

Accelerated Aging of Surgical N95 Filtering Facepiece Respirator (FFR) Straps: Pressure Reactor Vs. Oven Aging Methods

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ABSTRACT

Personal Protective Equipment (PPE), such as surgical N95 filtering facepiece respirators (FFR), undergoes oxidative degradation during extended storage, potentially compromising its effectiveness. This study aimed to develop a screening test for oxidative degradation of surgical N95 FFR straps. Straps from three respirator models were aged using traditional oven aging at 70 °C under ambient air or in a pressure reactor at room temperature under oxygen pressures of 20 or 40 bar. Characterization using tensile tests and Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy showed that pressure reactor aging significantly accelerated degradation more than traditional oven aging. Straps maintained stability up to a critical oxidative threshold, beyond which significant deterioration occurred. ATR-FTIR analysis underscored the complexity of assessing oxidative degradation due to variable chemical composition across models. This research highlights that mechanical properties, particularly modulus, can serve as reliable indicators of long-term stability and performance, offering a more streamlined and direct approach for future PPE evaluations. The pressure reactor aging at room temperature not only expedites degradation assessment but also potentially more closely mimics real-time aging on the shelf, which could simplify the design of future studies and support the development of standardized oxidative degradation screening tests for various types of PPE.

Keywords: accelerated aging, surgical N95 filtering facepiece respirators (FFR), personal protective equipment (PPE), PPE longevity, respirator straps, degradation screening

INTRODUCTION

During global health emergencies, the reliability and effectiveness of Personal Protective Equipment (PPE) are paramount. In some cases, the Strategic National Stockpile (SNS) may store respirators for up to 13 years (National Personal Protective Technology Laboratory 2020; Rottach and Lei Z. *et al.* 2017). However, long-term storage poses significant challenges due to material degradation resulting in sub-optimal performance (Brun *et al.* 2020; Yorio, Rottach, and Dubaniewicz 2019). In the case of surgical N95 filtering facepiece respirators (FFR), the straps are more prone to failure than the filtration components (Rottach and Lei Z. *et al.* 2017). The strap material, typically made from polyisoprene – a synthetic variant of natural rubber known for its elasticity but also its susceptibility to oxidative degradation (Hernández *et al.* 2019; Straus & Madorsky 1957).

The standard practice for estimating the shelf-life of polymeric devices involves accelerated aging at elevated temperatures and using the Arrhenius equation to extrapolate the results to ambient conditions. Standards, such as ASTM D7160-16 for the expiration dating of medical gloves (ASTM D7160-16 2012) and ASTM F1980-21 for accelerated aging of sterile barrier systems in medical devices (ASTM F1980 2016), provide guidelines for testing. However, these methods usually require testing at multiple temperatures, covering a range necessary to establish a lifetime estimation by extrapolation, to verify that the degradation processes occurring during the accelerated aging are representative of the real-time aging. Alternatively, the use of a conservative aging factor (Q10) of 2.0 is recommended for calculating the accelerated aging shift factor based on the ratio of reaction rates at elevated and ambient temperatures

(ASTM F1980 2016). However, assessing the effects of long-term shelf storage exceeding a decade would require impractically long test times using these traditional accelerated aging methods. For example, based on the Q10 relationship in ASTM F1980-21, matching the effects of 10 years of real-time aging would require accelerated aging at 60 °C for over 2 years. The practical application of these methods is further complicated by the limitation on how much the temperature can be increased without inducing non-representative degradation mechanisms, such as diffusion-limited oxidation (DLO), where accelerated surface reactions do not allow for or accurately reflect the bulk material degradation over time (M. C. Celina *et al.* 2013; Gillen, Bernstein, & Celina *et al.* 2005; Gillen, Bernstein, & Derzon *et al.* 2005).

Traditional accelerated aging methods at higher temperatures fail to accurately simulate real-world oxidative degradation mechanisms, necessitating excessively prolonged testing at temperatures marginally above ambient. Consequently, screening methods are crucial in the materials selection and testing process. These methods are designed to rigorously challenge the materials, allowing for an evaluation of their stability by comparing them against the performance of materials with known performance record under similar aggressive conditions. For example, ASTM F2003-02 (2022) recommends oxidative degradation of ultra-high molecular weight polyethylene (UHMWPE) for estimating its shelf-life by aging it in a pressure reactor with 5 bar O₂ gas pressure at 70 °C for 2 weeks (ASTM F2003-02 2010). However, this approach predominantly induces surface oxidation in UHMWPE, in contrast with the bulk oxidation typically observed after prolonged real-time shelf aging. Toohey *et al.* have demonstrated that pressure reactor aging at 25 °C promotes more bulk oxidation of UHMWPE than aging at 70 °C (Toohey, Blanchet, and Heckelman 2003).

Since polyisoprenes are inherently more susceptible to oxidative degradation than UHMWPE due to the unsaturation in their molecular structure (Azhar *et al.* 2023), we hypothesized that aging the surgical N95 FFR in a pressure reactor at similarly high temperatures may also lead to surface-limited oxidation. Therefore, the surgical N95 FFR straps were subjected to pressure reactor aging at room temperature, with the intent that ambient temperature conditions would allow for a more uniform degradation process simulating the oxidative aging that occurs over extended periods in real-world conditions. Since the efficiency of a respirator relies on both the filtration and the precise fit of the respirator (Forouzandeh, O'Dowd, and Pillai 2021), the modulus, a measure of material stiffness, is integral in ensuring an ideal fit. Therefore, our evaluation of aged respirator performance is predicated upon modulus as a critical performance indicator. Furthermore, Infrared Spectroscopy techniques were employed to quantify the level of oxidative degradation by calculating the oxidation index (OI) of the respirator straps. This method is commonly used for assessing oxidative degradation of UHMWPE and is described in ASTM F2102. Similarly, the peak area changes in hydroperoxide (-ROOH), centered at 3425 cm⁻¹, and carbonyl groups (-C=O), centered at 1717 cm⁻¹, were used to investigate the degradation of natural rubber under UV irradiation (Kim *et al.* 2016). A quantitative analysis of thermal degradation of polyisoprene also utilized the carbonyl band area ranging from 1680 cm⁻¹ to 1800 cm⁻¹ (Azhar *et al.* 2023).

In this study, the straps of surgical N95 FFR were subjected to aging either in a pressure reactor at 25 °C with oxygen gas pressures of 40 bar or 20 bar, or in a traditional oven at 70 °C. Tensile tests were performed to assess changes in mechanical properties of the straps, and ATR-FTIR was used to evaluate their degree of oxidation based on oxidative functional groups such as carbonyl groups, aldehydes, ketones, trans-vinylene, and bond breakage within the alkene group. This research provides a foundation for developing standardized oxidative degradation screening methods, with potential future comparisons to real-time aged respirators stored in the Strategic National Stockpile (SNS).

In summary, the objective of this research is to develop a more representative and efficient method for accelerated aging of respirator straps, leveraging ambient temperature conditions in a pressure reactor to mimic real-time degradation more closely than traditional high-temperature aging. This approach aims to establish a reliable screening method that uses modulus as a primary indicator of long-term respirator strap integrity and performance.

MATERIALS AND METHODS

Materials

Three different surgical N95 FFR were selected for this study. The respirator brands have been de-identified and are referred to as Respirator A (180mm x 7mm x 0.9mm), Respirator B (220mm x 7.5mm x 0.9mm), and Respirator C (220mm x 7.5mm x 1mm) throughout this study. The respirators were purchased from third party contractors and were tested within a month of receiving.

Accelerated aging

Three accelerated aging methods were employed, and each sample was treated to one of these methods: traditional oven aging (as per ASTM D7160-16) at 70 °C or modified accelerated aging using a 1 L pressure reactor (Parr Instruments, IL) at room temperature with oxygen gas pressurized to 40 bar or 20 bar. In oven aging, the respirator straps were suspended on shelves within the oven, ensuring uniform exposure to a constant temperature of 70 °C. In reactor aging, the pressure reactor was filled with oxygen gas up to the predetermined pressure and then left in a fume hood at room temperature. Samples were removed periodically for analysis under two aging conditions: oven aging and reactor aging. For oven aging, samples were removed at t0 (0 days), t1 (7 days), t2 (14 days), t3 (21 days), t4 (28 days), t7 (49 days), t11 (77 days), t16 (112 days), and t28 (196 days) (see Table S1). For reactor aging, the removal times included t0 (0 days), d1 (1 day), d2 (2 days), d3 (3 days), t1 (7 days), t2 (14 days), t3 (21 days), t5 (35 days), and t8 (56 days) (see Table S4). Each time, the samples were exposed to ambient conditions for approximately 120 minutes to perform mechanical tests and Attenuated Total Reflected Infrared Spectroscopy (ATR-FTIR) tests before being returned to the reactor to continue the aging process. This process was repeated for each sample to ensure consistent aging condition.

Tensile Tests

The mechanical properties (breaking force and % elongation at break) were measured using an Instron 33R 4465 tensile tester (Instron, MA, USA) with modified tensile testing method from ASTM D 412-16 2016. The dimensions of the respirator straps were 180 mm × 7 mm × 0.9 mm for Respirator A, 220 mm × 7.5 mm × 1 mm for Respirator B, and 220 mm × 7.5 mm × 1 mm for Respirator C (length × width × thickness). The initial length l_0 for tensile testing was carefully measured to 20 mm using a vernier caliper, marked on the strap, and cut with scissors to ensure uniformity, and the strain rate was 200 mm/min. Three samples were tested for each respirator at room temperature and humidity for every aging step, which included which included t0 (0 days), t1 (7 days), t2 (14 days), t3 (21 days), t4 (28 days), t7 (49 days), t11 (77 days), t16 (112 days), and t28 (196 days) for oven aging, and t0 (0 days), d1 (1 day), d2 (2 days), d3 (3 days), t1 (7 days), t2 (14 days), t3 (21 days), t5 (35 days), and t8 (56 days) for reactor aging. The straps were mounted on a self-tightening grip.

The breaking force (ultimate force) and elongation at break (ultimate strain) were calculated by finding the maximum force at break and maximum displacement, respectively. Modulus was obtained from the initial slope of the force-displacement curve. Toughness or the area under the force-displacement curve was calculated by integrating the area under the graph of force-displacement curve. It is important to mention that modulus data from this study is different from Young's modulus, which can be obtained by calculating the slope of true stress $\sigma = F/A$ (where F is the force required to break and A is the instantaneous cross-sectional area) versus true strain at break $\epsilon_T = \ln(l/l_0)$ (where l is the actual length of the respirator before it breaks and l_0 is the original length of the respirator or gauge length).

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR)

Infrared spectra were obtained using a Nicolet Summit FTIR spectrometer (Thermo Fisher Scientific) equipped with an ID7-ATR accessory, containing a diamond crystal with a fixed incident angle of 45°. The specimens were analyzed by absorbance spectra in the region between 4,000 and 400 cm^{-1} , with 32 scans at 4 cm^{-1} resolution using OMNIC software by Thermo Fisher Scientific. The collected spectra for each sample were baseline-corrected using Thermo Scientific OMNIC software. All the spectra were normalized

to the absorption peak centered at 1370 cm^{-1} peak. The carbonyl region includes contributions from ketone C=O stretching (around 1730 cm^{-1}), aldehyde C=O stretching (around 1740 cm^{-1}). These peaks collectively represent the oxidative features in the samples. Oxidation indices (OI) were calculated as the ratio of the area of the peak corresponding to the carbonyl (C=O) functional groups ($1650\text{--}1850\text{ cm}^{-1}$ for respirator A, $1700\text{--}1800\text{ cm}^{-1}$ for respirator B and $1600\text{--}1800\text{ cm}^{-1}$ for respirator C) to the area of the peak under the region $1330\text{--}1396\text{ cm}^{-1}$, which corresponds to the stretching of the alkyl (C-H) bonds.

Statistical Analysis

One-way analysis of variance (ANOVA) was employed as a statistical technique to assess whether there were significant differences in mechanical properties based on varying accelerated aging times, which served as the independent variable in the study. ANOVA allows us to compare multiple groups and determine if there are statistically significant differences among them.

Tukey's Honest Significant Difference (HSD) test was used post hoc. Post hoc tests are employed after an ANOVA to pinpoint specific pairwise comparisons that exhibit statistical significance. In this case, Tukey's HSD helped identify which specific combinations of aging times showed significant differences in mechanical properties. All statistics were conducted in JMP version 14 (SAS Institute Inc., Cary, NC).

RESULTS

Figure 1 presents force-displacement curves for untreated respirator straps from three surgical N95 FFR, assessed prior to any aging treatment. Tensile testing of three individual samples per respirator type confirmed intra-sample consistency, ensuring the reliability of the tensile properties for each type of respirator strap. Despite uniformity within each respirator type, inter-sample comparisons revealed distinct tensile behaviors between respirator models. Respirator B and Respirator C showed a similar maximum force at strap breakage (0.08 kN and 0.07 kN , respectively), while Respirator A had a significantly lower maximum force at breakage (0.03 kN) (Table S1-S3 in the supplemental materials). In terms of elongation, the average elongation at break for Respirators A, B, and C was measured at 460 mm , 550 mm , and 300 mm , respectively. The stress-strain slopes, indicative of the modulus before the yield point, were approximately 1.03 MPa for Respirator A and 1.92 MPa for Respirator C, with Respirator B showing a markedly higher modulus of 20 MPa (Figure 1, inset).

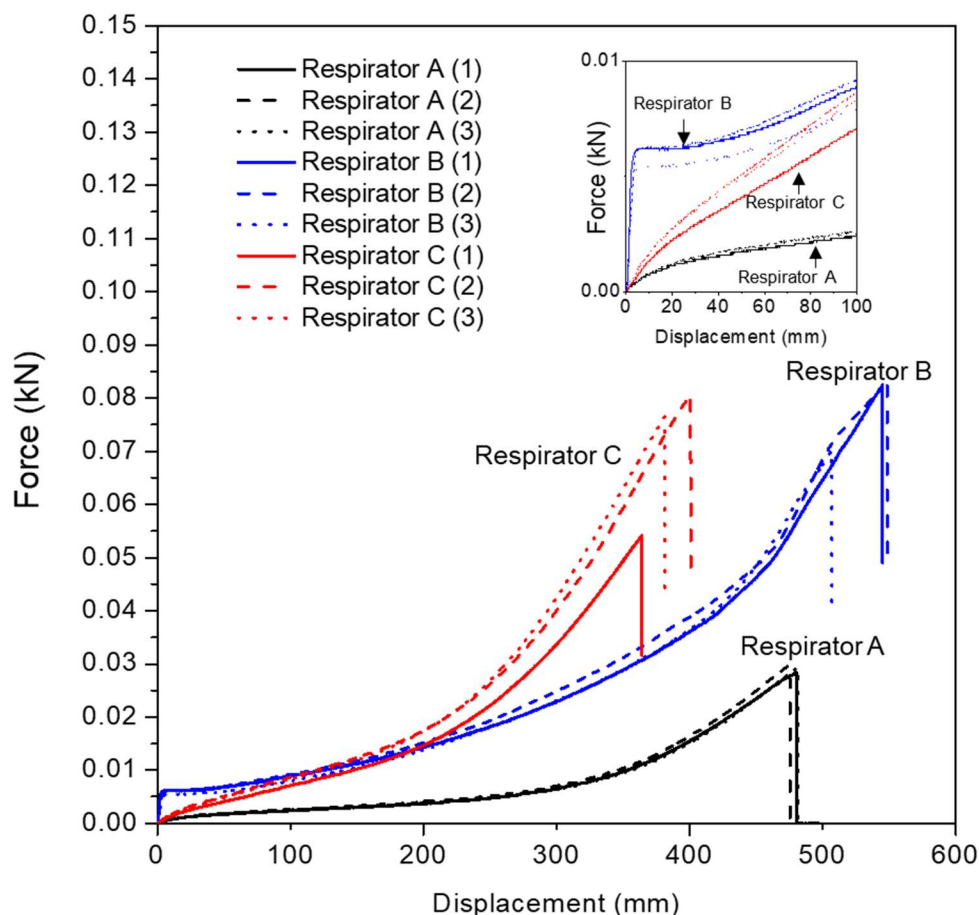


Figure 1. Force-displacement curve of untreated respirator straps (Respirator A, Respirator B, and Respirator C) tested at a rate of 200 mm/min. Zoom-in data of the region before yield point (insert).

Figure 2 shows the mean modulus values of the respirator straps following treatment under three different accelerated aging conditions. The observed changes in modulus over aging time reflect alterations within the polymer's bulk structure. Pressurized reactor aging at 25 °C with 40 bars and 20 bars of O₂ resulted in more pronounced and rapid degradation compared to oven aging at 70 °C. Initially, a decrease in elastic modulus is evident for all respirator straps at day 1 of aging at 25 °C, 40 bar and day 2 at 25 °C, 20 bar. Subsequently, the mechanical properties appeared to stabilize, suggesting a possible saturation of reactive sites available for further oxidation or compensatory mechanisms within the material's microstructure, such as cross-linking or other chemical transformations that might mitigate further degradation. However, the precise reasons for this stabilization remain unclear due to the proprietary material compositions of the respirator straps. This period prior to the observed stabilization marks a critical oxidative threshold or induction period that serves as a key point for evaluating the onset of significant oxidative changes. In contrast, oven aging resulted in negligible modulus variation over approximately 112 days (Figures S2-S4 in the supplemental materials).

The oxidative degradation of polymers such as polyisoprene that are commonly used in surgical N95 FFR straps, leads to the formation of various chemical species, including aldehydes, ketones, alcohols, carboxylic acids, hydroperoxides and trans-vinylene. While ATR-FTIR spectroscopy detects changes in functional groups due to accelerated aging, the unknown and potentially complex chemical composition poses challenges in precisely determining oxidative degradation mechanisms.

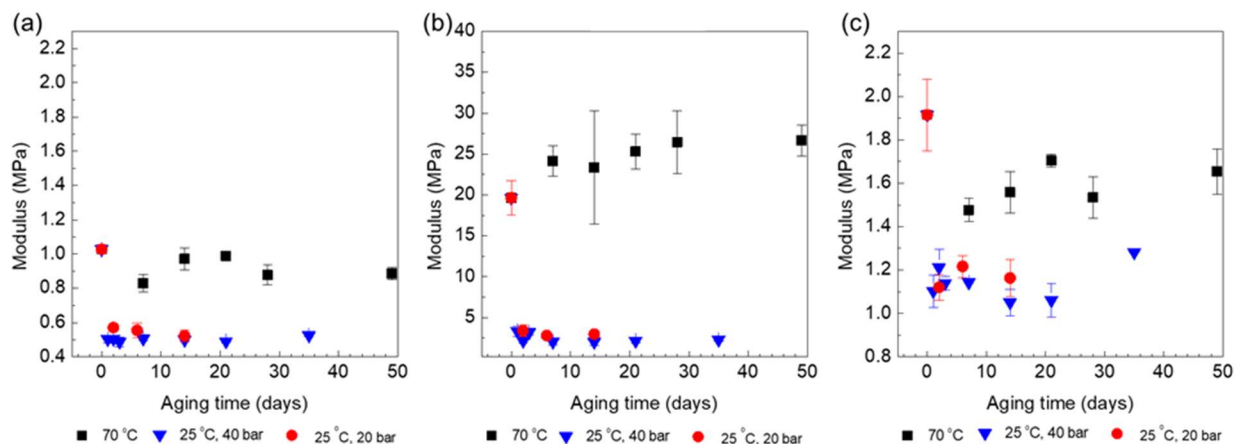


Figure 2. Modulus versus aging time graph: (a) Respirator A, (b) Respirator B, and (c) Respirator C. Samples aged in the oven at 70 °C are represented by black squares and samples aged in pressure reactors at 40 bars or 20 bars, both at 25 °C, are represented by blue triangles and red circles, respectively

Figure 3 illustrates the normalized infrared spectra of unaged respirators, highlighting distinct peaks that suggest variations in chemical composition across respirators. For instance, Respirators A and C exhibit a peak corresponding to C=C bonds near the 1640 cm^{-1} region, absent in respirator C. Only Respirator C showed a pronounced peak in the $3200\text{--}3600\text{ cm}^{-1}$ region, potentially indicating -OH or N-H groups. Both Respirator A and C displayed peaks corresponding to the trans-vinylene functional groups in the $800\text{--}1200\text{ cm}^{-1}$ region, not present in Respirator B, indicating differences in oxidation susceptibility. Additionally, Respirator C exhibits a strong, sharp peak near $1700\text{--}1730\text{ cm}^{-1}$, associated with N-H stretching vibrations, and a distinct peak around $1530\text{--}1590\text{ cm}^{-1}$, typically linked to the C-N bond stretching vibrations, suggesting that this respirator might be composed of polyurethane or similar nitrogen-containing polymers (Strankowski *et al.* 2016).

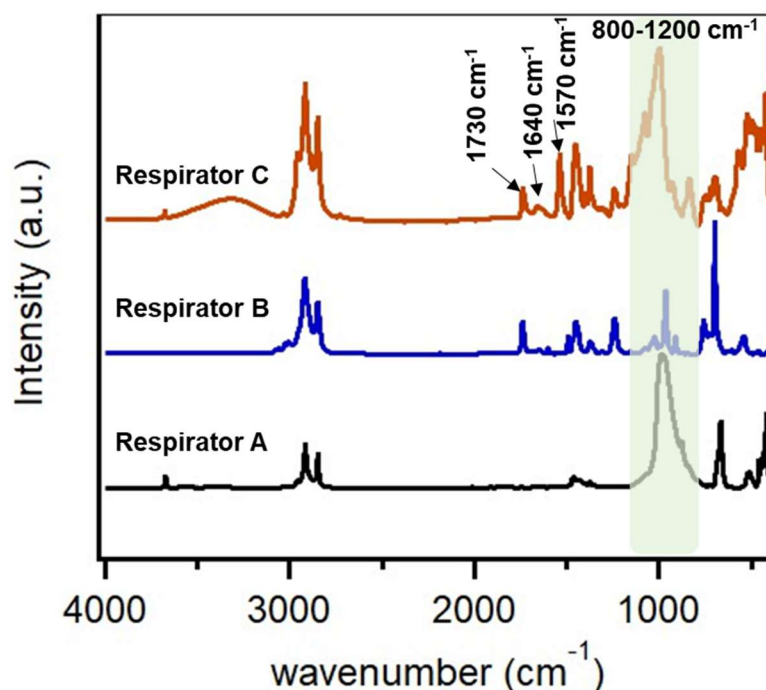


Figure 3. Representative ATR-FTIR spectra of untreated straps from Respirator A, Respirator B, and Respirator C, highlighting chemical characteristic peaks unique to each respirator model. The green-shaded region (800–1200 cm^{-1}) indicates trans-vinylene functional groups, while N–H stretching vibrations (1740 cm^{-1}), C=C bonds (1640 cm^{-1}), and C–N stretching peaks (1570 cm^{-1}) are marked with arrows.

Figure 4 displays the ATR-FTIR spectra of the C=O and C=C regions of the untreated, oven-aged at 70 °C on day 42 and day 84, and pressure reactor-aged at 25 °C, 40 bar O_2 on days 2, 14, and 56, for Respirators A, B, and C. All respirators showed a pronounced increase in the formation of C=O groups like aldehydes and ketones (1720–1740 cm^{-1}) and $-\text{CH}_2=\text{CH}_2-$ trans-vinylene groups (800–1000 cm^{-1}) (Figure S5 in the supplemental materials) with accelerated aging time. To quantify the oxidation levels of the aged respirators, the area under specific oxidation-related peaks of polymer was calculated and normalized to the area of the peak centered at 1370 cm^{-1} , following the method recommended in ASTM F2102. The oxidation index (OI) value was calculated based on the area of the carbonyl region (1600–1800 cm^{-1}), which encompasses C=O containing ketone and aldehyde groups (centered at 1720 and 1740 cm^{-1}) and the C=C groups (centered at 1660 cm^{-1}). Figure 5 presents the deconvoluted ATR-IR spectra in the 1600–1800 cm^{-1} region, analyzed using Gaussian curve fitting to determine the area under the curve. The oxidation index was calculated by dividing the total area of C=O and C=C groups by the normalization region's area, with the green line marking the baseline, the blue line the fitted data, the red line the raw data, and the black line indicating error, with fitted peaks shown in red.

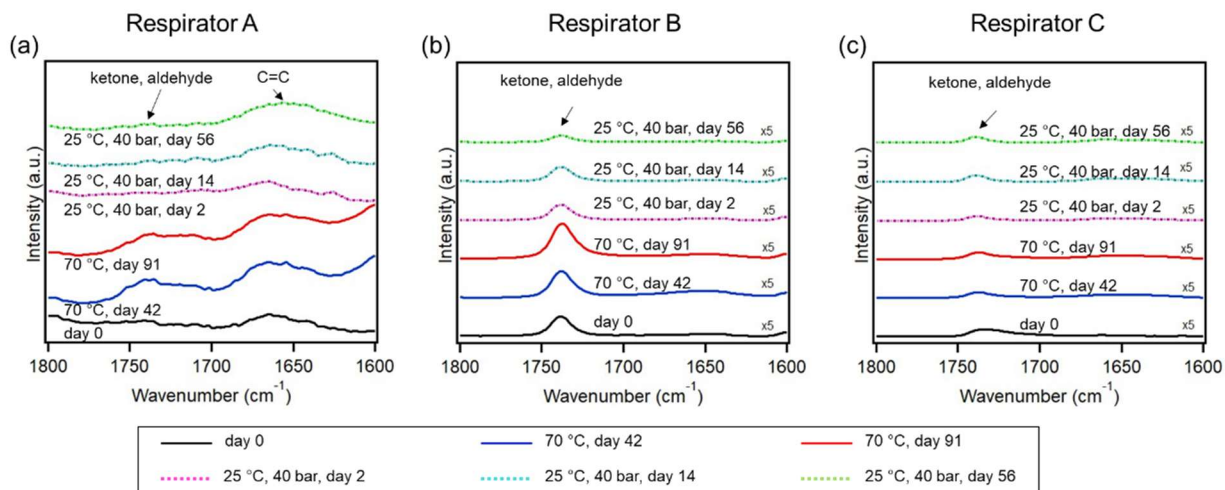


Figure 4. ATR-IR spectra of carbonyl C=O region and C=C region of (a) Respirator A, (b) Respirator B, and (c) Respirator C. The arrows highlight the C=C stretching region (1660 cm⁻¹) and C=O region (1720-1740 cm⁻¹).

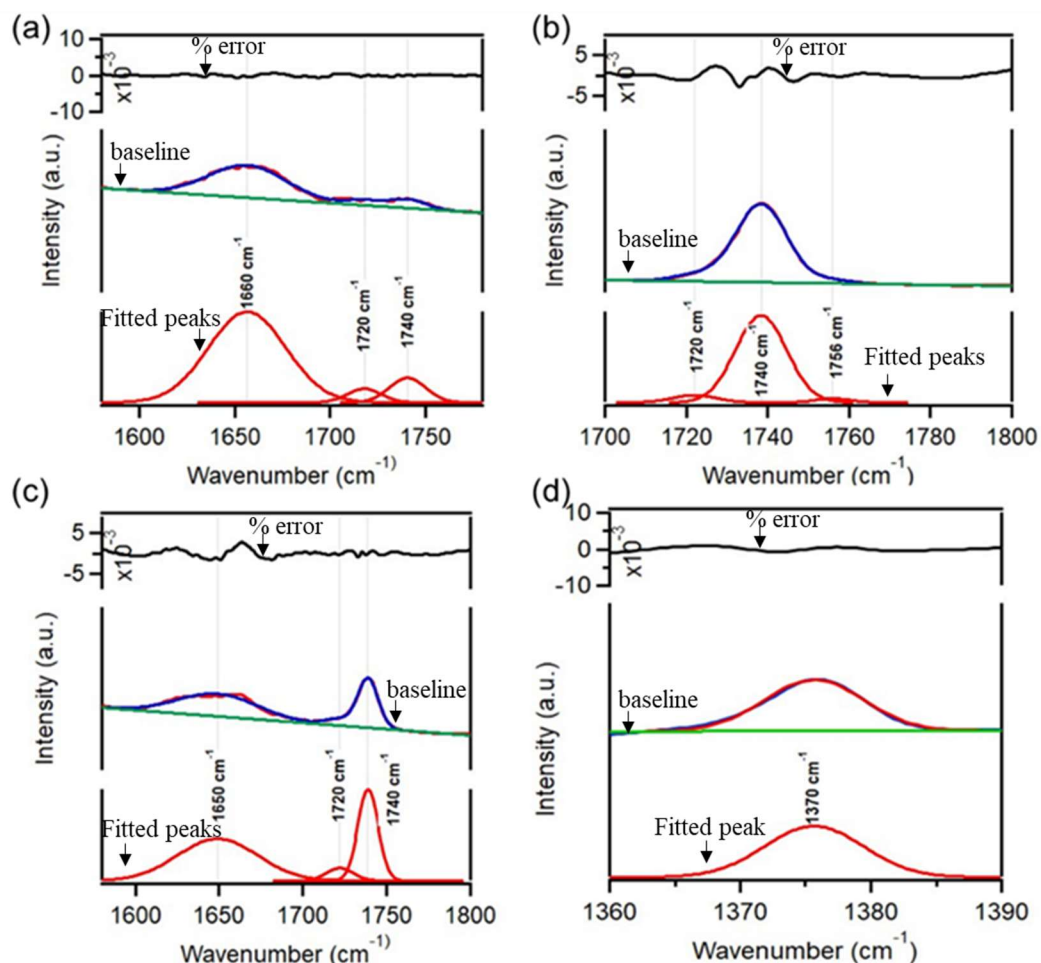


Figure 5. Representative deconvoluted ATR-IR spectra of Carbonyl region (1600-1800 cm⁻¹) for (a) Respirator A, (b) Respirator B, (c) Respirator C, and (d) normalization region (1330-1360 cm⁻¹).

Figure 6 presents the OI values obtained from ATR-FTIR deconvolution for Respirators A, B, and C after various durations of oven and pressure reactor aging. Notably, Respirator A's OI significantly increased from 1.84 to 3.58 ($p = 0.0384$) after 42 days of oven aging. Similarly, after 56 days of reactor aging, the OI value was 4.47, nearly 2.5 times higher than the unaged sample ($p = 0.0445$). Conversely, no significant changes in OI were observed for Respirator B and C under either aging condition.

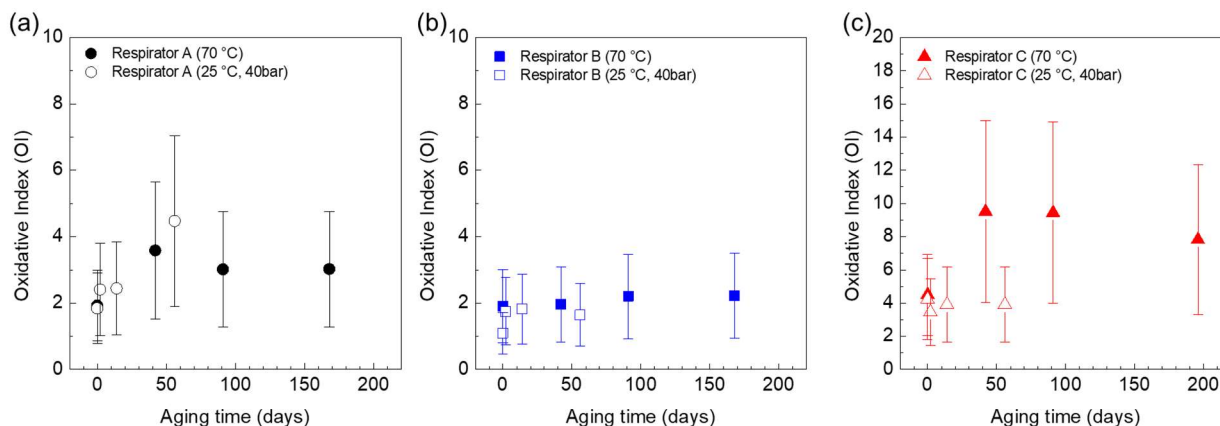


Figure 6: Oxidative index change with aging time of (a) Respirator A, (b) Respirator B, and (c) Respirator C treated with oven aging 70 °C or reactor aging at 25 °C, 40 bar. Respirator A showed an increase in oxidative index for both oven and reactor aging. Conversely, the oxidative index does not change for respirator B, and respirator C, with the aging treatment.

DISCUSSION

The differential responses observed under various aging conditions highlight the complexity of accelerated aging and its effects on respirator straps. Elevated temperatures in oven aging may initiate surface-specific degradation due to diffusion-limited oxidation (DLO) effect, where the rate of oxygen consumption on the surface exceeds the rate of oxygen permeation into the polymer bulk. The potential presence of DLO was assessed by analyzing the elongation at break for the aged respirator straps, which has been empirically observed to be less influenced by DLO (M. C. Celina 2013; M. Celina *et al.* 2000). This empirical observation has been hypothesized to be based on the rapid propagation of microcracks that originate at the oxidized surface and extend through the bulk of the material. As oxidation progresses, even if initially confined to the surface, these microcracks can influence the material's overall ductility, manifesting as changes in the elongation at break.

For Respirator A, the stability in mechanical properties such as elongation at break, breaking force, and toughness after 196 days of oven aging might indicate either inherent material resistance to oxidative degradation at the tested temperature or insufficient aging duration to effectuate detectable changes (Figure S2). In contrast, the observed increase in elongation and reduced breaking force for Respirator B (Figure S3) indicate material softening, likely due to plasticization effect of degraded polymer chains. For Respirator C, the unchanged modulus with reductions in elongation at break, breaking force, and toughness (Figure S4), suggests a degradation pattern consistent with DLO effect, where surface degradation restricts the material's ability to elongate without impacting its stiffness. These findings highlight the challenges of applying uniform accelerated aging conditions to different respirator types and compositions.

In contrast to oven aging, significant reductions in modulus were observed after just two days of reactor aging: 45-51% for Respirator A, 83-89% for Respirator B, and 42-43% for Respirator C (Tables S1-S9 in the supplemental materials). The straps exhibited initial mechanical stability, but a clear deterioration became evident beyond a critical oxidative threshold or induction period. This induction period serves as a robust metric for comparing resilience against oxidative stress between materials.

Chemical analysis via ATR-FTIR further illustrates the complexity of oxidative degradation processes. Distinct responses to aging treatments among the respirators, evidenced by variations in the intensity of C=C and C=O peaks, reveal differences in chemical compositional changes influenced by aging conditions. For instance, the intensity of the C=C peak at 1660 cm^{-1} in Respirator A remained constant after oven aging but increased after reactor aging treatments, whereas the C=O peak ($1720\text{--}1740\text{ cm}^{-1}$) increased after oven aging but remained unchanged after reactor aging. Similarly, Respirator A showed no increase in the -ROOH region over time, unlike Respirators B and C, which exhibited noticeable increases (Figure S5). These observations suggest differing mechanisms of degradation, with oven aging promoting the formation of aldehydes and ketones, while reactor aging appears to enhance hydroperoxide and alcohol formation.

Given the variability in chemical compositions and the resultant chemical changes, focusing solely on the carbonyl region to calculate OI values may not fully capture oxidative degradation-related changes in polymers without detailed compositional information. Instead, mechanical properties, particularly modulus, may offer a more direct and applicable indicator of respirator performance for assessing long-term stability. This study lays the groundwork for future research where real-time aged samples will be analysed to refine and validate accelerated aging parameters. By emphasizing modulus as a primary indicator, we aim to develop a standardized oxidative degradation screening method applicable across different types of respirators and potentially other PPE. This method promises to enhance the effectiveness and safety of PPE in healthcare settings, ensuring robust performance over extended periods.

CONCLUSIONS

This study evaluated various accelerated aging methods to develop an oxidative degradation screening test for estimating shelf-life of surgical N95 FFR straps. Three types of surgical N95 FFR straps were subjected to either conventional oven aging at $70\text{ }^{\circ}\text{C}$ or reactor aging with pressurized oxygen at 20 bar or 40 bar at room temperature. Results indicated that reactor aging significantly accelerated the rate of degradation compared to oven aging, identifying a critical oxidative threshold that could serve as a robust metric for assessing material's oxidative stability. Despite initial mechanical stability, significant deterioration occurred beyond this threshold.

The oxidation index, measured at various intervals, highlighted complex degradation pathways and underscored the limitations of chemical analysis due to the polymer's varied compositions. This finding reinforces the utility of mechanical properties, especially modulus, as a more direct and reliable indicator of respirator performance and longevity.

The insights from this research not only refine the approach for assessing long-term stability of respirators but also streamline the evaluation process by prioritizing measurable mechanical changes over complex chemical analyses. Future studies will focus on correlating accelerated aging results with real-time material performance to optimize aging parameters for the pressure reactor. This foundational work is anticipated to expedite the development of standardized oxidative degradation screening methodologies applicable to various types of PPE.

Conflicts of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions: K.H conducted all laboratory tests, modified experimental procedures, performed experiments, and authored the manuscript. T.J designed the project and experiments, provided feedback during its execution, and co-authored and edited the manuscript.

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