Deterioration Valuation of Polymer Materials in UV-ozone Generator using Microwave Plasma

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Abstract: - Various materials are used to sterilize medical instruments. Rubber and other products deteriorate owing to ozone and UV exposure. Ozone is capable of inactivating bacteria and fungi and is known to be effective in inactivating a wide range of viruses. Silent discharge is the mainstream method of ozone generation. The silent discharge method is also concerned with the generation of nitrogen oxides (NO_X) caused by nitrogen molecules in the air, and the deterioration of electrodes during use poses a problem. Furthermore, nitrogen oxides react with water in the gaseous phase to produce nitric acid. Nitric acid reacts with several metals to form nitrates. A sterilization device using high concentrations of ozone has not been put to practical use because of the lack of an efficient method for decomposing ozone and the corrosion of metals. If a medical device is altered, it cannot be used as a sterilizing device. In this study, we exposed polymeric materials, which are often used in medical instruments, to ozone and UV light to determine whether their properties changed. Elution tests were conducted on polymeric medical materials from the viewpoints of their physical and chemical properties, functional decline, and biological safety. This study investigates changes in mechanical strength and surface chemical properties, representing the physical and chemical aspects.

Key-Words: - microwave, ozone, UV, sterilizer, mercury bulb, active oxygen, polymer material.

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1 Introduction

Various materials are used in medical instruments that are subjected to sterilization. It is known that rubber and other products deteriorate due to ozone and UV exposure, [1]. If a medical device undergoes alterations, it becomes unsuitable for use as a sterilizing device. In this study, we exposed polymeric materials, which are often used in medical instruments, to ozone and UV light to determine whether their properties changed.

Specifically, we exposed hard polymer materials like polyethylene, polypropylene, polyethylene terephthalate, and polyvinyl chloride, as well as soft polymer materials such as natural rubber, fluororubber, and silicone rubber—common in medical settings—to UV ozone exposure. Polyethylene is widely used in artificial lungs, colostomies, infusion bags, packaging films, etc [2], [3], [4], [5], [6]. Polyethylene terephthalate (PET) is used as a relatively large-diameter artificial blood vessel because it undergoes little tissue reaction and is less susceptible to in vivo deterioration. Polypropylene is stable to drugs, biochemically inert, and is used as a material for rigid medical devices such as disposable syringes, indwelling needles, and catheters[6]. Polyvinyl chloride has excellent flexibility, processability, and durability and is used in large quantities in disposable medical devices such as tubes and bags for infusions and extracorporeal circulation. Fluororubber is a general term for synthetic rubbers prepared by the polymerization or copolymerization of monomers containing fluorine atoms, [7]. Although it has been reported to deteriorate under alkaline and high-temperature conditions, it is known as a rubber that can be used even in harsh environments, [8] and is used for endoscopes, scope tip covers, etc. Silicone rubber is made into a rubber-like material by adjusting the molecular weight of silicone and is used for rubber tubes and external shunts for blood access for extracorporeal circulation. For comparative purposes, natural rubber, composed of linear isoprene molecules (C5H8), [9] and known for its degradation by ozone, [1], was included. For polymeric medical materials, elution tests are conducted from the viewpoints of physical and chemical properties, functional decline, and biological safety, [10], [11], [12]. In this study, changes in mechanical strength and surface chemical properties were investigated as physical and chemical properties.

1.1 Ozone

Ozone is represented by the molecular formula O_3 and has a molecular structure in which three oxygen atoms are bonded in an isosceles triangular shape. It is in an unstable state with one extra oxygen atom bonded to a stable oxygen, decomposes naturally, and returns to oxygen, [13].

1.2 UV

UV radiation can be classified into three regions based on wavelength: UVA (320–400 nm), UVB (320–280 nm), and UVC (280–200 nm). UV lamps are a technologically mature field, and many products are already in use. DNA is damaged by short-wavelength UV light (254 nm) emitted by germicidal lamps, [12]. UV is used in a variety of fields, and it must be used in a way that prevents it from directly irradiating the human body, [13].

1.3 Mercury Excitation by Microwaves

Atoms become excited when they receive external energy such as light, heat, electric, or magnetic fields. After a short time, the excited atom transitions to a lower energy level, emitting light in the form of photons. The energy of these photons corresponds to the difference between the two energy levels. The mercury atoms in this study were excited by 2.45 GHz microwaves. The electromagnetic waves emitted dominant wavelengths of 184.957 nm and 253.652 nm, [13].

1.4 Principles of Ozone Generation and Decomposition

In this study, ozone was generated via a photochemical reaction, as shown in Figure 1. UV light at a wavelength of 184.9 nm decomposes oxygen molecules into atomic oxygen. When ozone combines with the surrounding oxygen molecules, ozone is generated. In this study, a glass low-pressure mercury-sealed bulb that generates ozone is referred to as a UV-ozone-generating bulb. By contrast, ozone decomposition requires a wavelength of 253.7 nm. Ozone is excited by 253.7 nm UV and separates into atomic oxygen and oxygen molecules. The two oxygen atoms react with each other, resulting in oxygen molecules.

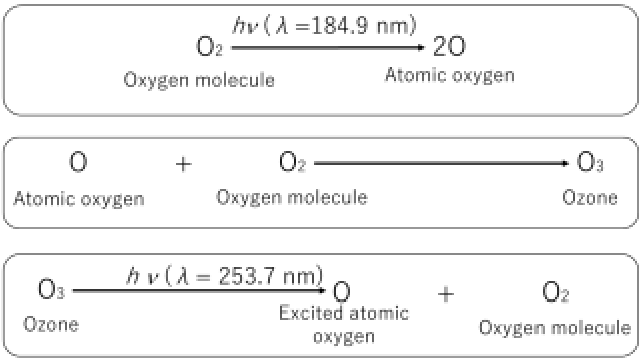

Fig. 1: Ozone generation and decomposition process

Additionally, as shown in Figure 2, atomic oxygen reacts with water molecules in the gas phase to generate OH radicals. Quartz was used as the UV-transmitting glass; however, impurities were added to the UV-ozone decomposition bulb to block 184.9 nm UV. Therefore, ozone was not generated, and only UV light with a decomposition wavelength of 254.7 nm was emitted.

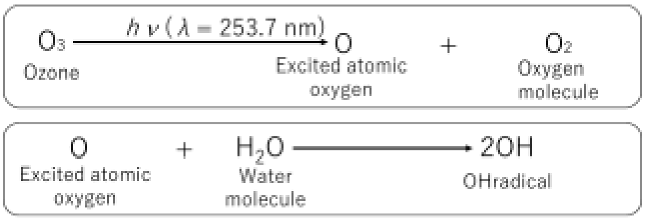

Fig. 2: Products during ozone decomposition

2 Experiments

A hard polymer material was cut into pieces 1 mm thick, 70 mm long, and 10 mm wide, placed 15 cm from the device, and exposed for a specified time. Then, a three-point bending test was performed using a rheometer (CR-500DX-S), as shown in Figure 3**.** This tert involved a distance between fulcrums of 40 mm, a pushing speed of 5 mm/min, and a pushing distance of 10 mm after the sample begins to bend, from which a stress-strain curve was created.

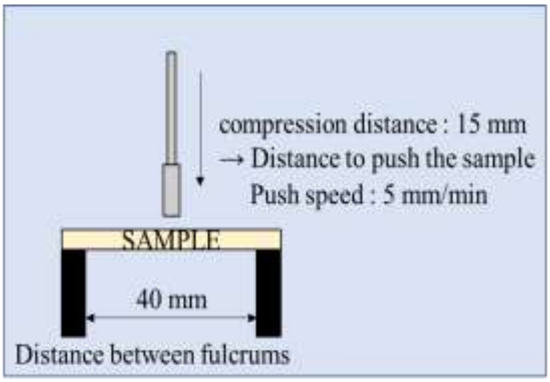

Fig. 3: Three-point bending measurement conditions

For the tensile test, each piece of soft polymer material was cut into a dumbbell shape with a thickness of 1 mm, length of 70 mm, width of 10 mm, and both ends of 20 mm, and placed 15 cm from the device and 10 mm of the total length. The material was exposed for a specified time while being stretched by 7 mm, corresponding to [specific percentage]. The material was exposed in a stretched state because when a soft polymer material is stretched by 10–20%, the material changes significantly owing to oxidation, [1].

Thereafter, using a rheometer (CR-500DX-S), a tensile test was performed at a distance between chucks of 60 mm, a tensile distance of 15 mm, and a tensile speed of 100 mm/min as shown in Figure 4, and a stress–strain curve was created. In addition, changes in the surface chemical properties of the polymer materials before and after all the UV ozone treatments were measured using ATR-IR spectroscopy.

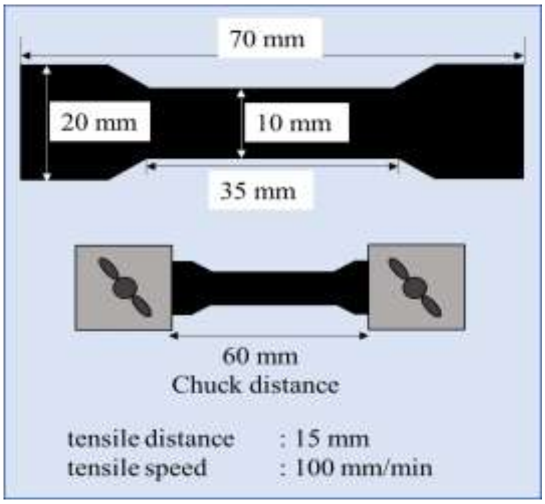

Fig. 4: Tensile measurement conditions

3 Results and Discussion

3.1 Hard Particle Molecular Material

The stress-strain curve for the three-point bending is depicted in Figure 5. The bending stress is the force applied to a material, the bending strain is the amount of deformation caused by the applied force, and the elastic modulus is the slope of the straight line in the elastic region of the stress-strain curve, which is the value of stress divided by strain. The harder the material, the greater the elastic modulus and the closer it becomes vertical. The yield point is the point at which the material begins to yield (plastic deformation). The stress at this time is called the yield stress; the higher the stress, the less plastic deformation occurs, and the higher the durability against bending loads. In other words, the elastic modulus indicates the hardness of the material, and the yield stress is the stress at which the material cannot return to its original shape. The material was deemed unaffected by the device if no significant changes were observed in the elastic modulus or yield stress.

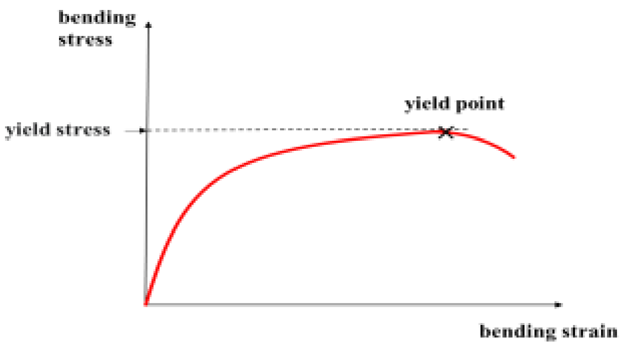

Fig. 5: Stress strain curve in three-point bending

Figure 6, Figure 7, Figure 8 and Figure 9 display the stress-strain curves for polyethylene, polyethylene terephthalate, polypropylene, and polyvinyl chloride, respectively. Figure 10 illustrates the post-treatment elastic modulus, normalized to 1 as the ratio, and Figure 11 depicts the yield stress after treatment, also normalized to a baseline of 1 for comparison. The elastic modulus ratio and yield stress ratio were compared, but no significant differences were found, regardless of the ozone exposure time.

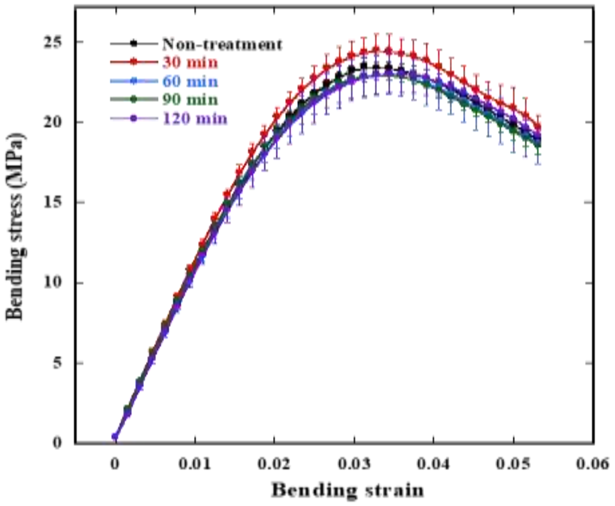

Fig. 6: Stress strain curve of polyethylene

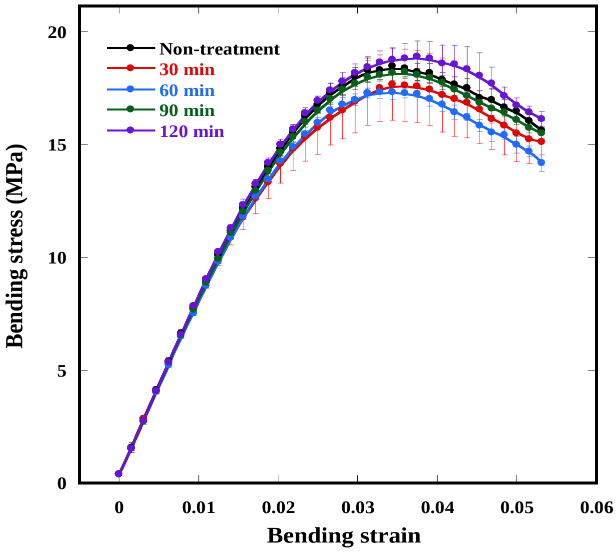

Fig. 7: Stress strain curve of polyethylene terephthalate

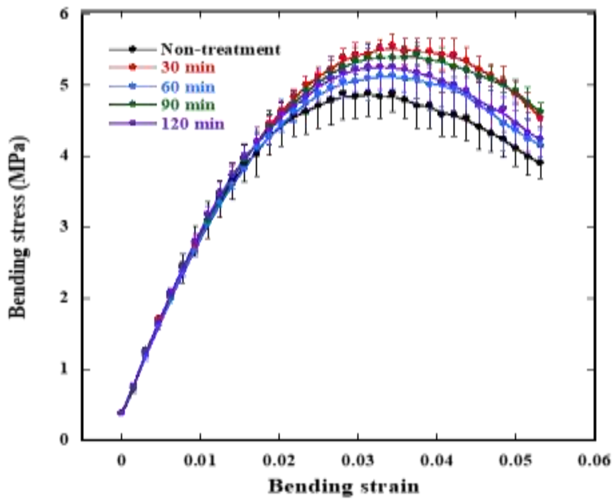

Fig. 8: Stress strain curve of polypropylene

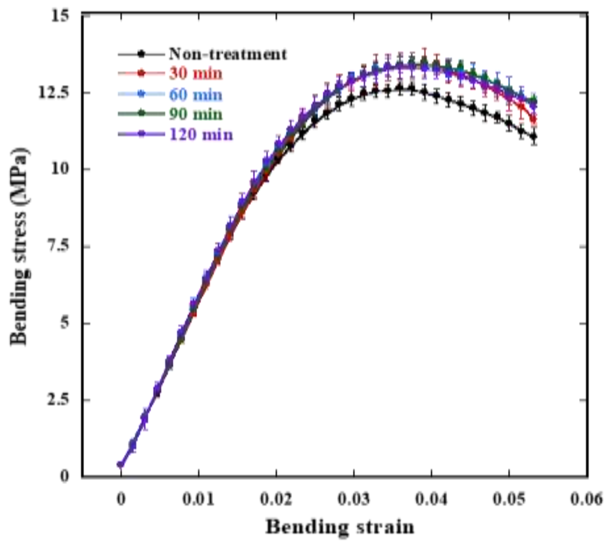

Fig. 9: Stress strain curve of Polyvinyl chloride

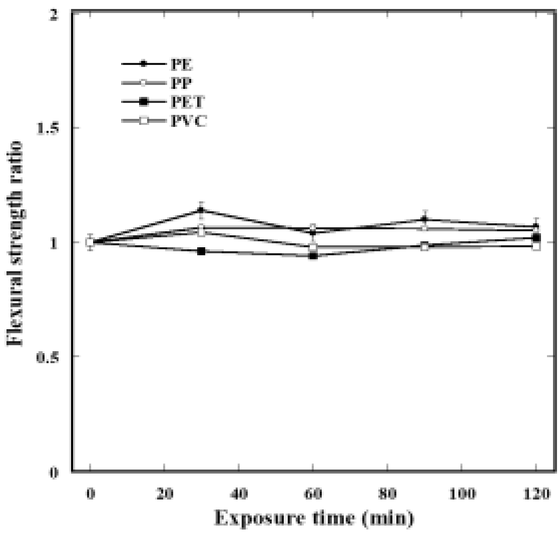

Fig. 10: Elastic modulus ratio

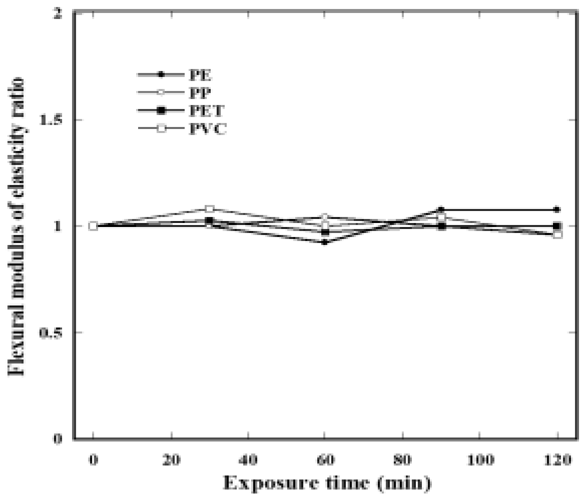

Fig. 11: Yield stress ratio

The results of the IR spectral analysis used to investigate the surface conditions are shown in Figure 12, Figure 13, Figure 14 and Figure 15. No significant changes were observed in the surface conditions of polyethylene, polypropylene, and polyvinyl chloride. However, only in polyethylene terephthalate, a peak believed to be derived from hydroxyl or carboxy groups, [14] was confirmed at absorbance around 3500 cm^{-1} (arrow in the figure). Previous reports indicate that UV treatment induces scission reactions in the molecular main chain of polyethylene terephthalate, [15]. Additionally, studies have shown that the contact angle with different liquids decreases, enhancing wettability, [14]. This suggests that the UV light from this device alters the surface properties.

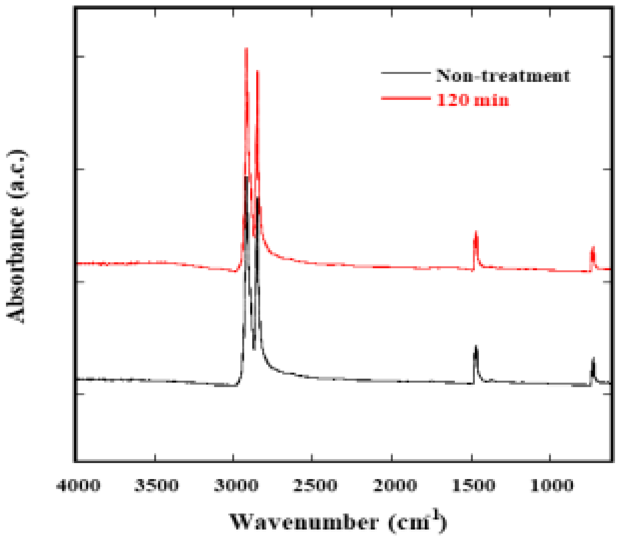

Fig. 12: IR spectrum analysis of polyethylene

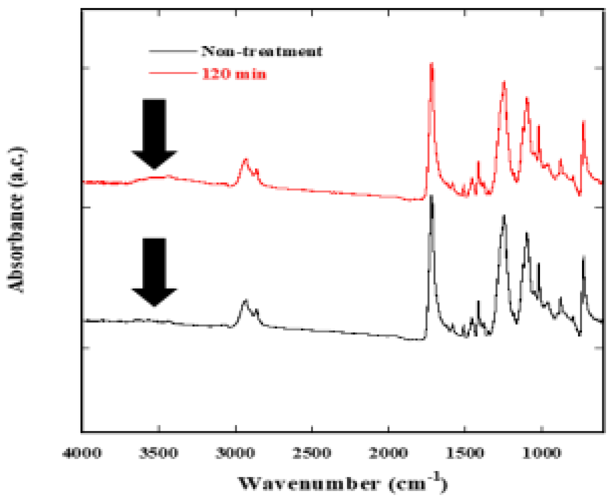

Fig. 13: IR spectrum analysis of polyethylene terephthalate

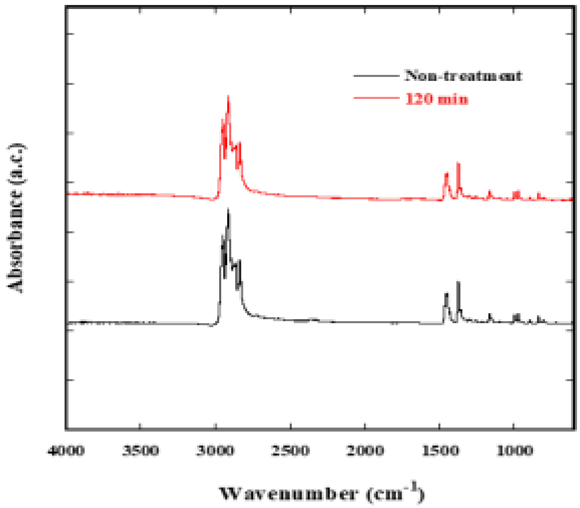

Fig. 14: IR spectrum analysis of polypropylene

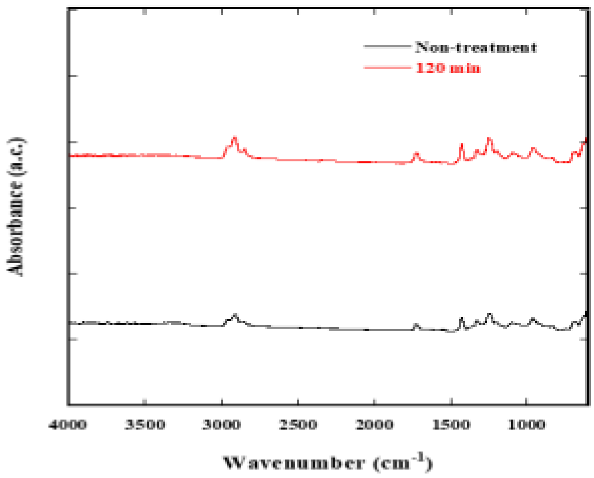

Fig. 15: IR spectrum analysis of Polyvinyl chloride

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3.2 Soft Polymer Material

The stress-strain curve under tension is shown in Figure 16. The stress on the vertical axis represents the force applied to the material, and the strain on the horizontal axis represents the amount of deformation caused by the applied force. The elastic modulus is the slope of the straight line in the elastic region of the stress-strain curve (the region that returns to its original state after being stretched). The harder the material, the larger the elastic modulus, and the closer it becomes vertical. Tensile strength is the limiting strength of a material, and the higher the tensile strength, the higher the durability against tensile loads. If the stress decreased as the strain increased, it was determined that the material had fractured.

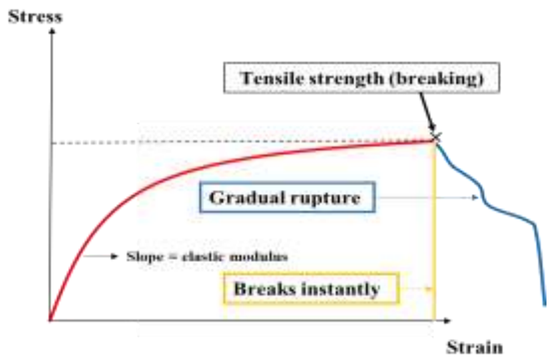

Fig. 16: Stress strain curve in tension

Figure 17 shows the stress–strain curve of the fluorororubber, and Figure 18 shows the results of the IR spectrum analysis used to investigate the surface conditions. It seems that the elastic modulus ratio of the fluororubber gradually decreases as the ozone exposure time increases, but if the fluorubber becomes softer (elastic modulus decreases) by exposure to UV ozone, then it increases with exposure time. The elastic modulus should decrease with increased exposure time. However, the increase in elastic modulus after 90 minutes of exposure suggests a possible error in the size of the cut material. No change in the surface conditions was observed in the IR spectrum analysis. It has also been reported that no macroscopic deterioration occurs even when ozonated water is treated, [8]. This is because the carbon-fluorine bond in the main chain is extremely stable even in ozone water. Another factor contributing to its stability is that it is shielded from ozone and OH radicals by the highly electronegative F atoms, [14]. However, the alkyl moiety that forms the crosslinking point is oxidized and decomposed in ozone water, [14]. A similar reaction generating ozone at high humidity is thought to occur in this device. Therefore, the reaction of fluororubber is likely influenced by the specific device used. However, the ozonated water exposure time was 60 h, and in this experiment, the exposure was for 300 min. Considering that it was in the gas phase, it was necessary to expose it for a longer time to understand the changes in more detail. If certain conditions are met, it may be possible to achieve effective sterilization by limiting the number of sterilization procedures.

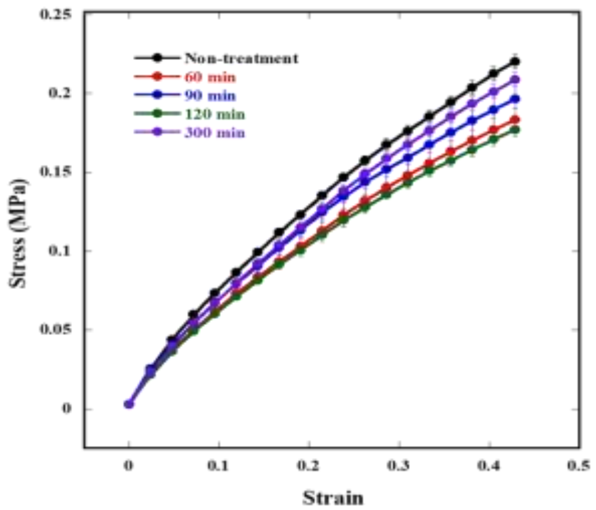

Fig. 17: Stress-strain curve of fluororubber

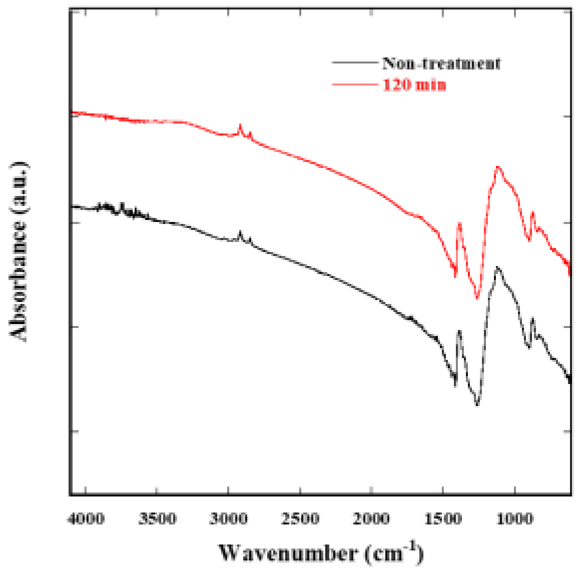

Fig. 18: IR spectrum analysis of fluororubber

The stress–strain curve of the silicone rubber is shown in Figure 19, and the IR spectrum analysis results are shown in Figure 20. The elastic modulus increased as the UV ozone exposure time increased but decreased again after 300 min of exposure. This implies that the material was hardened and softened by the device. However, no change in the surface conditions was confirmed by IR spectrum analysis. Silicone rubber decomposes under acidic and alkaline conditions, [14]. However, there are few evaluations of deterioration from ozone alone. The surface of silicone rubber, treated with combined UV irradiation and ozone generated via corona discharge, was evaluated using X-ray photoelectron spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy, [16]. Silicone rubber surfaces undergo specific structural changes in the polymer backbone, [17]. Therefore, even in ozone water, silicone rubber may exhibit a different deterioration behavior than other general-purpose rubber materials. This is thought to apply in this experiment, in which ozone was generated at high humidity. It should be noted that ozone water treatment confirmed changes in the silicone rubber after 60 days of exposure; therefore, it is thought that there was little change in the 300 min of this experiment.

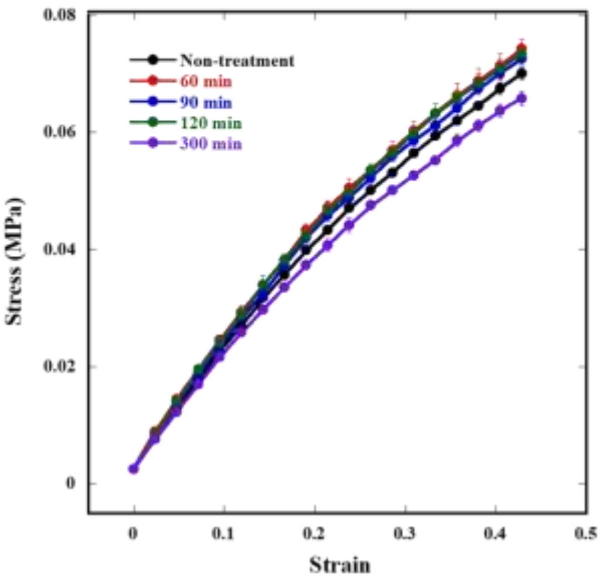

Fig. 19: Stress-strain curve of silicone rubber

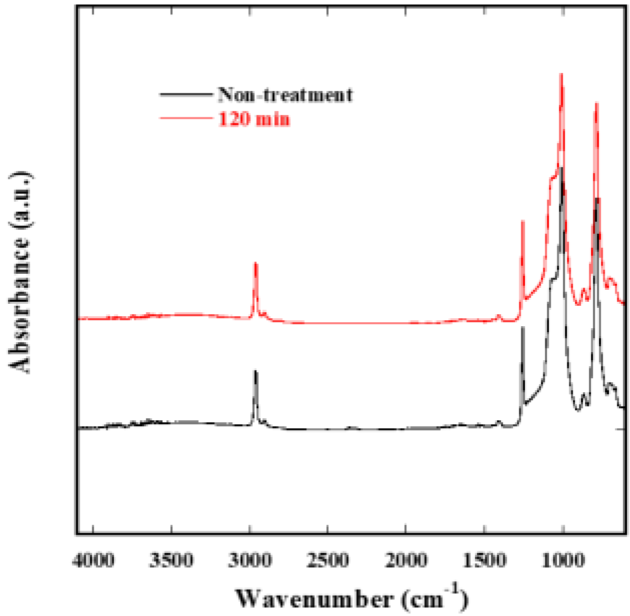

Fig. 20: IR spectrum analysis of silicon rubber

The stress–strain curve of natural rubber is shown in Figure 21, and the IR spectrum analysis results are shown in Figure 22. The elastic moduli and tensile strengths decreased after 15 min of exposure. The decrease in the elastic modulus occurs because the UV ozone exposure leads to changes in natural rubber, making it softer. It could elongate significantly under low stress. Furthermore, the reduced tensile strength suggests that the natural rubber tore under the stress experienced during this time. At an exposure time of 60 min, the material ruptured, and a tensile test could not be performed. Ozone forms a bond called ozonide, [1], in the carbon-carbon double bond of the isoprene unit, [18] of natural rubber, as shown in Figure 23. This is reflected in the absorption wavelength of 1500 cm^{-1} in the IR spectrum analysis, and it can be seen that the peak that existed without exposure decreased after 60 minutes of exposure (arrow in the figure). It is considered that the elastic modulus decreases because of this change. As shown in Figure 24, the elastic modulus ratio with an untreated elastic modulus of 1 indicates that natural rubber was the only material in which significant deterioration occurred.

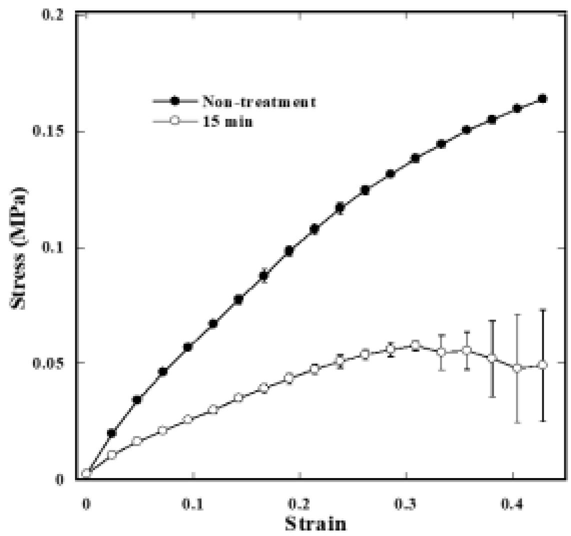

Fig. 21: Stress-strain curve of natural rubber

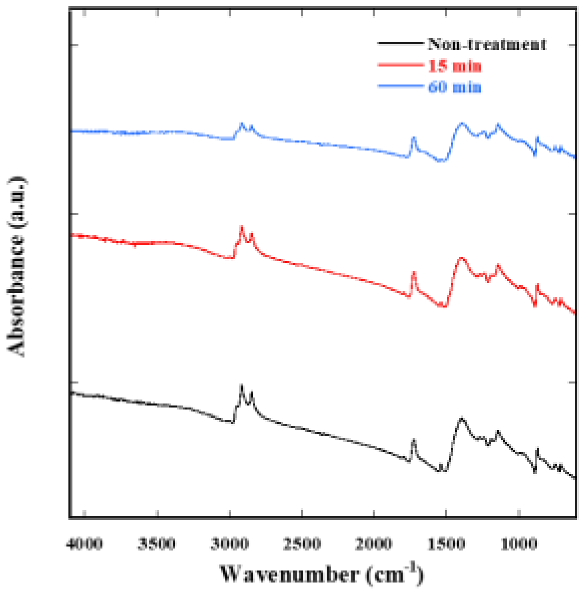

Fig. 22: IR spectrum analysis of natural rubbe

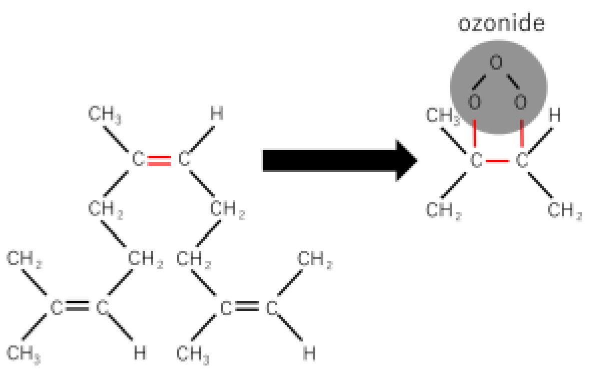

Fig. 23: molecular structure of natural rubber

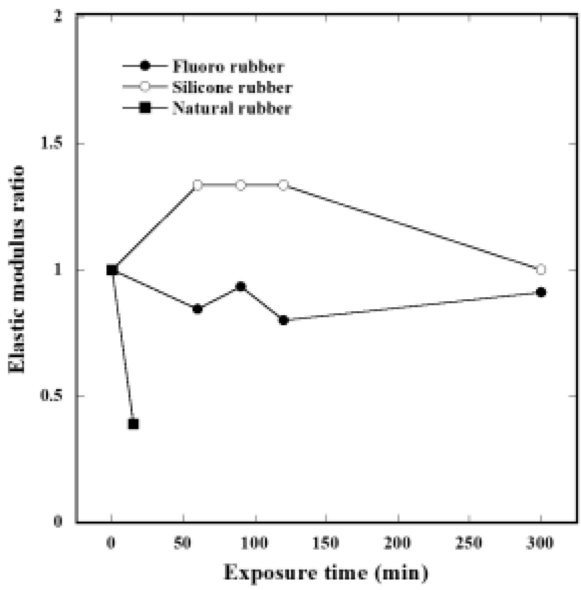

Fig. 24: Elastic modulus ratio of soft polymer material

4 Conclusion

The main results of this study are as follows:

(1) By investigating the UV resistance and ozone resistance of typical polymer materials often used in medical devices, we found that polyethylene, polypropylene, and polyvinyl chloride have excellent mechanical strength, and no change in the surface condition was observed.

(2) However, changes in the surface conditions of PET, fluorourubber, and silicone rubber due to long-term exposure to ozonated water have been reported. It was found that natural rubber should not be sterilized using this device because, in addition to the change in the surface conditions, the mechanical strength was significantly reduced. It is thought that not only ozone but also OH radicals and excited oxygen atoms are involved.

(3) The results showed that this device can sterilize instruments made of polyethylene, polypropylene, and polyvinyl chloride.

(4) Given that the sterilization process is repeated frequently, the absence of changes in mechanical strength or surface conditions after 300 min does not preclude alterations occurring over several tens of hours. Consequently, further testing with extended exposure times and increased concentrations is necessary.

(5) However, it is a useful new sterilization option in the field of medical engineering.

(6) We are planning to confirm whether UV ozone sterilization is effective for the other materials used in the medical field.

(7) Additionally, we will consider the possibility of deploying UV ozone sterilizers to general households to prevent pandemics such as the new coronavirus infection.
(8) Furthermore, using actual medical instruments, we will compare the degree of material deterioration with other sterilization methods and UV ozone sterilization.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- Naoki Kusumoto devised a sterilization system using ozone.
- Atsuya Watanabe sterilized the bacteria.
- Hiraoka developed a microwave generator.
- Norimich Kawashima developed the low-pressure mercury bulb-issuing system using microwaves.
- Yoshikazu Tokuoka provided extensive guidance, including adjustment and preparation of the entire experiment.
- Hitoshi Kijima supervised the study.

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Conflict of Interest

The authors declare no conflicts of interest relevant to the content of this article.