, D. Kocak, and M.S. Ozen, "Investigation of the Filtration Properties of Medical Masks", in *Medical and Healthcare Textiles,* S.C. Anand, et al., Editors. 2010, Woodhead Publishing. p. 93-97.
15. Dunnett, S., "Filtration Mechanisms ". Aerosol Science: Technology and Applications, ed. I. Colbeck and M. Lazaridis. 2014: Wiley.
16. Van de Voorde, M.H. and C. Restat, "Selection guide to organic materials for nuclear engineering", *Report No. CERN 72-7.*, CERN, Geneva, 1972.
17. Kremser, T., M. Susoff, S. Roth, J. Kaschta, and D.W. Schubert, "Degradation studies of a commercial radiation-resistant polypropylene sterilized by gamma and electron beam technology before and after subsequent accelerated aging cycles", *Journal of Applied Polymer Science,* **137**(10), 7, 2020.
18. AATCC 22-2017, "Water Repellency: Spray Test, standard by American Association of Textile Chemists and Colorists", 2017.

A REPORT FOR STERILIZING PERSONAL PROTECTIVE EQUIPMENT BY IONIZING RADIATION

J.M. YUN[1], H. KIM[1], H.S. KIM[1], S.J. KIM[2], Y.M. LIM[1], J.H.HA[1], B. KIM[1*]

[1]Radiation Utilization and Facilities Management Division, Advanced Radiation Technology (ARTI), Korea Atomic Energy Research Institute (KAERI), 29 Geumgu-gil, Jeongeup-si, Jeollabuk-do 56212, Republic of Korea

[2]Radiation Research Division, Advanced Radiation Technology (ARTI), Korea Atomic Energy Research Institute (KAERI), 29 Geumgu-gil, Jeongeup-si, Jeollabuk-do 56212, Republic of Korea

Abstract

This study is to investigate the effect of ionizing radiation on the structure and filtration performance of KF94 respiratory mask using electron beam accelerator and Co-60 gamma irradiation facility. From the SEM and TGA analyses, all filters showed no significant and measurable structural changes irradiated up to 24 kGy in air and vacuum conditions. However, compared to the pristine KF94 mask, filtration efficiency of electron beam treated KF94 masks was decreased from 99.4% to ~55-67% due to the reduction of electrostatic force by ionizing radiation.

1. INTRODUCTION

As numbers of COVID-19 infections increase, shortages in respiratory masks such as a model KF94 widely used by hospital staff and the general population are a big problem in many countries. For the reason, many governments are looking for a practical reuse method for used respiratory masks. In typical, there are several methods to sterilize personal protective equipment using UV light, chemicals or radiation. Among them, ionizing radiation such as electron beams and gamma is widely used to sterilize medical devices and healthcare products prior to their use. In particular, radiation sterilization method is efficient for eliminating microorganisms such as bacteria and viruses even at a lower dose than 25 kGy. Thus, it is urgently needed to evaluate whether radiation sterilization is a feasible method for solving shortages of respiratory mask or not. To investigate that radiation is a reuse method for used respiratory masks or not, electron beam and gamma irradiation tests were conducted using a commercially available and widely used KF94 mask, which filter out at least 94 per cent of external particles with an average size of 0.6 micrometres.

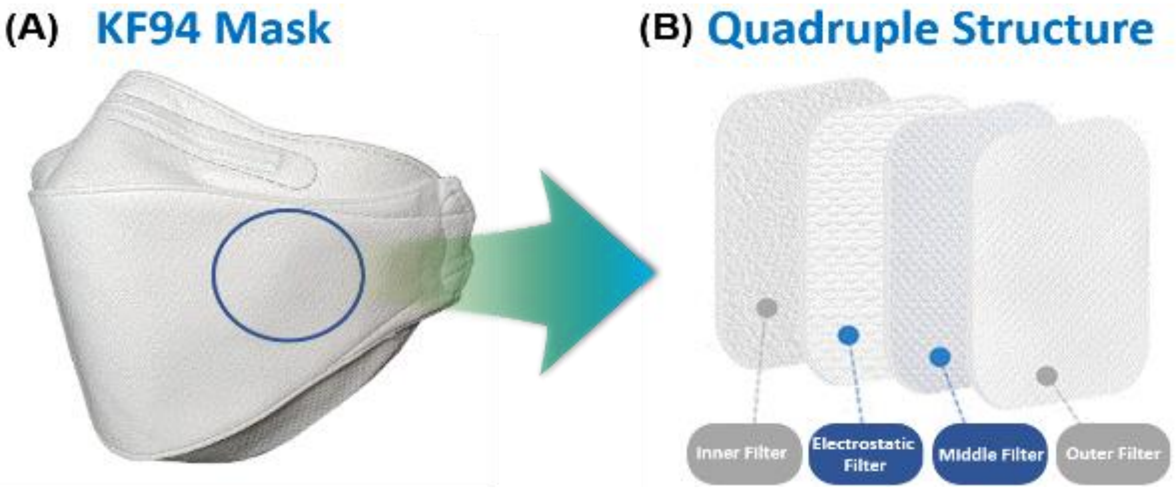


FIG. 1.1 (A)Photograph of a commercial KF94 mask and (B)the corresponding images of each protection filter

2. MATERIALS AND METHODS

As shown in FIG. 1.1, the KF94 respiratory mask is composed of four layers such as inner, electrostatic, middle and outer filters prepared using a low molecular weight polypropylene polymer.[1] The KF94 mask manufactured by melt blown method. Particles larger than ~1 micro meter were filtered by outer and middle filter. In particular, the electrostatic filter is the most important for determining filtering efficiencies in KF94 mask because sub-miro meter sized aerosol, dust or charged particles are efficiently filtered by pore size and electrostatic effects. The outer filter is typically used to maintain a mask shape and to improve wearability.

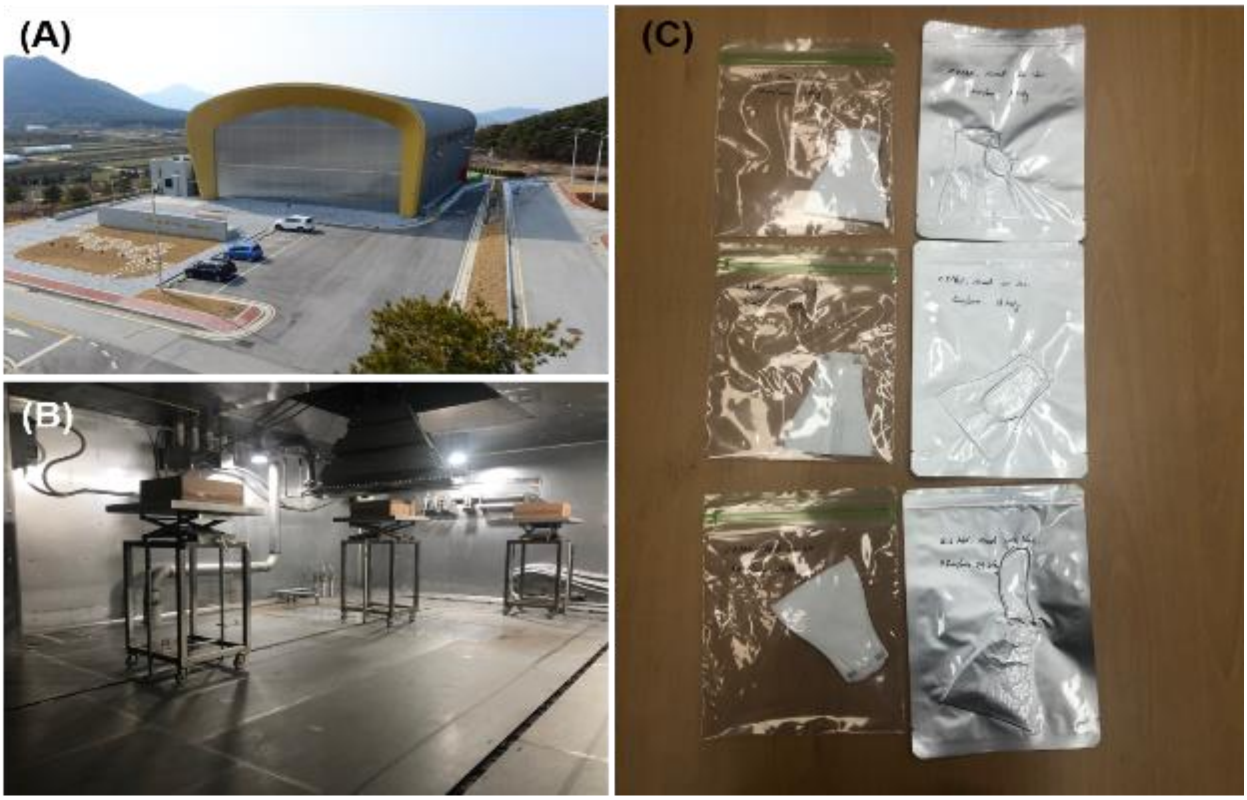


FIG. 1.2 (A)Electron Beam Demonstration and Research Building (B)2.5MeV electron beam accelerator(Model: ELV-8, Manufacturer: EB-Tech, Korea) (C)Samples before electron beam and gamma irradiation under air(left) and vacuum(right) condition

2.1 Electron beam irradiation

Electron beam irradiation on pristine masks both in air and vacuum sealed samples and detailed irradiation conditions are described in TABLE 1.1

TABLE. 1.1 DETAILED ELECTRON BEAM TREATMENT CONDITIONS USING THE ELV-8 (2.5 MEV, 100 KW)

Dose(kGy)	Energy (MeV)	Dose Rate(kGy/s)	Remarks
-	-	-	Commercial KF94 mask
9	2.5	18	Air/vacuum condition
18	2.5	18	Air/vacuum condition
24	2.5	18	Air/vacuum condition

3. RESULT

3.1 Observation of morphological changes

Because each filter is important to maximize filtering efficiencies, we investigated effects of electron beam or gamma radiation on inner, electrostatic, middle and outer filter, as described above. Additionally, air-exposed or vacuum-packed four filters were irradiated to check an unexpected oxygen-induced chemical reaction.[2] Followed by this motivation, we prepared samples as shown in FIG. 1.2. Electron beam irradiation was performed using 2.5 MeV electron accelerator at dose rate of 18 kGy.s^{-1} and gamma ray irradiation at the same doses (9 kGy, 18 kGy, and 24 kGy) at the dose rate of 5 kGy.h^{-1}.

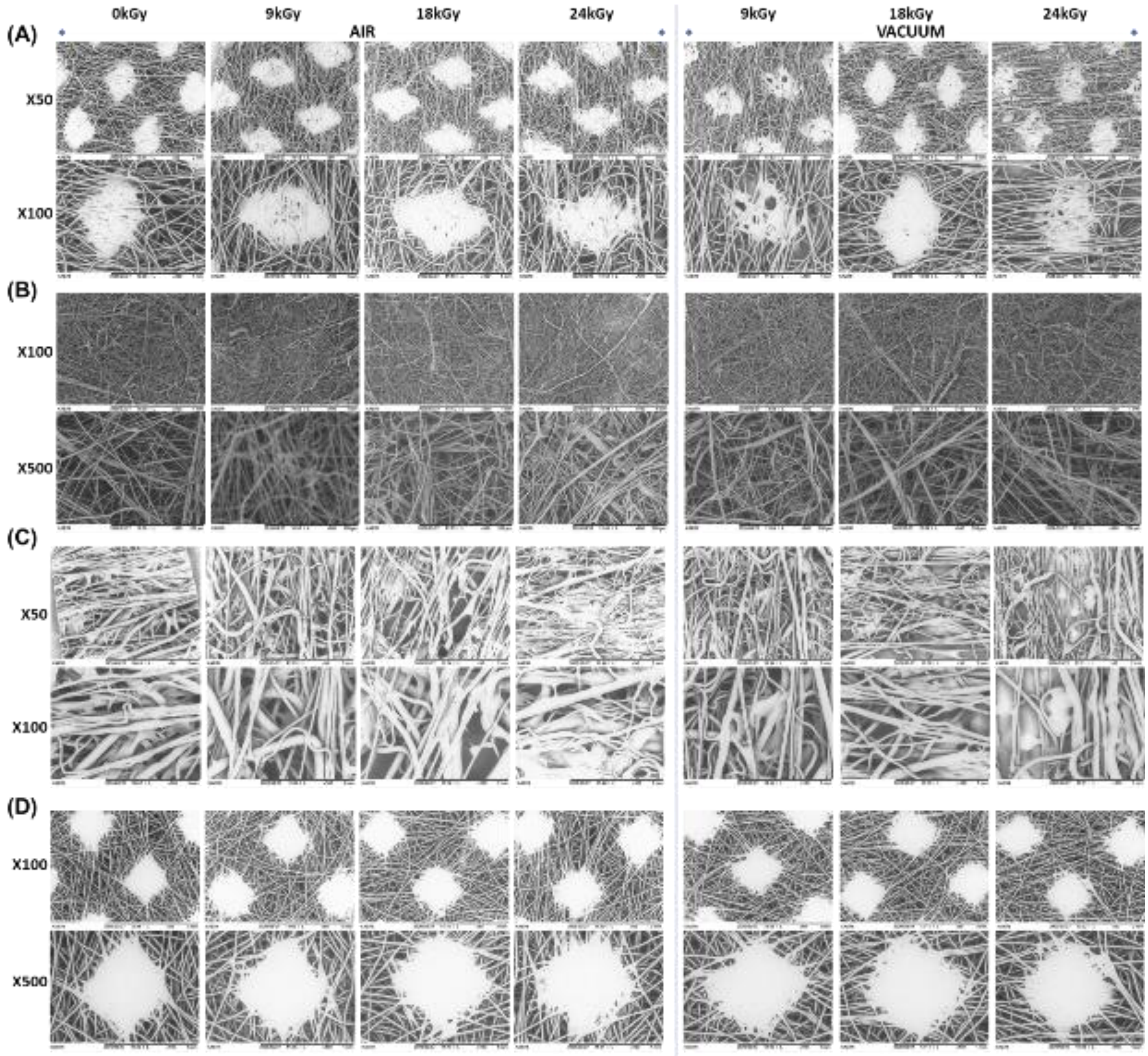


FIG. 1.3 SEM images of (A)inner, (B)electrostatic, (C)middle and (D)outer filters before and after electron beam irradiation

To evaluate whether electron beam irradiation induce crosslinking or decomposition reaction or not, SEM analyses were conducted as shown in FIG. 1.3. In addition, each filter sample irradiated under air and vacuum condition was analysed using the SEM instrument to check an unexpected oxygen-induced chemical reaction.

As a result, there was no significant changes in measurable structural changes when irradiated up to 24 kGy in air and vacuum conditions. In particular, we cannot find structural changes in the SEM images of the electrostatic filter after exposed to 24 kGy dose of radiation despite that electrostatic filter is vulnerable to deform from radiation. These results clearly showed that electron beam radiation up to 24 kGy does not change the structure of KF94 mask filter.

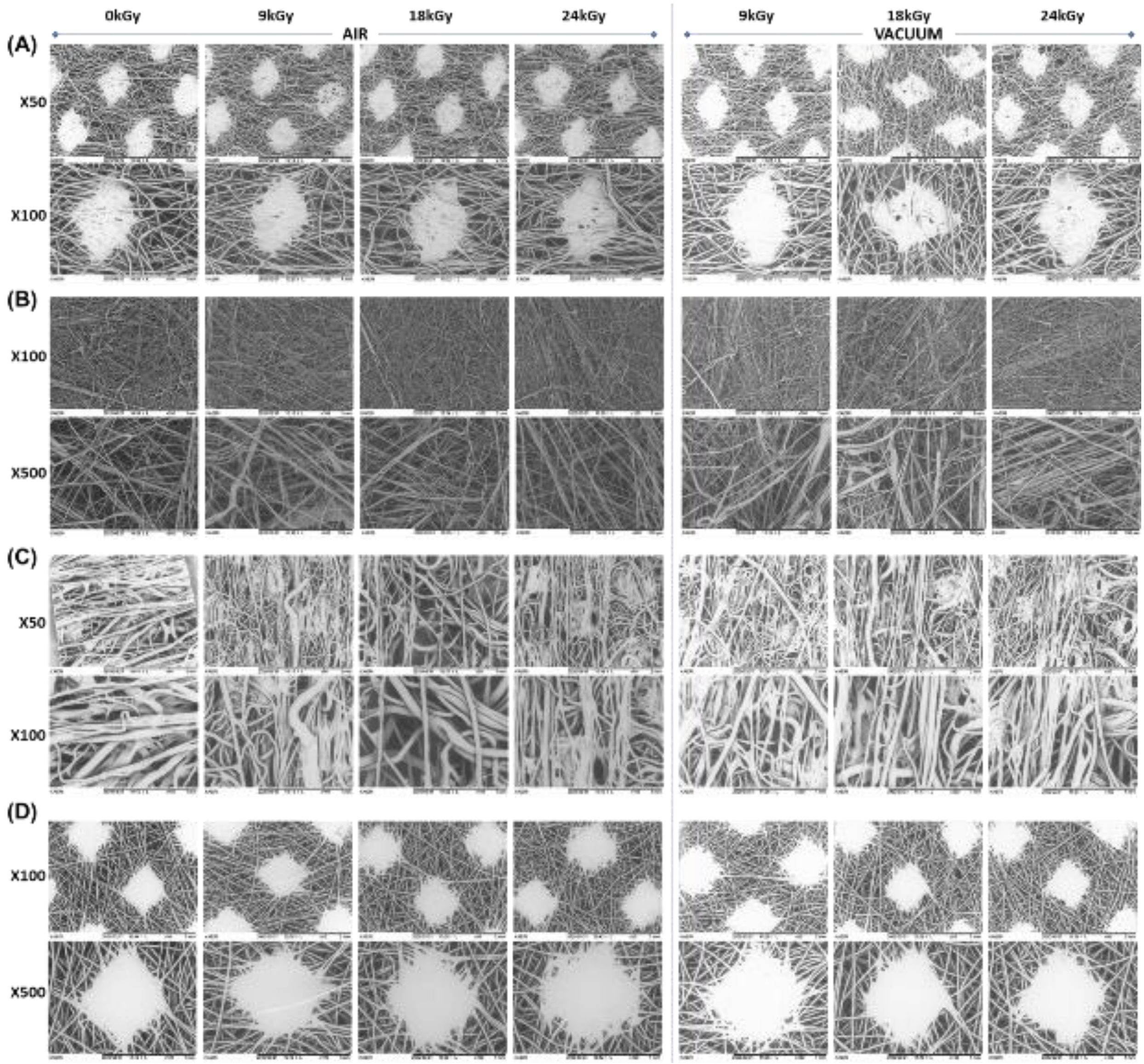


FIG. 1.4 SEM images of (A)inner, (B)electrostatic, (C)middle and (D)outer filters before and after gamma irradiation

3.2 Observation of thermal properties after irradiation

To check whether gamma irradiation changes in the filter structure or not, the same experiment was conducted, as seen in FIG 1.4. As a result, we cannot find any significant structural changes in all filter when exposed to 9, 18 and 24 kGy dose of gamma radiation.

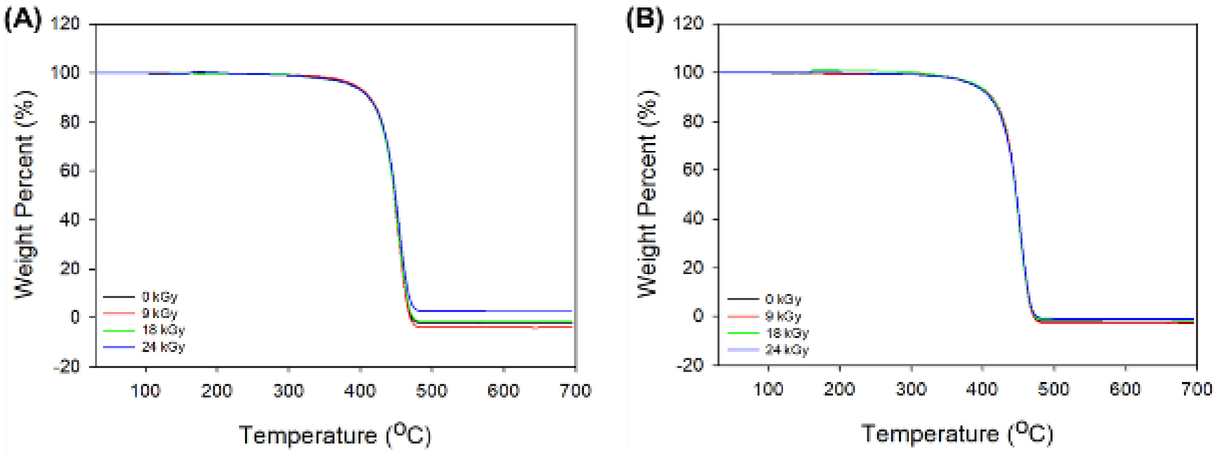


FIG. 1.5 TGA results of electron beam irradiated electrostatic filter under (A)air and (B)vacuum condition

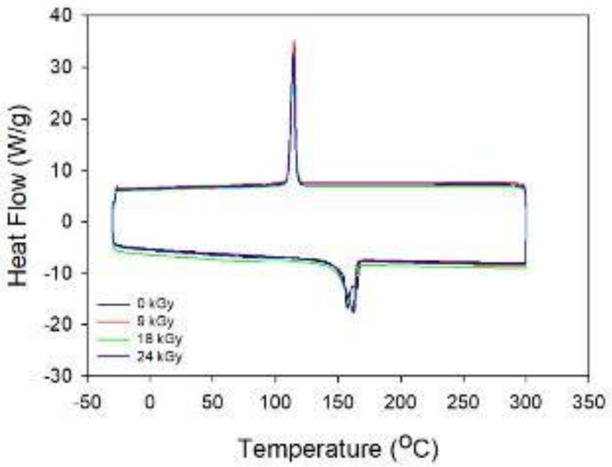


Fig. 1.6 DSC result of electron beam irradiation electrostatic filter under air

To further check the possibility for crosslinking or decomposition reaction of respiratory mask filter in details, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) were conducted after irradiated at a dose of 9, 18, 24 kGy. Here, we tested only electron beam treated samples in air and vacuum. As can be seen in FIG. 1.5 and 1.6, thermal decomposition (T_g) temperature of each sample exposed to the 9, 18 and 24 kGy dose of electron beam radiation is identical to that of pristine case irrespective of irradiation conditions. This result indicates that electron beam irradiation does not induce a measurable chemical reaction such as crosslinking or chain scission and crystallinity.

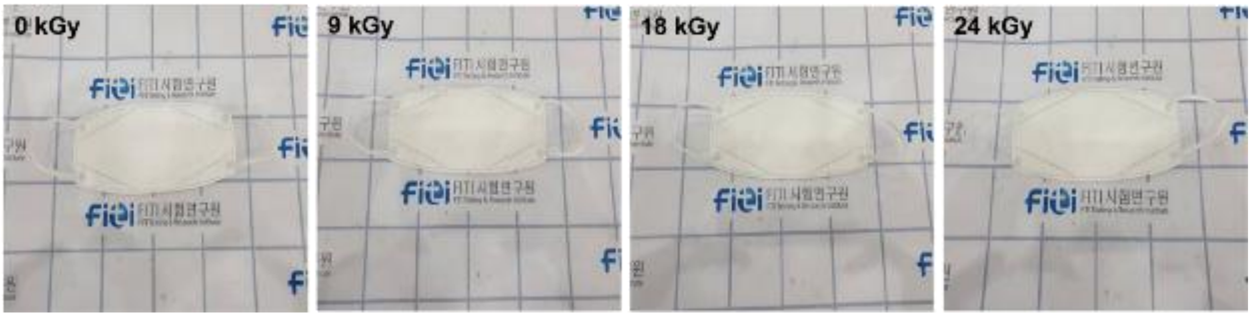


FIG. 1.7 Photographs of KF94 masks for NaCl aerosol-based filtration efficiency test

3.3 Filtration test of irradiated masks

Finally, we performed NaCl aerosol-based filtration efficiency of KF94 masks with and without electron beam irradiation in air. (*Here, filtration efficiency was tested only one case due to a limited time and the rest cases are currently underway in KAERI.*) The filtration test was carried out by the authorized institute (FITI) by Korea Food and Drug Administration (KFDA). All sample preparation, test procedures and conditions are the same to those of KF94 respiratory mask (see FIG. 1.6).[3] Compared to the pristine KF94 mask, filtration efficiency was decreased to ~57-67% when exposed to electron beam as can be seen in TABLE 1.2. This result is a similar to the previous result.[4] One possible reason for this reduction is that electrostatic force is vanished by ionizing radiation. For the reason, the electron beam treated KF94 mask may be more difficult to filter out polar sodium and chloride ions.

TABLE. 1.2 NACL AEROSOL-BASED FILTRATION EFFICIENCY OF KF94 MASKS BEFORE AND AFTER ELECTRON BEAM IRRADIATION IN AIR CONDITION

	0 kGy	9 kGy	18 kGy	24 kGy
#1	99.2%	56.6%	61.9%	68.4%
#2	99.4%	57.5%	64.2%	67.9%
#3	99.4%	59.8%	66.1%	66.4%
Average	99.3%	57.9%	64.1%	67.6%

4 CONCLUSION

For the result from repeated tests, the mechanical and thermal properties such as morphology of SEM, TGA and DSC of KF94 masks are not significant changes at doses from 9 to 24 kGy of electron beam and gamma radiation. However, filtering efficiency of irradiated masks were declined do severely after sterilization using ionizing radiation. It is supposed that the electrostatic effect of the mask was reduced by electron beam irradiation. It can be considered that sterilization is sufficiently possible to personal protective equipment by irradiation such as with electron beam and gamma ray, however it is difficult to apply for recycling of respiratory masks due to reduced filter performance.

ACKNOWLEDGEMENTS

We would like to thank Ph. D. candidate J.O. Jeong, and master course students Y.A. Kim, and D.M. Yun for their experimental support.

REFERENCES

[1] http://www.xn--hz2b19jzoas5b990b40dw2g.kr/bbs/sub5_1/34450

[2] B.Keene et al. "Characterization of Degradation of Polypropylene Nonwovens Irradiated by γ-Ray", *J. Appl. Polym. Sci.*, **2014**, *131*, 33917

[3] https://www.fiti.re.kr/en

[4] A. Cramer et.al. "Disposable N95 Masks Pass Qualitative Fit-Test But Have Decreased Filtration Efficiency After Cobalt-60 Gamma Irradiation", preprint doi:https://doi.org/10.1