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TITLE

Durability of disposable N95 mask material when exposed to improvised ozone gas disinfection

Key words

Virus, virucidal, viricidal, COVID-19, PPE, N95, Surgical mask, reuse, decontamination

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Authors

Robert G Dennis, PhD
Associate Professor, UNC & NC State Joint Department of Biomedical Engineering
Owner, Micro-Pulse LLC
Co-Owner, Cortical Metrics, LLC
Co-Owner, Flux Health LLC

Benham Pourdeyhimi, PhD
Klopman Distinguished Professor
The Nonwovens Institute
North Carolina State University

Avery T Cashion, PhD
Research and Development Engineer, Sandia National Laboratories[1]

Steve Emanuel, MSE
Technical Staff, UNC & NC State Joint Department of Biomedical Engineering

Devin Hubbard, PhD
Teaching Assistant Professor, UNC & NC State Joint Department of Biomedical Engineering

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Statement of Conflict of Interest

The authors Dennis, Cashion, Emanuel and Hubbard have no financial or commercial interest in any of the material presented in this report, and claim no intellectual priority or rights. This information is offered entirely in the public interest, without restriction or limitation. The author Pourdeyhimi and NC State University hold IP on the base materials tested in this report.

ABSTRACT

The principle finding of this report is that both commercial and a novel material used for N95 mask filters can endure many cycles of disinfection by ozone gas (20 ppm for 30 minutes) without detectable degradation or loss of filtration efficiency.

N95 masks and surgical masks (hereafter referred to as masks) typically use a filtration material fabricated from meltblown polypropylene. To achieve maximum filtration efficiency while maintaining a reasonable pressure drop, these nonwoven fabrics are also electrostatically charged (corona discharge is the most common method used), to maximize attraction and capture of aerosols and solid particulates. Under normal circumstances, the reuse of masks is generally discouraged, but in times of crisis has become a necessity, making disinfection after each use a necessity. To be acceptable, any disinfection procedure must cause minimal degradation to the performance of the filter material. Possible performance degradation mechanisms include mechanical damage, loss of electrostatic charge, or both. One of the most practical and direct ways to measure combined mechanical and electrostatic integrity, and the subsequent ability to reuse mask filter material, is by the direct measurement of filtration efficiency.

In this paper, we report that small numbers of disinfection cycles at reasonable virucidal doses of ozone do not significantly degrade the filtration efficiency of meltblown polypropylene filter material. By comparison, laundering quickly results in a significant loss of filtration efficiency and requires subsequent recharging to restore the electrostatic charge and filtration efficiency.

A common assumption among biomedical scientists that ozone is far too destructive for this application. However, these direct measurements show that mask materials, specifically the filtration material, can withstand dozens of ozone disinfection cycles without any measurable degradation of filtration efficiency, nor any visible discoloration or loss of fiber integrity. The data are clear: when subjected to a virucidal dose of ozone for a much longer duration than is required for viral inactivation, there was no degradation of N95 filtration efficiency.

The specific dosages of ozone needed for ~99% viral inactivation are thought to be at least 10 ppm for up to 30 minutes based upon an extensive literature review, but to standardize our testing, we consider a dose of 20 ppm for 30 minutes to be a reasonable and conservatively high ozone disinfection cycle. The material tested in this study withstood dosages of up to 200 ppm for 90 minutes, or alternatively 20 ppm for up to 36 hours, without detectable degradation, and further testing suggests that up to 30 or more disinfection cycles (at 20 ppm for 30 minutes) would result in less than a 5% loss of filtration efficiency. This report does not address the effect of ozone cycling on other mask components, such as elastics.

CAVEATS and CAUTIONS

This paper discusses the potential use of ozone as an improvised virucidal strategy during a period of national crisis and severe shortages of protective supplies and sanitizing agents. Before undertaking any such action, note that this strategy is not approved by the FDA, and that safety and efficacy has not been established by any federal agency**.**

FDA NEWS RELEASE

FDA Reminds Patients that Devices Claiming to Clean, Disinfect or Sanitize CPAP Machines Using Ozone Gas or UV Light Have Not Been FDA Authorized

“The FDA has identified several manufacturers that are marketing ozone gas or UV light-based products claiming to clean, disinfect or sanitize CPAP devices and accessories in the home,” said William H. Maisel, M.D., M.P.H, director of the Office of Product Evaluation and Quality in the FDA’s Center for Devices and Radiological Health. “Exposure to high levels of ozone gas may worsen a patients’ existing chronic respiratory diseases or increase the chance of a respiratory infection. UV light-based products could cause burns, eye damage or increase the risk of skin cancer due to over exposure. The FDA has contacted manufacturers of products making these claims and asked them to submit data demonstrating their safety and effectiveness.”

The official safety communication from the FDA:

Potential Risks Associated With The Use of Ozone and Ultraviolet (UV) Light Products for Cleaning CPAP Machines and Accessories: FDA Safety Communication

It is also important to note that occupational exposure to ozone is regulated by OSHA (enforceable) and NIOSH (as guidelines). Some regions or localities, such as California, may restrict or prohibit the use of ozone generators. For links to these and other resources, please see the links at the end of this manuscript in these two sections in REFERENCES:

Links to FDA, CDC, and NIH advice on the reuse of N95 respirators

Links to FDA, OSHA, and NIOSH resources and communications regarding ozone safety

INTRODUCTION

During the COVID-19 coronavirus crisis, the shortage of personal protective equipment (PPE) has been severe, especially regarding the availability of N95 and equivalent masks. A great deal of effort has gone into the challenge of the safe reuse of N95 masks, and many strategies have been proposed for the rapid and repeated disinfection of these masks and other PPE. Most of the initial progress has been made by re-purposing existing disinfection technologies in large institutions, such as high-concentration hydrogen peroxide vaporizers (HPV) that are available in large hospitals. Less formal scientific thought has been given to the pressing need for improvised solutions for the more widely distributed need, such as small clinics and medical/dental offices, EMS stations, fire and police, rest homes and care facilities, city, county, and state offices and public services such as water and waste handling facilities, home health care, food distribution and delivery, postal services, and the needs of individuals as they occasionally must venture out for food, fuel, and medicines, not to mention those who work in the many under-appreciated critical functions not directly related to medical care. Also of importance is the reuse of PPE in austere environments, which will be a perennial challenge long after the shortages due to the covid-19 crisis have abated in the large cities of advanced nations. The re-purposing of existing disinfection technologies already in place in large hospitals addresses none of these needs. We consider the use of ozone gas.

Unlike many other disinfectant agents, ozone is uniquely well suited to these exigencies. As a dry gas, it is easily generated at the point-of-use, requires only the initial purchase of a simple corona-discharge ozone generator, which costs less than 100 dollars, and a large plastic box with a tight-fitting lid, and thereafter requires only a standard electrical outlet and atmosphere. No other supplies are required or consumed. But the widespread use of ozone as an improvised disinfectant may be limited by some common misconceptions.

Ozone (O_3) is an extremely potent oxidizer and has been used on a large industrial scale to kill microorganisms, mostly in waste-water treatment and agricultural processing. In particular, ozone is an extremely effective germicide against viruses and bacteria (Dennis et al., 2020; Farooq & Akhlaque, 1983; Gray, 2014; Hudson et al., 2009; Katzenelson et al., 1974, 1979; Li & Wang, 2003; Rojas-Valencia, 2014; Roy et al., 1981; Solomon, Clement; Casey, Peter; Mackne, Colleen; Lake, 1998; Sunnen, 2003; C.-C. Tseng & Li, 2006; C. Tseng & Li, 2008; Wolf et al., 2018; Zhang et al., 2004) . Ozone acts to destroy virus particles through non-specific oxidation of envelope, capsid and nucleic acids (Farooq & Akhlaque, 1983; Lowe, 2020; Rojas-Valencia, 2014; Roy et al., 1981; C.-C. Tseng & Li, 2006; C. Tseng & Li, 2008). In a recent report (Dennis et al., 2020) we discuss the scientific justification of gaseous ozone disinfection, calculate a practical virucidal dosage based on literature, and demonstrate an extremely simple and inexpensive system for generating and maintaining ozone levels in large plastic containers (24- and 61-liter volume). These systems produced ozone concentrations that are likely sufficient for virus deactivation in 10 to 30 minutes, using inexpensive and commercially available components.

As a highly reactive oxidant, ozone is also known to degrade polymers through oxidation of bonds. It is also notable that for materials such as rubbers, ozone is well known to rapidly degrade their mechanical performance to the point of failure (Cataldo, 2001; Clark et al., 1989; Lee et al., 2003; Leusink, 2018; Ma et al., 2010). Coatings such as waxes have been shown to be effective at preventing degradation of rubber (Cataldo, 2001; Ma et al., 2010) an indication that for completed disposable masks with rubber elastic straps, there may be techniques to protect them from ozone during decontamination.

Additionally, masks could be modified to make them more durable in an ozone atmosphere. As a simple example, new straps can be attached with adhesives or small magnets on the inside and outside of the mask to avoid penetration. As another example, mask straps could be replaced with short lengths of fabric (attached to the masks by adhesive, magnets or sewn and sealed with wax) and the fabric lengths can then be tied together with a rubber band. In this second example, the rubber bands are a disposable component which provides the convenient elasticity to hold the masks tight to the face, and the masks can be disinfected many times without elastic degradation.

Collectively, we now realize that the ability to reuse otherwise "disposable" personal protective equipment (PPE) is of great consequence during times of pandemic crisis and shortage, but also a persistent challenge in parts of the world where such disposable items are always in short supply. With or without authorization, people on the front lines of healthcare delivery often have no alternative than to re-use PPE. The question arises: is it safe to do so (Clinical Evidence Assessment ECRI, 2020)? Disinfection and reuse of PPE, a necessity during the time of the COVID-19 crisis, is happening worldwide without much data on the effectiveness or durability and degradation of disposable PPE materials when subjected to laundering and/or disinfection cycles. A rapid, dry, virucidal method is desirable that reliably deactivates virus particles without significantly degrading the substrate PPE material, especially filter and barrier material. In times of extreme crisis, a widely achievable and rapidly scalable disinfection method must be developed, and may require the use of improvised equipment and supplies.

Among the many virucidal strategies under discussion, ozone rarely rises to the top. This is probably due largely to a lack of information and some common misconceptions. For example, many biomedical technologists responded to the suggestion that ozone be considered as a potential disinfectant for disposable PPE with such statements as:

> "Ozone destroys whatever it touches."
>
> "Ozone is known to destroy [a specific material used in PPE]."
>
> "Ozone will create toxic byproducts (or degradation products)."
>
> "That is not FDA approved."
>
> "Ozone is just a pollutant, not a disinfectant."
>
> … and often, "That just won't work."

However, when asked to identify the source of the information that forms the basis for their opinion, or any data which suggests that ozone is ineffective for the purpose of disinfection and reuse of PPE, none was forthcoming. These statements were therefore taken largely as "common sense", without a strong scientific basis; or more specifically, a blanket oversimplification to a nuanced scientific topic. To inform decisions on this topic, *we test the hypothesis that ozone can be applied to two different types of polypropylene N95 mask filter material, in virucidal doses for many cycles, without mechanical damage or degradation of filtration efficiency*. We do not directly address the issue of FDA approval, nor do we measure potentially toxic or harmful byproducts. However, ozone is classified by the FDA as a "generally recognized as safe" (GRAS) component for food processing and is approved by the USDA as an antimicrobial substance for use in the production of meat, poultry, and egg products (FDA, 2019; USDA-FSIS, 2019). We do attempt to show that there is no evidence of degradation of performance of mask filter materials at virucidal doses of ozone exposure. And this, along with further study, may lead to eventual consideration of ozone disinfection for PPE by regulatory agencies as a viable strategy, given that many misconceptions related to mask degradation in ozone have been addressed.

It is important to note that the filtration efficiency of N95 mask material depends not only upon mechanical integrity of the base filter material, but also upon the electrostatic charge that is applied to the material during manufacture. There is always the danger that any method of disinfection may cause loss of electrostatic charge. For example, it is known that saline solutions or even distilled water will cause a very significant loss of electrostatic charge in N95 mask material, as will common disinfectant liquids such as alcohols which can eliminate the electrostatic charge in as little as 15 seconds (Martin & Moyer, 2000).

The primary questions being addressed in this report are:

(1) Do multiple disinfection cycles using ozone exposure (20 ppm for 30 minutes) damage the base polypropylene fiber material?

(2) Do multiple disinfection cycles using ozone exposure (20 ppm for 30 minutes) reduce the electrostatic charge on the filter material?

Both degradation mechanisms result in, and are detectable by, a reduction of filtration efficiency.

In short, the brief answer is “no.” We find that up to 30 cycles at this ozone exposure did not damage the base filter material, nor did it reduce the electrostatic charge, as indicated by the fact that no loss of filtration efficiency was detected until excessive ozone dosages were applied for extreme durations, greatly exceeding 30 exposures at 20 ppm for 30 minutes.

We carry out mechanical testing on mask filter materials with load-deformation analysis to detect the degradation of the base material itself. Mechanical assessment is important because the mechanical properties of the mask account for the initial ~80% of filtration efficiency and the basic mechanical integrity of the mask, required for it to be a practical protective garment that can maintain a seal around the face. We carry out filtration efficiency measurements to detect any degradation of the base material plus electrostatic charge, which must remain intact to retain high (~95%) levels of filtration efficiency.

METHODS

Two types of mask filter material are tested in this report. One is a novel microfiber spunbond polypropylene material (MSP) which is proposed for new N95 mask technology, and the second is the melt blown media (MBM) material classically used in N95 respirator masks.

For the first set of experiments, a special class of microfiber spunbond polypropylene (MSP) filter material was fabricated at the Nonwovens Institute (NWI) at North Carolina State University[1]. The structure is composed of continuous filaments entangled by a series of waterjets. The waterjets result in microfibrillation of the filaments and create fibers that are in the suitable dimension for filtration and are similar to meltblown filter media currently used. This was accomplished on a large scale 1.2-meter-wide pilot line at NWI's facilities. The material in this study was tested in the as-received (uncharged) condition: no corona treatment was used.

For the second set of experiments, NWI fabricated a classical N95 (MBM) filter charged by corona to achieve the 95% filtration efficiency required to meet the industrial standard for N95 mask filtration performance. This represents the standard filter material used most commonly in commercial N95 masks. It is the ability of this material to endure multiple cycles of ozone disinfection that is most directly relevant for the reuse of commercial N95 masks after decontamination by ozone.

Ozone exposure:

Samples pairs of each material were initially razor-cut to 5.2" x 10.4" rectangles, from random locations in a bolt of freshly made fabric. Each sample pair was then split in half to yield paired samples, each 5.2" x 5.2", where each pair is comprised of a control and an ozone-exposed sample from the same location on the bolt of fabric. Sample pairs were numbered with consecutive numbers, odd numbers destined for ozone exposure, even numbers held as paired controls. Thus, each final sample had dimensions of 5.2" by 5.2", and each had a paired control from a nearly identical location on the original fabric. For ozone exposure, each sample was suspended in an open acrylic frame in a small improvised ozone chamber (Figure 1) (Dennis et al., 2020), or loosely rolled to fit into the much smaller chamber for the higher-concentration (200 ppm) experiments.

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[1] High-efficiency spunbond filter medium, US Patent Application Filed, February 2020

Figure 1. Samples of filter material being exposed at controlled ozone concentration in an improvised ozone disinfection chamber.

These sample preparations resulted in two sets of controls: baseline controls as well as paired controls, to prepare for the possibility the fabric was highly variable in terms of filtration efficiency. The additional controls turned out to be unnecessary, but all control data are reported nonetheless, and serve as a clear demonstration of the consistency of the fabrication process.

For the purposes of this study, ozone was generated from room air (not enriched or medical-grade oxygen) by corona discharge using consumer-grade ozone generators as described elsewhere (Dennis et al., 2020). For this study, the "A2Z" brand "bubbler" ozone generator was used, which is functionally equivalent to other "bubbler" ozone generators that deliver ~ 600 mg ozone/hr through a 3/16" ID flexible silicone tube. Regular air was used because the results of this work are intended to inform improvised efforts at disinfection with ozone, where enriched sources of oxygen may not be available, or might be reserved for other uses (such as respiration support). The use of ordinary atmosphere rather than enriched oxygen will result in the generation of many compounds other than ozone (O_3), due to the large amount of nitrogen in atmosphere that is also subject to recombination and reaction under corona discharge.

Ozone concentration was monitored continuously in the same manner as previously reported (Dennis et al., 2020) and held to the test concentrations (10 ppm, 20 ppm, and 200 ppm), within 10%. Testing conditions were: room temperature = 72 - 74 °F and 45% – 55% relative humidity. Ozone levels were achieved within 1 minute and were maintained for the times reported at the ozone concentrations reported +/- 10%.

The first set of experiments were conducted only on the novel MSP material and involved low and very high ozone exposures, using two sets of samples. An initial set of baseline controls was set aside, with no ozone exposure. Samples to be exposed to ozone were given an exposure based on the dosage that is required to achieve a reliable virucidal effect. Ozone *dosage* is calculated as concentration in parts per million (ppm) x exposure time in minutes. For the first set of samples, ozone concentrations of 10 ppm and 20 ppm were used for 60 minutes each. Based on the initial finding that these ozone dosages had no detectable effect on filtration efficiency or degradation by microscopic inspection, a second set of samples were tested using much higher ozone concentration, some with much longer duration. The maximum achievable stable ozone concentration for our apparatus was used: 200 ppm. This very high concentration could only be achieved if the test chamber volume was significantly reduced, and the ozone concentration was determined ratiometrically by air sample dilution. This prevented continuous ozone monitoring at the highest ozone concentration, but allowed for maximum ozone concentration. Sets of samples were exposed to 200 ppm ozone for 15, 90, and 720 minutes.

The second set of experiments involved classical N95 meltblown material (MBM) as well as the novel MSP filter material used earlier. Samples of identical size were cut as above, and designated “C” for corona-charged classical N95 MBM, “F1” for MSP material which was triboelectrically charged prior to ozone exposure, and “FR” for MSP filter material that was triboelectrically charged immediately after ozone exposure. Smaller samples were also cut, 12.7 mm x 50 mm, for tensile testing the materials before and after ozone exposure, along (“A”) and transverse to (“T”) the roller direction on the large scale 1.2-meter-wide pilot line at NWI’s facilities.

After ozone exposure, samples were allowed 1 hour to degas in regular room atmosphere, and thereafter were placed into folders for transport to the flow testing laboratory for filtration efficiency.

Laundering of the MSP filter media:

As a comparative disinfection strategy, samples were put cycles of laundering which simulate household washing. Filtration efficiency was tracked after decontamination through multiple cycles of laundering.

Accelerated laundering of the NWI spunbond filter media (MSP) was performed according to AATCC Test Method 61-1996. Briefly, samples are tumbled in a canister with water, detergent, and steel balls and then removed and rinsed with deionized water. 5 samples were laundered at 5, 10 and 15 cycles. Laundering was done as a separate experiment, on separate samples, without ozone exposure.

Only MSP material was laundered in these experiments. The meltblown filter media (MBM) material would be destroyed in the laundering process due to the fact that the meltblown structures are fragile and can be dimensionally disturbed easily. Therefore, no samples of meltblown filter media were laundered.

Electrostatic Corona Charging:

After laundering, some samples were charged by corona discharge and their filtration efficiency measured. Charging was accomplished by a table-top unit (Simco) with one charging bar. The samples were charged for 5 seconds on the face and 5 seconds on the back.

When the meltblown webs are charged continuously, normally, multiple charging bars are used to ensure that the filters can be charged at full speed.

Filtration Efficiency Measurements:

TSI 8130 Certitest instrument used for NIOSH certification was used to determine the penetration obtained based on the measurement of the flux of light scattering from particles upstream and downstream of the media. Initial penetration levels for polydisperse NaCl particles were measured to avoid a loading effect for better comparison and correlation with other tests. The test face velocities were set at 5.3 at a flow rate of 32 L/min. This flow rate is used for flat media but for actual N95 masks, a higher flow rate of 85 L/min is used. This is due to the fact that the N95 mask surface area is much larger than that of a flat specimen being tested. Five test specimens (5.2” squares) were used for each of the experimental groups studied.

It is important to keep in mind that the base materials (MSP and classical N95 MBM) do not inherently have a filtration efficiency near 95%. As a base material, efficiency may be closer to 80%. They must be electrostatically charged to achieve higher levels of filtration efficiency. One of the concerns about ozone disinfection was whether it would damage the filter by reducing the electrostatic charge.

Tensile Testing:

To detect changes in mechanical integrity that may not have been reflected directly in filtration efficiency, we included a series of basic mechanical tensile tests. Unfortunately, during the early peak of this crisis, mechanical testing facilities were not available as they are considered “non-essential”. Therefore, tests were performed using an improvised tensile tester constructed with a precision Wilson FDIX load cell (50 N, 0.05N resolution) with an RS232 interface at 100 samples/second, and a precise, recently calibrated and tuned CNC mill bed to control strain rate at 1.0 mm/second. Samples were razor-cut using a laser-cut stencil mask. Samples were simple rectangles: width 12.7 mm (0.500”) x 30 mm gauge length. Samples were handled and stored on (or in) polyethylene PE box material (HDPE or TYVEK), because PE and polypropylene are adjacent on the triboelectric chart, and thus spurious triboelectric effects on the specimen materials could be minimized. Four tensile specimens were tested in each group. Specialized sample holder clamps were designed to prevent breakage at the clamp interface. All samples were tested to tensile failure, and samples with a failure within 4 mm of the end clamps were to be excluded from further analysis. Uncharged MSP materials were given a tribo-electric charge by rubbing on a very smooth maple wood surface for 5 seconds. F1 samples were MSP materials triboelectrically charged prior to ozone exposure, whereas FR samples were MSP material triboelectrically charged after ozone exposure.

RESULTS

Ozone:

In the first set of experiments, the objective was to find the limits of ozone exposure where filtration efficiency begins to degrade on MSP filter material. The baseline MSP filtration efficiency was found to be very consistent, with values generally in the range of 81 to 82%, as shown in Figure 1. Paired controls also have nearly identical filtration efficiency. For the ozone concentrations of 10 and 20 ppm for 60-minute exposures, no change in filtration efficiency was detectable. During initial ozone exposures, no loss of filtration efficiency could be detected. In subsequent experiments, with much higher ozone concentration (200 ppm) and much longer exposure times, loss of filter efficiency was evident. A filtration efficiency loss of 4% was observed at very high ozone exposures (200 ppm for 90 minutes), and a functionally important > 50% loss of efficiency at the highest ozone dose (200 ppm for 720 minutes). The results from the first and second experiment are combined onto a single graph (Figure 2).

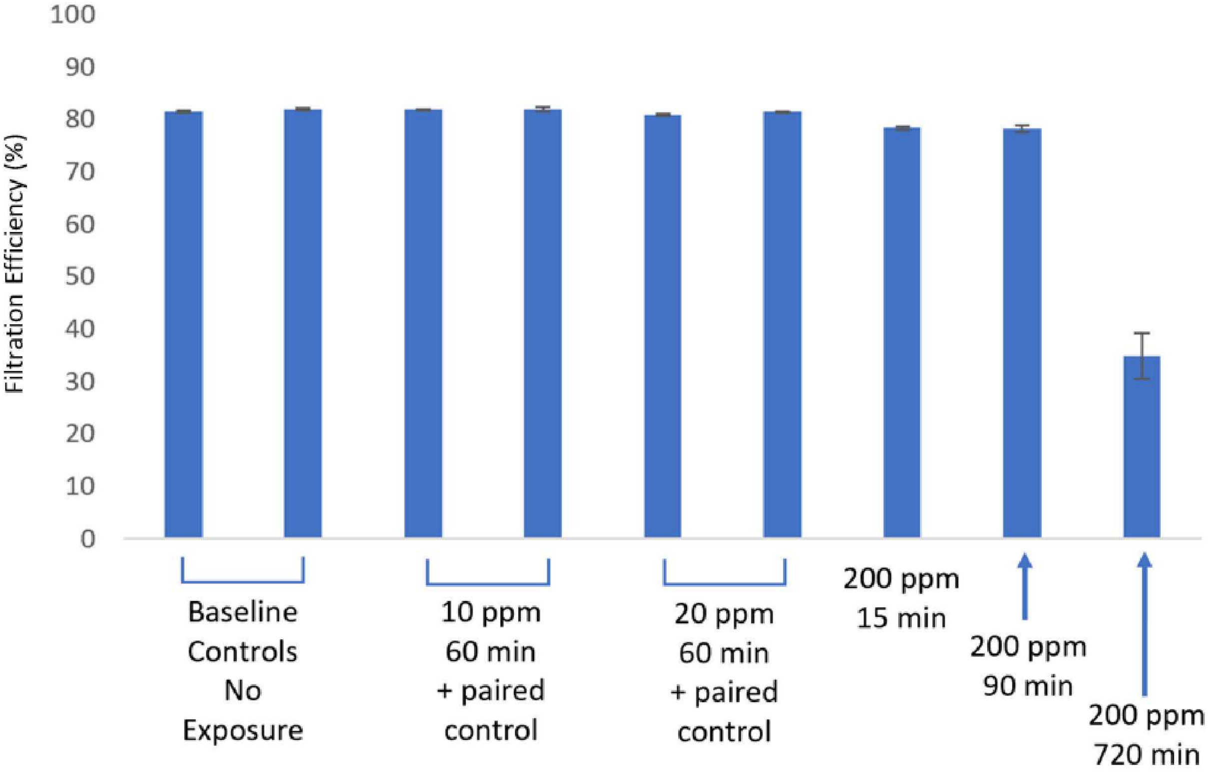

Figure 2. Filtration efficiency of uncharged MSP. The first six bars (to the left) each represent seven samples, whereas the three bars to the right, for the highest ozone dosages, represent 5 samples each. Filtration efficiency was not detectably changed when comparing control fabric samples to those exposed to 10ppm or 20ppm ozone, always achieving a filtration efficiency of 81% to 82%. A small but detectable drop in filtration efficiency was indicated at 200 ppm for 15 minutes and 90 minutes (filtration efficiency dropped to 78.4% and 78.2%, respectively). This is a small reduction in filtration efficiency, corresponding to an ozone disinfectant dosage of 18,000 ppm-minutes. Only at the most

extreme ozone dosage, 200 ppm for 720 minutes, is a major reduction in filtration efficiency observed, down to 34.9%, at an ozone dose of 144,000 ppm-minutes. Mean and standard error bars are shown.

In the most conservative case, and based on the published literature on ozone inactivation of virus, an ozone exposure of 20 ppm for 30 minutes would be considered a very reliable dosage to achieve excellent (> 99%) viral inactivation, which corresponds to a dosage of 600 ppm-minutes (Dennis et al., 2020). The filtration efficiency appeared to drop less than 5% for all but the most extreme ozone dosage. The highest ozone dosage at which filtration efficiency was retained within 5% of control was 200 ppm for 90 minutes, which corresponds to a dosage of 18,000 ppm-min. This suggests that MSP polypropylene fiber N95 filtration mask material could be exposed to 30 disinfection cycles at a conservatively high ozone dosage (20 ppm for 30 minutes) without experiencing more than 5% loss of filtration efficiency in the mechanical aspect of the filter.

It is also of note that before and after ozone exposure, the fabric samples were visually inspected and no visible discoloration or loss of fiber integrity was observed. Also, the filter material was easily able to withstand ozone concentrations that destroyed the Buna-N seals on the original ozone test chamber. Tests had to be paused for maintenance, then resumed after the seals were replaced with a durable silicone sealing gasket material.

Laundering:

The results for laundering tests (no ozone exposure) show that filtration efficiency drops to about 60% following the initial five cycles, with little change thereafter (Figure 3).

The process of laundering can result in structural changes on the filter media. It can also potentially remove any inherent charge in the samples. Note that the spunbond MSP samples were not charged by corona and were therefore assumed to be only mechanical filtration devices. However, the process used in the fabrication of the spunbond process can result in some inherent charge which is partially lost by laundering. This hypothesis is confirmed by the fact that the laundered samples, after subsequent corona charging, can recover filtration efficiency (Figure 4).

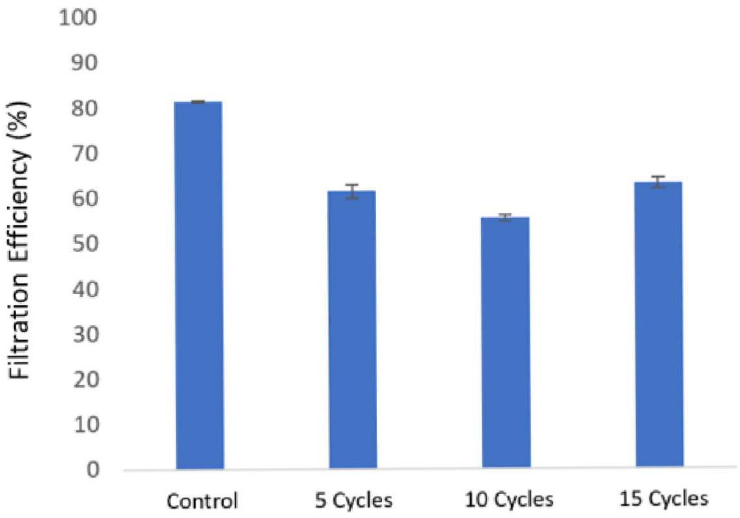

Figure 3. Filtration efficiency of the novel MSP material after laundering.

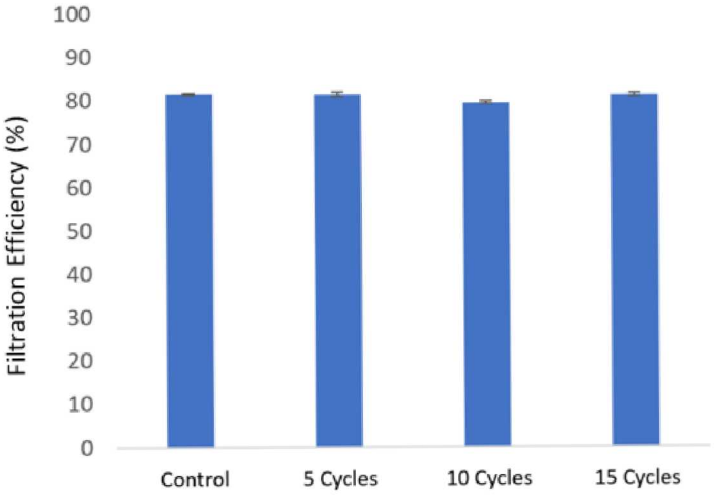

Figure 4. Filtration efficiency of MSP material after laundering followed by electrostatic charging.

Electrostatic charge and filtration efficiency:

In the above experiments, testing was limited to the novel MSP material. To test the ability to expose commercially-available N95 masks to ozone disinfection using ozone, we then ran a series of tests using both the novel MSP filter material and the classical electrostatically-charged N95 MBM filter material. Materials were exposed to ozone at 20 ppm for:

zero minutes (control)

30 minutes (representing one 30-minute disinfection cycle)

3 hours (representing 6 half-hour disinfection cycles)

36 hours (representing 72 half-hour disinfection cycles)

The materials were tested for filtration efficiency initially as-delivered, then after application of an electrostatic charge following ozone exposure, as shown in Figure 5.

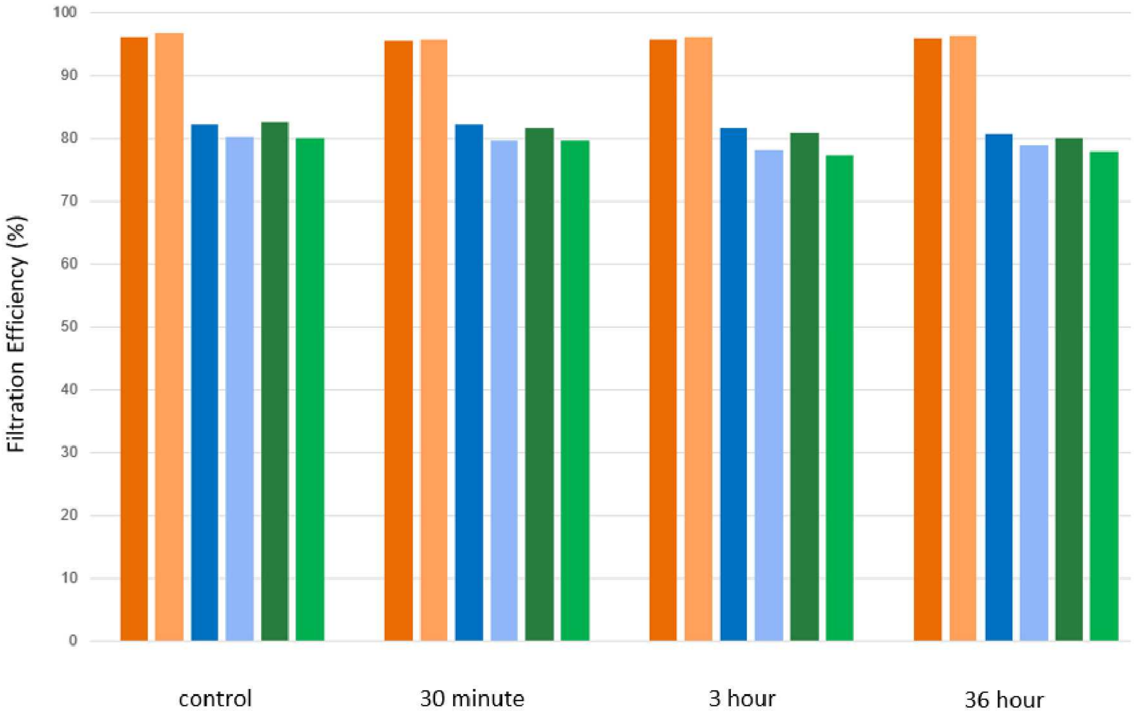

Figure 5. Effect of ozone exposure on charged classical N95 MBM and novel MSP. Orange bars show the effect of ozone on the filtration efficiency of the classical N95 material. Dark orange is tested after ozone exposure without any re-charging afterward, light orange shows the results of the material being recharged after ozone exposure. Blue and green bars show the effect of ozone exposure on triboelectrically-charged (F1) MSP filter material, dark blue is before corona recharge following ozone exposure, light blue is after ozone exposure then corona recharge. Similarly, green bars show the effects on FR material.

Figure 5 demonstrates that ozone exposure of up to 72 disinfection cycles at 20 ppm of 30 minutes each has no measurable effect on filtration efficiency for any of the filter materials or charge conditions tested. Crucially, electrostatically-charged N95 mask filter material in common commercial use (dark orange bars) did not lose its filtration efficiency, and therefore did not lose significant surface charge, even after an equivalent exposure to 72, half-hour ozone disinfection cycles. Before ozone exposure, the mean filtration efficiency was 96.74% (+/- .36% SD), whereas the mean efficiency was at 96.29% (+/- .68% SD) after 72, half-hour ozone exposure cycles (20 ppm).

Tensile Testing:

To fully verify that the mechanical integrity of the filter materials was maintained throughout ozone exposure, basic tensile testing was also carried out. The resulting data were analyzed and are presented using physical units that we feel will most directly address concerns that might arise regarding the mechanical integrity of mask filter materials. This analysis includes questions regarding changes to the peak load capacity of the materials, their stiffness, and their toughness, namely the energy required to distort the material to levels of 20% and 100% of the peak load capacity. These numbers relate directly to the ability of the mask filter material to retain its shape, its elasticity, and to resist tearing during use.

The tested materials show strong anisotropic properties with regard to the roll direction as the material is fabricated. The term “along” refers to tensile properties along the rolling direction, and “transverse” refers to properties measured orthogonal to the rolling direction (Figure 6). The energy required to achieve 20% (Figure 11) and peak load (Figure 10) are also presented.

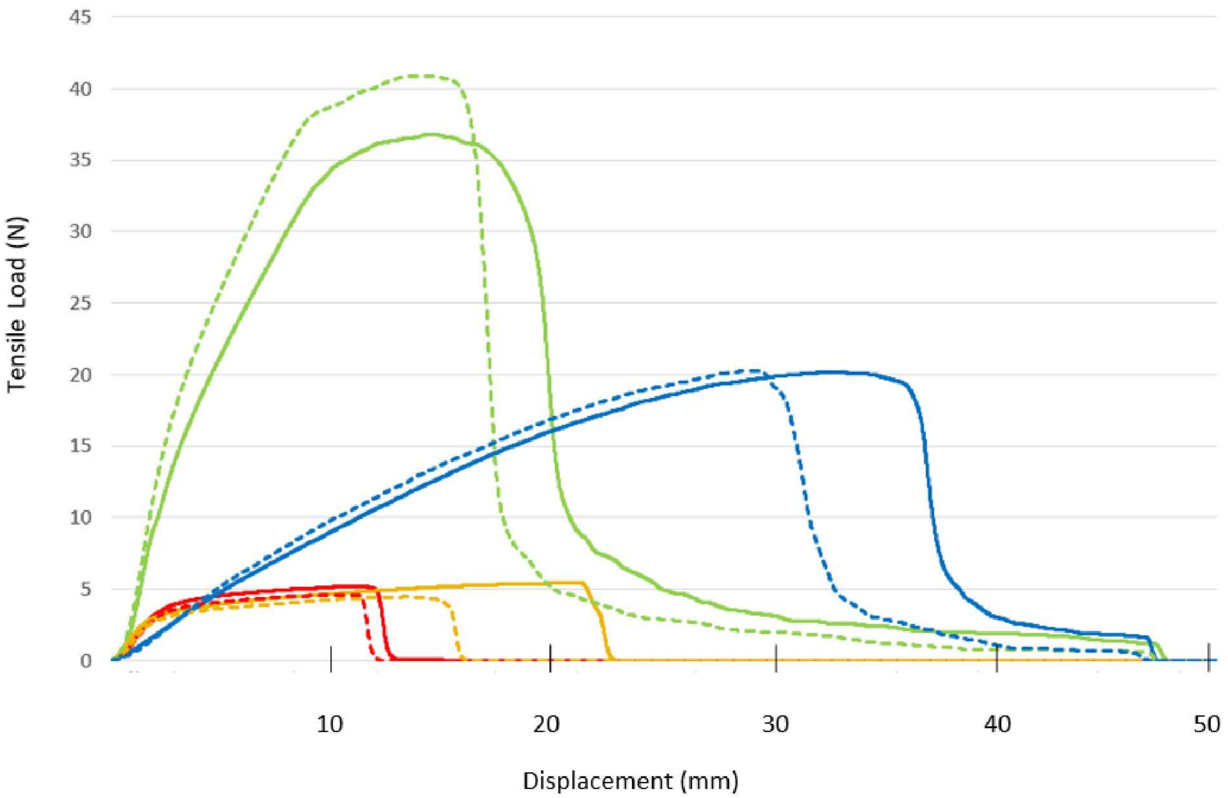

Figure 6. Typical load-deformation curves for the filter material, showing the strong anisotropic behavior of these materials. Red and yellow lines represent classical N95 MBM. Red is along the roll direction, yellow is transverse. Green and blue lines are MSP material. Green lines are along the roll direction, blue is transverse. Solid lines represent materials before ozone exposure, dashed lines represent properties after ozone exposure (20 ppm for 36 hours).

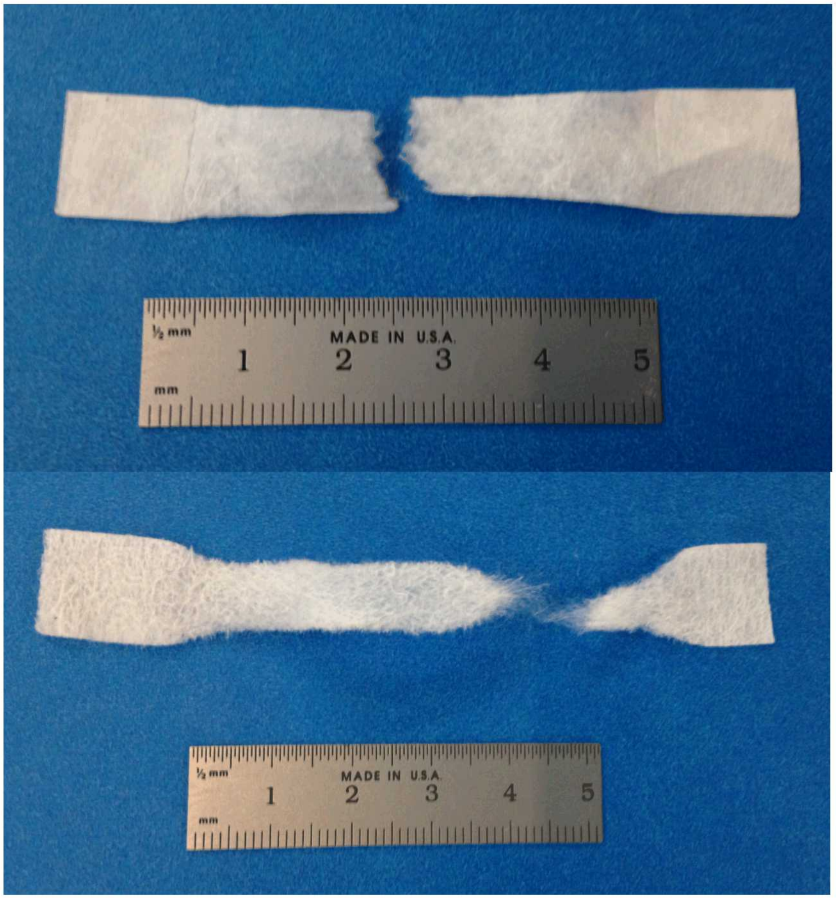

Figure 7. Typical tensile specimens after loading to failure. The classical N95 mask (MBM) filter fabric (above) failed at much lower load and elongation than the MSP filter material (below)

Tensile specimens generally broke at or near mid-gage during testing (Figure 7), and specimens with failures at the end clamp were excluded from further consideration. The tensile specimens exhibited extensive permanent deformation of the fibrous structure when loaded to failure, so it was decided that a better measure of mechanical durability of the filter material would be the energy to 20% strain (Figure 11) and fabric stiffness (Figure 12).

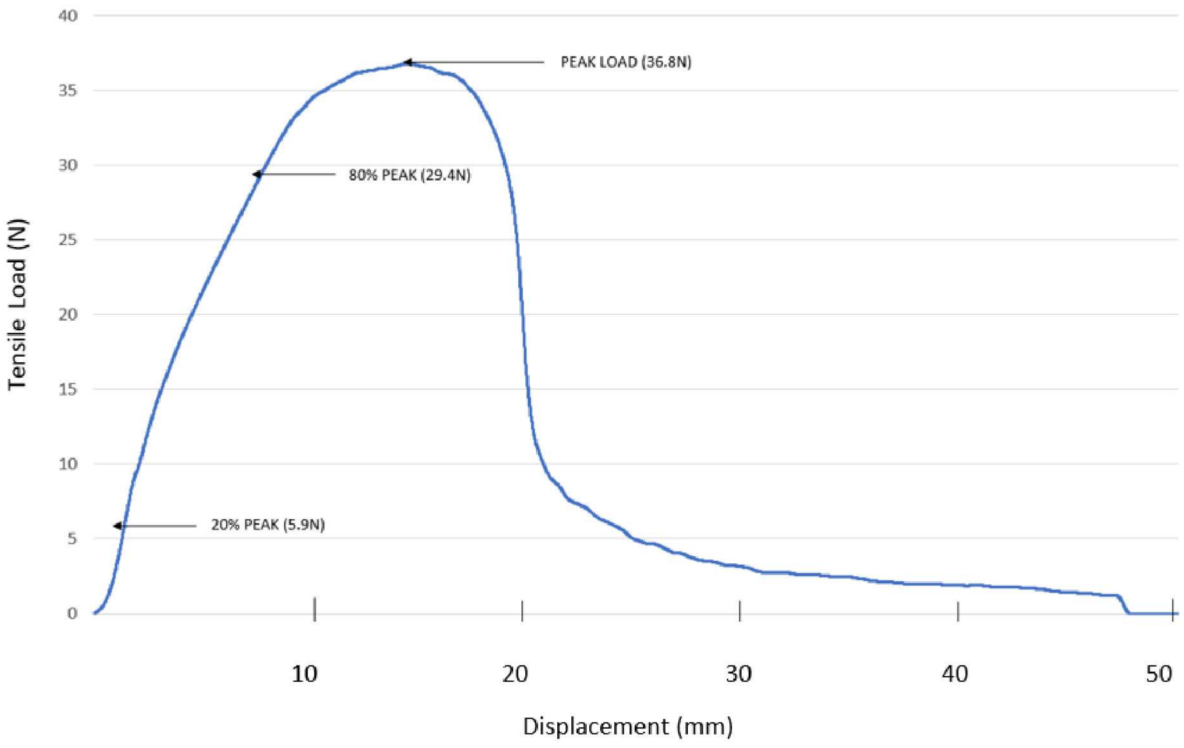

Figure 8. Indication of the key points for calculations on each tensile data chart: peak load, 80% peak load, and 20% peak load. Toughness energy calculations represent a calculation under the curve from zero to the indicated point (20% or peak) in units of mJ.

For tensile testing, three different material conditions were tested (C, F1, FR), in two directions (A, T) each at four different ozone exposure time points (20 ppm ozone for zero, 30 minutes, 3 hours, and 36 hours). "C" designates the classical N95 mask MBM material, corona charged prior to ozone exposure; "F1" is the novel MSP material charged triboelectrically before ozone exposure; and "FR" is the MSP material charged triboelectrically immediately after ozone exposure. The letter "A" designates tensile testing specimens oriented along the roll axis of the fabric as it is manufactures, whereas "T" designates an orientation of the tensile specimen transverse to the roll direction. The summary results for the peak load, strain energy to peak load, strain energy to 20% peak load, and material stiffness are shown in Figures 8 – 11, respectively.

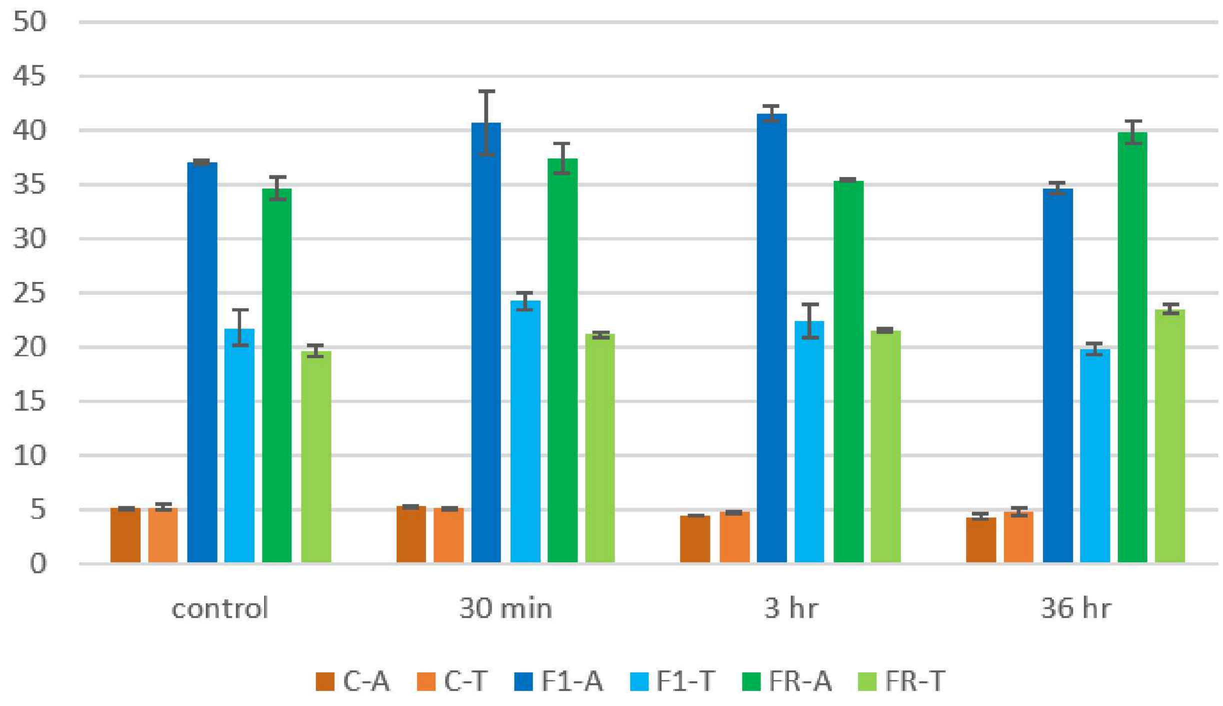

Figure 9. Peak Load (N) for each of the materials tested, along and transverse to the rolling direction during fabrication. Ozone exposure times were zero (control), 30 minutes, 3 hours, and 36 hours. For any given material and test axis orientation, no effect of ozone exposure was evident up to 36 hours at 20 ppm (equivalent to 72 half-hour (30-minute) disinfection cycles).

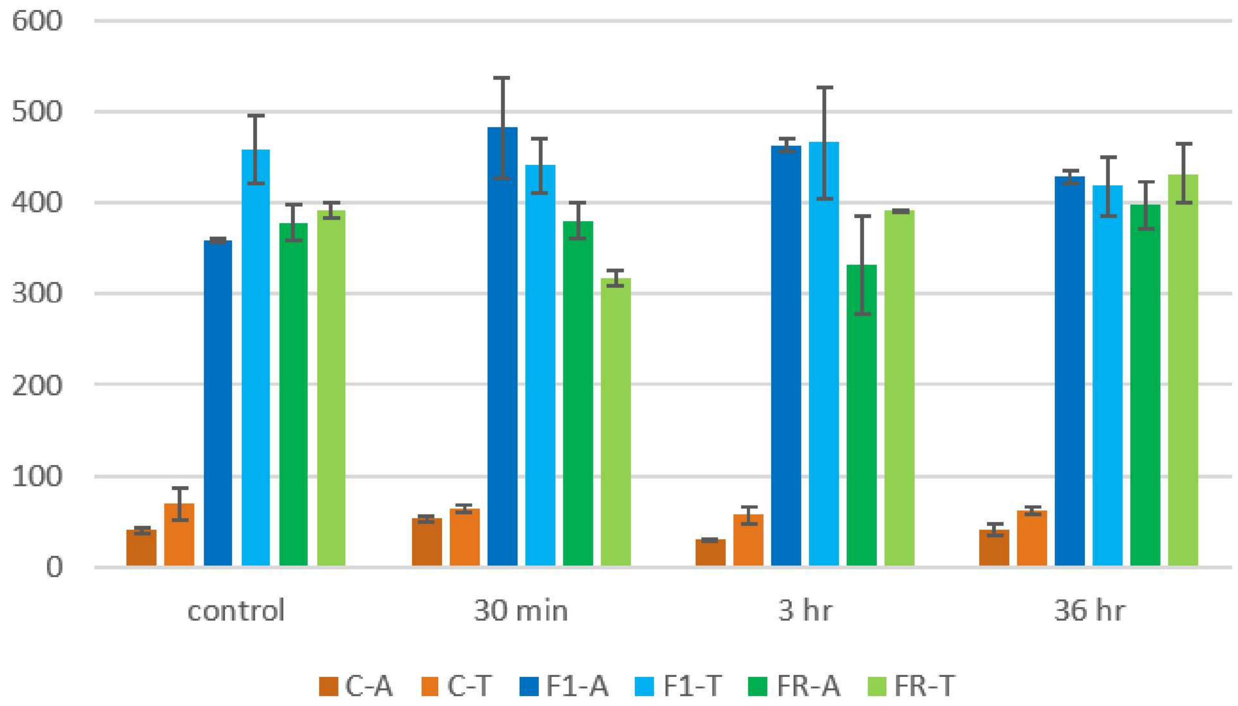

Figure 10. Strain energy (mJ) from zero to peak load for each of the materials tested, along and transverse to the rolling direction during fabrication. Ozone exposure times were zero (control), 30 minutes, 3 hours, and 36 hours. The number of data samples was small, but no trend suggesting a degradation of performance is evident. For any given material and test axis orientation, no effect of ozone exposure was evident up to 36 hours at 20 ppm (equivalent to 72 half-hour disinfection cycles).

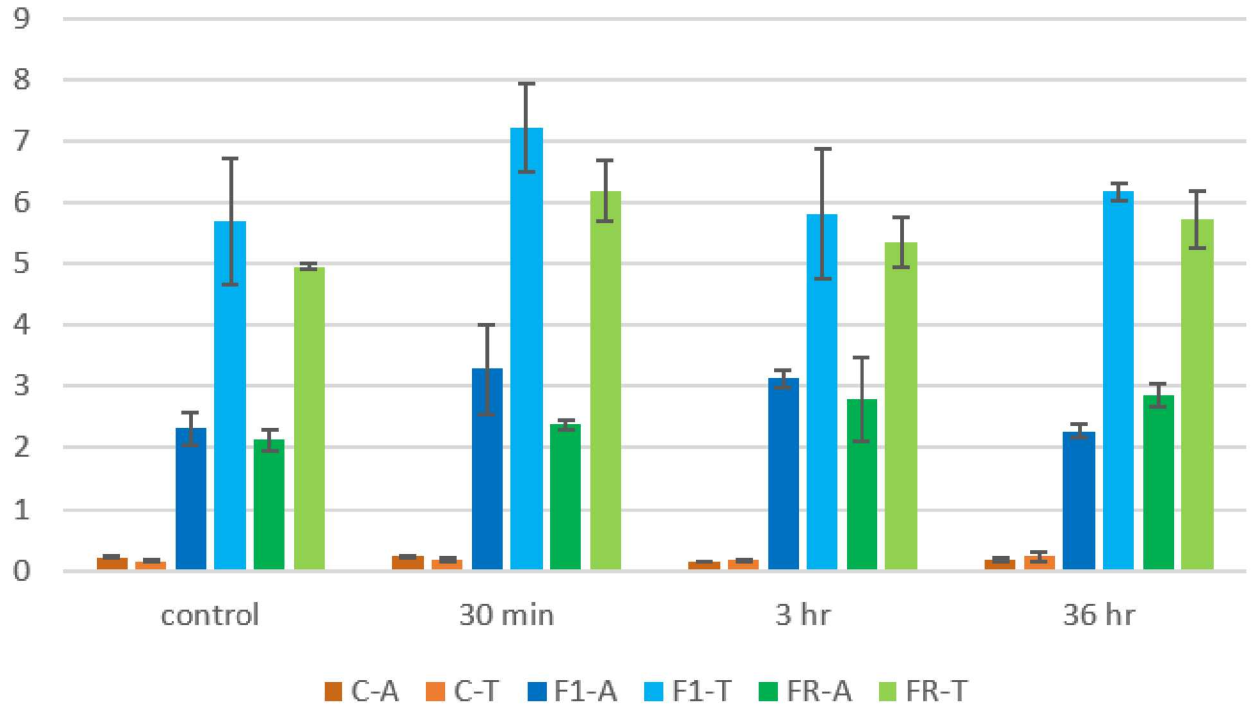

Figure 11. Strain energy (mJ) from zero to 20% peak load for each of the materials tested, along and transverse to the rolling direction during fabrication. Ozone exposure times were zero (control), 30 minutes, 3 hours, and 36 hours. For any given material and test axis orientation, no effect of ozone exposure was evident up to 36 hours at 20 ppm (equivalent to 72 half-hour disinfection cycles).

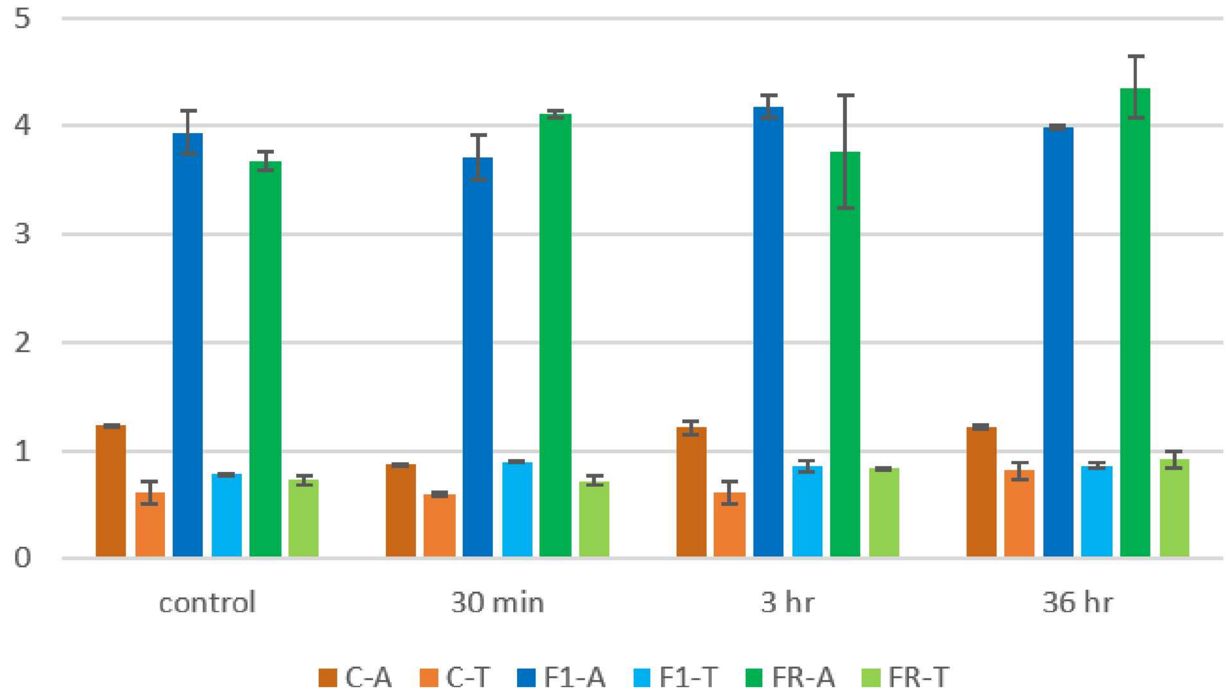

Figure 12. Stiffness (N/mm of gage length elongation) from 20% to 80% peak load for each of the materials tested, along and transverse to the rolling direction during fabrication. Ozone exposure times were zero (control), 30 minutes, 3 hours, and 36 hours. For any given material and test axis orientation, no effect of ozone exposure was evident up to 36 hours at 20 ppm (equivalent to 72 half-hour disinfection cycles).

SUMMARY and CONCLUSIONS

The ozone concentration sufficient to deactivate virus is generally accepted to be in the range of 10 to 20 ppm, for exposure durations on the order of 10 to 30 minutes at relative humidity around 55%. Higher humidity environments require less ozone. For the purposes of this report, and based upon previously published values, we assume a conservatively large ozone disinfection cycle of 30 minutes at 20 ppm. Two types of N95 mask material were tested: classical meltblown material (MBM) with an electrostatic charge applied by corona, and microfiber spunbond polypropylene material (MSP) with an electrostatic charge applied triboelectrically either before or after ozone exposure. Initial testing of MSP exposed to high concentrations of ozone for one hour showed no detectable amount of decreased performance based upon filtration efficiency measures, the key metric for the effectiveness of a filter when filtering aerosols and solid particles. Subsequent experiments demonstrated no loss of filtration efficiency or mechanical properties for either material when subjected to up to 36 hours at 20 ppm ozone, equivalent to 72 disinfection cycles of 30 minutes at 20 ppm.

Durability testing yielded the following results:

Laundering of MSP material resulted in the partial loss of any process-induced charge while ozone appears to have no detectable influence on the performance of these filters. Laundering can also result in structural damage. While this was not observed in this study, it is conceivable that home laundering can result in potential loss of performance. Laundering was not studied further.

The same filter materials (MSP) withstood extremely high ozone concentrations for a duration far in excess of the 10 to 30 minutes necessary for viral inactivation.

Subsequent measurements indicate that ozone exposure had no measurable effect on either classical N95 meltblown material (MBM) or the novel MSP material: no reduction of base filtration efficiency, nor any loss of electrostatic charge as indicated by retention of filtration efficiency, nor any detectable degradation of mechanical properties for up to 72 standardized ozone disinfection cycles (20 ppm for 30 minutes).

Tensile testing showed some variability in tensile specimen mechanical properties as expected, but in no case was there a clear indication of a trend in the reduction of peak load, strain energy, or stiffness as a result of up to 36 hours of ozone exposure at 20 ppm. Comparison of the 36-hour exposure samples to control samples did not indicate a loss of any measure of mechanical integrity greater than 10%, our *a priori* established threshold for detectable mechanical degradation, and therefore we conclude that these materials were not mechanically degraded by ozone exposure (72, 30 min cycles at 20ppm equivalent) to the extent that such would interfere with the mechanical performance of the mask filter material during actual use.

Our measurements and calculations suggest that the N95 filter material tested at high ozone concentration (200 ppm) would withstand the concentration-time equivalent of 30 cycles of a conservatively high virucidal dose of ozone (20 ppm for 30 minutes, or 600 ppm-min) before the loss of > 5% of filtration efficiency, suggesting that high-concentration ozone flash disinfection is also feasible, but was not further studied in the scope of this report.

It is unlikely that the other components of a disposable N95 mask would withstand such repeated ozone exposures, especially elastic bands, and therefore we conclude that mechanical damage and loss of integrity of either of the filter materials tested is likely not the primary failure mode for N95 masks resulting from ozone exposure.

Finally, we conclude that virucidal ozone dosages, which are easily and inexpensively achieved using improvised methods and equipment, may allow multiple reuses of N95 masks without loss of filtration performance. Other components of the N95 mask may not endure this ozone cycling as well as the filter material, and therefore may need to be modified or replaced by improvised means during a crisis.

REFERENCES

Relevant Links:

Links to FDA, CDC, and NIH advice on the reuse of N95 respirators

US FDA advice on N95 Respirators and Surgical Masks (Face Masks)

https://www.fda.gov/medical-devices/personal-protective-equipment-infection-control/n95-respirators-and-surgical-masks-face-masks

Pre-print of article: Assessment of N95 respirator decontamination and re-use for SARS-CoV-2

https://www.medrxiv.org/content/10.1101/2020.04.11.20062018v1

CDC infographic on N95 respirators versus surgical masks

https://www.cdc.gov/niosh/npptl/pdfs/UnderstandDifferenceInfographic-508.pdf

NIH Study Validates Decontamination Methods for Re-Use of N95 Respirators

Three Methods Effectively Sanitized Masks for Limited Re-Use

https://www.niaid.nih.gov/news-events/nih-study-validates-decontamination-methods-re-use-n95-respirators

Appendix A to §1910.134—Fit Testing Procedures (Mandatory)

https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.134AppA

CDC advice on the Decontamination and Reuse of Filtering Facepiece Respirators

https://www.cdc.gov/coronavirus/2019-ncov/hcp/ppe-strategy/decontamination-reuse-respirators.html

List N: Disinfectants for Use Against SARS-CoV-2

All products on this list meet EPA’s criteria for use against SARS-CoV-2, the virus that causes COVID-19

https://www.epa.gov/pesticide-registration/list-n-disinfectants-use-against-sars-cov-2

Links to FDA, OSHA, and NIOSH resources and communications regarding ozone safety

https://www.fda.gov/news-events/press-announcements/fda-reminds-patients-devices-claiming-clean-disinfect-or-sanitize-cpap-machines-using-ozone-gas-or

https://www.fda.gov/medical-devices/safety-communications/potential-risks-associated-use-ozone-and-ultraviolet-uv-light-products-cleaning-cpap-machines-and" https://www.fda.gov/medical-devices/safety-communications/potential-risks-associated-use-ozone-and-ultraviolet-uv-light-products-cleaning-cpap-machines-and

https://www.cdc.gov/niosh/topics/ozone/default.html" https://www.cdc.gov/niosh/topics/ozone/default.html

https://www.osha.gov/chemicaldata/" https://www.osha.gov/chemicaldata/

Quick reference links for ozone information

https://www.ozonesolutions.com/knowledge-center/osha-and-ozone.html" https://www.ozonesolutions.com/knowledge-center/osha-and-ozone.html

https://www.oxidationtech.com/ozone/ozone-production/corona-discharge.html

https://www.oxidationtech.com/ozone/o3-half-life.html

Materials ozone resistance chart. Oxidation Technologies, LLC. https://www.oxidationtech.com/blog/materials-ozone-resistance-chart/

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