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Controversies related to real protection against SARS- CoV-2 virus of the most frequently used face masks

ABSTRACT

Face masks serve to protect the respiratory system from unwanted aerosol droplets, in which various types of pathogens or pollutants are present. They are particularly important during a pandemic, like SARS-CoV-2 pandemic we are withessing. The efficiency of filtration of aerosol droplets, which contain the virus particles, is generally unsatisfactory, especially in conditions of extremely virulent environments, for the most of commercially available masks. Therefore, the challenge is to produce masks with increased filtration efficiency, in order to reduce the percentage of virus penetration through the mask. Hence, it is crucial to correctly define the possibilities and limitations of today's most commonly used epidemiological masks, in order to successfully define completely new concepts of face masks manufacturing, which would enable the most effective protection not only of medical workers but also patients, especially in areas where virus concentrations are extremely high. Also, it has been shown that, in addition to the concentrations of infectious pathogens in a given environment, the conditions in which infection with a given pathogen occurs, such as temperature and humidity within a given contaminated space, are also important.

Keywords: *face mask, nanoparticles, filtration efficiency, aerosol transfer mechanism, SARS-Cov-2, cotton canvas.*

1. INTRODUCTION

The main route of virus transfection is over "droplets of respiratory fluid", between 10 and 5 μm in size, and an aerosol droplets less than 5 μm. Such droplets can spread viruses through the air, contacts and fomites. Airborne transmission of the virus leads to direct infection due to the inhalation of air droplets. Transmission by contact assumes transfer infection from some person infected by virus, like SARS-CoV-2, to one or more another uninfected persons when they come into contact. Airborne droplets and contact droplets are transmissible within 1 m of a person infected with the virus [1-4].

Studies have reported that the SARS-CoV-2 virus can remain viable and contagious for hours in aerosols and days depending on the surface.

Aerosols created by coughing or sneezing of an infected patient can greatly spread the virus. The use of innovative and existing technologies for the production of face masks is one of the primary research interests in this situation. Various researches investigate the idea of reducing, reusing and recycling existing masks in order to find optimal design solution. Modification of existing materials, as well as changes in their design, consequently improves their multifunctional properties [4,5]. Accordingly, filtration efficiency of hybrids (such as cotton-silk, cotton-chiffon, and cotton-flannel) is between 80% and 90% for particles above 300nm. The improved performance of hybrids is probably due to the combined mechanical and electrostatic effect, which are present during filtration [6,7].

Still, insufficient data are available on the performance of common canvas materials (used in canvas masks), especially related to their filtration efficiency depending on the size distribution of aerosol droplets in the range from ~10nm to 10μm.

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This fact is important in order to determine the relative efficiency of transmission of SARS-CoV-2 virus over different droplet sizes.

The aerosol filtration process itself follows the following five basic mechanisms: gravitational, sedimentary, inertial impact, interception, diffusion, and electrostatic attraction. The first two mechanisms play the most important role for aerosols larger than approximately 10µm. Aerosol ejection energy and gravitational force have a primary effect on large droplets, while for droplets in the range of 100nm to 1µm two crucial mechanisms are diffusion and mechanical interception of droplets by canvas fibers. For particles as small as a few nanometers, which can easily pass between the openings in the filter fiber network, electrostatic attraction is the predominant mechanism for removing low-mass particles, which bind to the fibers [8-13].

Electrostatic interactions are usually present in a variety of natural and synthetic fabrics. Some fabrics, such as silk, are extremely effective in filtering nano-aerosols since it possess the surface electrostatic charge, and therefore it is used for production of hybrid masks in combination with cotton or linen [8,9]. Cotton canvas in a four-layer mask in combination with silk show very high filtration efficiency, reaching a value of about 80% over the entire range of aerosol droplet size distribution from 10nm to 6µm [10,11]. For nanometer-sized aerosol droplets by combining a single layer of 600 TPI cotton with two layers of silk, a mask efficiency of about 90% is obtained. This value is comparable to the performance of a standard FFP2 masks when it comes to aerosol droplets above 300 nm and slightly less effective than masks FFP2 above 300nm [12,13].

Taking in mind that FFP2 masks and respirators are designed and engineered to capture more than 95% of particles above 300 nm, their insufficient efficiency in filtering aerosol droplets below 300nm is not surprising. The combination of cotton with silk, provides high efficiency in filtration experiments on the nano-scale (below 300nm) and micron scale (300nm to 6µm), probably due to the combined effects of electrostatic and physical filtration [14-18].

2. BRIEF EXPLANATION OF THE MAIN INTERACTION MECHANISMS BETWEEN MASK MATERIALS AND AEROSOL DROPLETS

In aerosol droplets in the range of 1 - 10 µm, gravitational deposition, in addition to the inertial impact induced by its ballistic effect, is a crucial mechanism of interaction between aerosol droplets and exhaled masks [19, 20].

Inertial impact has a significant effect when the inertia of the aerosol droplet is large enough to cause changes in the direction of movement of the aerosol droplet carried by the air flow. Droplets of larger dimensions and velocities will have greater inertia. Such droplets collide with the fibers of the mask and adhere to it. The effect of Brownian motion is also significant for such aerosol droplet sizes. The diffusion mechanism is usually the primary aggregation mechanism for particles smaller than 0.2µm, while for particles above 0.2 µm the basic mechanism is inertial impact [19-21].

Interception occurs when an aerosol droplet following the primary airflow comes in contact with the filter material. Such an interaction is typical for aerosol droplets up to 0.6µm in size. It is not explicitly determined by the flow rate of aerosol droplets. Nevertheless, it is more pronounced for smaller droplet sizes. Unlike an inertial aerosol droplet impact, in which droplets follows a typical ballistic trajectory, the mechanism of the interception assumes droplets streaming in a central air flow, until it comes in contact with the mask. Consequently, when the size of aerosol droplets is reduced to values between 100nm and 1 µm, the predominant mechanism is the diffusion caused by Brownian motion and the mechanical interception of aerosol droplets by the canvas fibers of the face mask [19-21].

Therefore, the diffusion of enormously tiny aerosol droplets is more important than interception. As the size or velocity of aerosol droplets decreases, the diffusion mechanism becomes more pronounced. At lower speeds, the retention period of aerosol droplets by the filter medium of the mask increases. As a result, the probability of a collision between aerosol droplets and filter medium increases dramatically. Various tests have shown that when the most of aerosol droplets enter the mask matrix, their velocity decreases sharply due to diffusion within the mask. With such a mass transfer mechanism, a general model of Fick's First law can be applied, which describes the diffusion of mass through a unit of surface area per unit time [21,22],

Electrostatic attraction is a process when electrostatic attraction and suspension of large and small aerosol droplets carried by air streaming occurs. This means that the electrically charged fibers of the silk or other kind of similar materials absorb the oppositely charged particles from the air stream. These types of filters are very useful at low respiratory rates [23,24].

Some studies also deal with the effect of thermal rebound on the filtration performance of nano-salts. The thermal rebound is well described by the critical velocity and kinetic energy of the aerosol droplets. As the mean thermal velocity of Brownian motion increases, so does the rate of capture of aerosol droplets. Also, as the size of the aerosol droplets decreases, the probability of their separation from the canvas surface increases. Finally, very small aerosol droplets do not appear to agglomerate on impact due to their mean thermal velocity, which exceeds the capture rate. As the size of the aerosol droplets decreases, so does their adhesion. In addition, smaller droplets adhere less to the canvas surface. These nano-droplets, thanks to Brownian motion, due to their extremely small size (order of the clusters or molecules) show behavior typical for molecules [25,26].

The efficiency of the mask canvas depends on the particle size. In the range of particle sizes larger than 300 nm, their efficiencies are in the range of 5–80%, i.e. 5–95% for each individual layer of the mask. Considering multiple layers and using a specific combination of different fabrics, such as cotton-silk, cotton-chiffon, cotton-flannel, this efficiency ranges from 80% to 90% for aerosol droplets above 300 nm [25-27].

For sub-micrometer particles filtered by mechanical filters, interception and diffusion are the most dominant mechanisms. At the same time, the inertial impact is negligible, when the contribution of each of these mechanisms is estimated to the depth of aerosol droplet penetration. [28-30].

3. WEAKNESSES AND STRENGTHS OF DIFFERENT TYPES OF PROTECTIVE MASKS

Filters used in respirators and medical masks should allow the user to breathe freely. Increasing the number of layers inside the masks improves its performance, but makes breathing difficult. This effect also depends on the structure of the used canvas material. The fibers diameter inside the mask, the density of their packaging, and the thickness of the canvas in each layer affect the filtration characteristics of the protective face masks. With the increase of the canvas thickness, the penetration depth of the aerosol droplets also increases, with all other parameters being constant. In other words, by reducing the thickness of the fibers, increasing their packing density, or the density of their charge, the filtration efficiency of the mask increases. Therefore, FFP2 masks protect us from viruses somewhat better then surgical masks, but they are not as comfortable as surgical masks. Due to the stronger hydrophobic effect, they repel water droplets somewhat stronger and have slightly better antibacterial protection. The transmission of the virus from the outer surface to the inner surface of the face mask can be also limited by reducing the effective capillary radius, increasing the thickness and angle of contact. Besides, condensation of water vapor, increased temperature and humidity are suitable for cultivation and reproduction of bacteria, increasing the health risks [31-36].

Among numerous parameters that affect the masks‘filtration efficiency, the size of the aerosol droplets and the flow rate are the most important. It was shown that for droplets larger than 0.5 μm the mechanisms of gravity, inertia and interception are predominantly responsible, while for droplets smaller than 0.2 μm the diffusion mechanism becomes dominant. For low flow rates, electrostatic and diffusion mechanisms dominate, while for higher flow rates, interception becomes the dominant mechanism. Parameters such as increase in humidity, temperature, inhalation frequency and changes in flow into cyclic flow decrease filtration efficiency, while increase in thickness and number of layers, packing density, fiber charge density and decrease in fiber diameter, increase filtration efficiency [37,38].

Besides, it is crucial to properly fit the masks, which should adhere well to the different contours of each person's face, as well as to regulate the movement of the masks in a controlled way, especially during the sleep. As a result of inadequate mask fitting, leakage can occur which significantly reduces the mask filtration efficiency. Considering the advantages, disadvantages and possibilities of different types of masks, it seems that there is a lot of opportunities to improve their design, especially by applying 3D technology and artificial intelligence [39,40].

4. DO FFP2 AND FFP3 MASKS PROTECT US SATISFACTORY IN VIRULENT ENVIRONMENTS?

Why FFP2 and FFP3 masks are recommended from World Health Organization (WHO), although they are insufficiently effective, particularly in red zones with high SARS-CoV-2 concentrations, is the main question that must be ask. Although different materials are effective for filtering large droplets, aerosols generated by sneezing, coughing, and speech pass relatively easily through them, regardless of their tissue density, because they ensure only a very weak physical barrier to virus passage. To confirm such evidences, certain researchers performed study based on a probability model to assess the risk of infection at 30s (corresponding to a rapid examination of the patient) and 20 minutes (required for intubation of the patient), by a physician located in such virulent zones. This study includes situations (in the room with a patient infected with SARS-CoV-2), when the mask was not worn, when FFP2, FFP3 or a surgical masks weres worn, as well as when masks made of various materials such as silk or cotton were worn [40,41].

A mean efficiency of 95% and 99% was assumed for FFP2 and FFP3 masks, respectively. The infection risk assessment values were compared at exposures of 20 minutes and 30 seconds, and it was found that the mean risk of infection was reduced by 24 to 94% and 44 to 99%, respectively, depending on the used mask design. At the same time, the risk strongly increases with the increasing the exposure time to the virulent medium. The largest reduction in the estimated infection mean risk was for FFP3 masks, which reduced the initial mean risks by 94% and 99%, respectively, for exposures of 20 minutes and 30 seconds. The risk with FFP2 mask is similar to surgical mask and the previously discussed multilayer mask made from natural origin materials, like cotton and silk. In highly contaminated environments, the risk of infection becomes very high, even for very short contact times between an infective patient and doctor or nurses, and it increases rapidly with the time of their delay in such infective environment [42,43].

Long-term wearing of FFP2/FFP3 masks influences serious contamination because bacteria or viruses accumulate in them more and more over time. To solve such a problem, a significant modification of the FFP2/FFP3 mask can be expected in near future [42,43].

5. TYPICAL MATERIALS FOR MASKS

The materials for masks can be produced by various techniques. One among them is the melt blowing technique, during which charges are incorporated inside of the canvas creating a quasi-permanent electric field that provides adequate particle filtration by electrostatic force. It is well known that membrane filtration efficiency depends on structure (pore size, fiber organization), fiber charge, fiber thickness and diameter, packing density, etc. Consequently, it has been shown that small diameter fibers and large areas that create small gaps compared to long fibers lead to increased filter efficiency [37-43].

Hence, polymeric materials with high electrical resistance and stability, such as polypropylene (PP), polyethylene, polyacrylonitrile (PAN), etc., are the best choice for masks and respirators. However, it is necessary to improve the hydrophilicity of such polymer surfaces to more efficiently capture and filter water droplets. Filtration takes place by the mechanism of electrostatic attraction between the matrix of masks and aerosol particles and depends on the dielectric properties of the material [37-43].

The use of nanofibers in masks and respirators has become dominant over the last decade. Nano-sized fibers offer a very high surface area per unit mass that can improve aerosol capture efficiency. They have a small gap size, low weight, improved permeability and good gap interconnection. Electrospray techniques are most commonly used to produce nanofibers. Surgical masks with a built-in nanofiber filter reduce airflow resistance and improve filtration efficiency compared to commercially available masks. A study of the usability of traditional N95 FFPR (filtering face piece reusable) mask with nanofiber shows that it has a significantly higher efficiency of bacterial filtration than commercially available masks that appear on the market [40-43].

The latest research speaks of the production of nanofiber composites made of PP coated with cellulose acetate (CA) and polyvinylidene fluoride (PVDF) to meet the requirements of FFP2 masks and respirators. Different ratios of CA and PVDF were chosen for testing. The filtration efficiency depended exclusively on the air flow resistance and the gap size, which at best was 5.71 μm. With fibrous membranes made of polyetherimide-silicon dioxide (PEI-SiO_2) produced by the electro-spinning technique, they had a filtration efficiency of 99.992% with better self-cleaning [40-43].

6. RECENT TECHNOLOGIES OF PRODUCING SUPER-HYDROPHOBIC COTTON CANVAS FOR FACE MASKS

The crucial factors in the fabrication of a super hydrophobic surface of various kinds of canvas are an appropriate hierarchical design with stable micro/nanoparticle structures and a low energy surface. For textiles with a fibrous structure on a micro scale, the usual strategy is to incorporate nanoscale particles onto the fiber surface to achieve a desirable micro/nanoscale structure and subsequent fluorination to achieve the request related to minimal surface energy requirements. The most common methods for preparing robust super-hydrophobic canvas surfaces include physical and chemical approaches, as they are wet chemical deposition, electro-assisted chemical deposition, spray deposition, polymer grafting methods, sol-gel processing, chemical etching, plasma treatments „in situ” influencing formation of nanotubes or/and particle growth, CVD and plasma processing technique, etc. [44,45].

The polymer grafting method is based on polymerization techniques. The highly controlled chemical reactions are used in this method to ensure high hydrophobicity of the cellulose fibers in cotton canvas, preferentially. Bearing in mind that cellulose $(C_6H_{10}O_5)n$ is a long-chain polysaccharide of glucopyranose repeating units linked together by a β-1,4 glycoside bond, it is obvious that hydroxyl groups of cellulose (partially or completely) can chemically react with different types of polymer molecules with a special structure and functions, forming cellulose and lignocellulose derivatives. These introduced polymers modify the surface of canvas to achieve the desired hydrophobic or super hydrophobic properties through derivatization reactions [46,47].

The coating immersion method is based on the functionalization of cotton canvas with nanoparticles, nano-filaments or a film layer to achieve the required roughness. Nanoparticles, such as SiO_2, TiO_2, ZnO are often used to create not only necessary roughness and consequently a stable super-hydrophobic surface, but also to enhance mechanical durability [48,49].

The chemical deposition technique (CDT) is based on the control of various deposition parameters, such as pH, bath temperature, composition of chemical mixture and deposition time. These parameters play a decisive role in the process thin films deposition. Using this method, numerous organic nanoparticles were synthesized by imidization of a copolymer of poly (styrene-maleic anhydride) in the presence of palm oil, as a final coating on cellulose substrates. The obtain results showed that the surface treatment of canvas with organic nanoparticles gave super-hydrophobic surfaces, characterized by a static contact angle of 148° [50, 51].

Electrostatic layering assumes a layer-by-layer (LbL) deposition approach to functionalize cotton canvas. It is based on alternating adsorption of oppositely charged polyelectrolyte of nanoparticles on the substrate surface, successfully achieving super-hydrophobicity of the canvas by applying a versatile electrostatic method of self-assembly. LbL and post-fluoridation strategy are significant in the construction of multilayer polyelectrolyte/silicon nanoparticle surfaces. Prior to electrostatic self-assembly, the intact cotton canvas can be treated with a specific solution to obtain an electrified polymer film. The surface morphology and hydrophobicity of the cotton fabrics can be adjusted by using multiple layers of nano silicon dioxide [52].

Chemical deposition from the gas (vapor) phase (CVD) is a chemical process in which gaseous precursor molecules (mainly halides) are transformed into a solid phase, in the form of a thin film on the surface of the cotton canvas substrate. The CVD approach is a simple and effective method of applying super-hydrophobic coatings of cotton fibers. During the precipitation from the vapor phase, the reaction temperature in the chamber must be higher than the boiling point of the precursor. Cotton canvas is firstly placed in a closed chamber for a certain time, in which a vapor of precursors should be introduced. During CVD this precursor is finally adsorbed on the surface of cotton fibers, penetrating into the fibers and influencing a reaction between precursor's halides and hydroxyl groups [52, 53].

Chemical etching method for modification of various kinds of canvas is based on the increase of the surface roughness of the canvas fibers, influenced by chemical etching, using a various coating solution containing poly (vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP), fluoroalkylsilane (FAS) and a volatile solvents [54].

7. RECENT IMPROVEMENTS AND FUTURE PERSPECTIVES

Recently, some kind of surgical masks enables the detection of infectious patients by using temperature-sensitive, thermo-chromatic dyes in masks, which can change color to 32–33°C, even when the temperature changes are very small (only 1°C). If the infected patients use such kind of face masks, they can be easily recognized and isolated from public space. Besides, by using of more thermo-chromic dyes, they can be designed to monitor the temperature rise, relative to normal body temperature. New multifunctional materials with satisfactory antibacterial efficiency and filtration performance from renewable sources can be also successfully manufactured [55-57].

The most important factor in the achieving increased protection of the face masks filters (made from canvas) is fabrication of a super-hydrophobic surfaces with appropriate hierarchical structure which enables stable micro/nanoparticles design and a low energy surface. For canvas with a fibrous structure on a micro scale, the usual strategy is to bind nanoscale particles to the fiber surface to achieve a micro/nanoscale structure and thus the minimal surface energy on the canvas surface [58-62].

To date, many innovative methods have been introduced for the production of super-hydrophobic coatings on a variety of cellulose-based materials, ranging from simple one-step processes to sophisticated multi-step processes, which produce unique coatings with different properties. Super-hydrophobic coatings on cellulose-based materials offer a sustainable and environmentally friendly alternative to fossil fuel-based polymers. In addition, super-hydrophobic coatings usually have several functions that cannot be achieved with traditional water repellency treatments. In the production of super-hydrophobic coatings on cellulose-based materials, wet chemical methods are useful for creating excellent coating durability, which is crucial in applications where the materials must withstand abrasion and multiple washing cycles. The advantage of dry methods is simplicity, simple one-step processes, avoiding organic solvents and any additional drying or curing steps [62-65].

8. CONCLUSIONS

Investigations of the filtration efficiency of various natural fabrics used for manufacturing of protective masks, to prevent the transmission of aerosol-based viruses in the size range of ~10 nm to ~6 µm, have shown that they can provide good protection, usually above 50% in the whole virus size range. A higher number of threads per unit area, in cotton with a denser weave, results in better filtration efficiency, so that a cotton cloth with about 600 TPI can provide an average filtration efficiency of 79 ± 23% (in the range 10-300nm) and 98.4 ± 0.2% (in the range 300nm - 6µm). This efficacy is comparable to the efficacy of epidemiological FPP2 masks.

Also, it has been shown that FPP2 and FPP3 masks, although showing slightly better filtration properties than multilayer masks with canvas made of natural materials, do not show satisfactory protection against SARS-CoV-2 virus, particularly in virulent environments, when their efficiency does not exceed 94% even for very short exposure times.

Besides, it was shown that there is no statistically significant difference in the effectiveness of SARS-CoV-2 protection between the surgical mask and FPP2, and even FPP3 masks, because the virus is about 100 nm in diameter and it is significantly smaller than the diameter of cavities in any face mask used today.

Therefore, in this paper, special attention is paid to the application of new technologies in the production of protective masks that would actively protect both medical workers and the population, since they would be based on a completely different concept. Instead of passive protection, it is possible to achieve active protection by applying such technologies, impregnation of the mask canvas with nanoparticle active systems, which would significantly increase their efficiency against SARS-CoV-2 and other pathogens.

Besides, the paper gave an overview of all the mechanisms by which the aerosol comes into contact with the canvas of the mask and its propagation into its interior. Knowledge of such mechanisms is important for the selection of the optimal technology for mask manufacturing as a hybrid combination in which several kind of canvas are involved, as layers of a multilayer mask.

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IZVOD

KONTROVERZE U VEZI SA STVARNOM ZAŠTITOM OD VIRUSA SARS-COV-2 RAZLIČITIM NAJČEŠĆE KORIŠĆENIM MASKAMA

Maske za lice služe da zaštite respiratorni sistem od neželjenih kapljica aerosola, u kojima su prisutne razne vrste patogena ili zagađivača. Posebno su važne tokom neke pandemije, kao što je pandemija SARS-CoV-2 virusa, kokoj smo svedoci.. Efikasnost filtracije kapljica aerosola koje sadrže virus kod većine komercijalno dostupnih maski je uglavnom nezadovoljavajuća, posebno u uslovima ekstremno virulentnih sredina. Stoga je izazov proizvesti maske sa povećanom efikasnošću filtracije, kako bi se smanjio procenat prodiranja virusa kroz masku. Zbog toga je ključno precizno definisati mogućnosti i ograničenja današnjih najčešće korišćenih epidemioloških maski, da bi se uspešno definisali potpuno novi koncepti proizvodnje maski za lice, koji bi omogućili što delotvorniju zaštitu ne samo medicinskih radnika, već i pacijenata, posebno kada se nalaze u područjima gde je koncentracija virusa izuzetno visoka. Takođe, pokazano je da su pored koncentracije infektivnih patogena u datoj sredini važni i uslovi u kojima dolazi do infekcije datim patogenima, kao što su temperatura i vlažnost unutar datog kontaminiranog prostora.

Ključne reči: *maska za lice, nanočestice, efikasnost filtracije, mehanizam prenosa aerosola, SARS-Cov-2, pamučno platno.*

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