Effect of Sterilization on the Mechanical Properties of Silicone Rubbers

Emilie Gautriaud, Keith T. Stafford, Jennifer Adamchuk, Mark W. Simon and Duan Li Ou*

Saint-Gobain, Northboro R&D Center, 9 Goddard Road, Northborough, MA, 01532, USA

Abstract

In the medical and biopharmaceutical fields, millions of silicone rubber-based tools and devices must be sterilized on a daily basis. During the sterilization process, silicone components are commonly exposed to various types of treatments, including single or multiple doses of radiation. While these processes are essential for sanitizing rubber parts, they often have an adverse effect on the integrity of the material. In this study, we evaluate the mechanical properties of three types of commercially available silicone rubbers (platinum cured liquid silicone rubber LSR, platinum cured high consistency rubber HCR, and peroxide cured high consistency rubber HCR) before and after sterilization (gamma irradiation, e-beam irradiation, and ethylene oxide EtO treatment). Our findings on the compatibility of various sterilization mechanisms with different silicone types will provide guidance to medical device designers on material selection and sterilization limitations.

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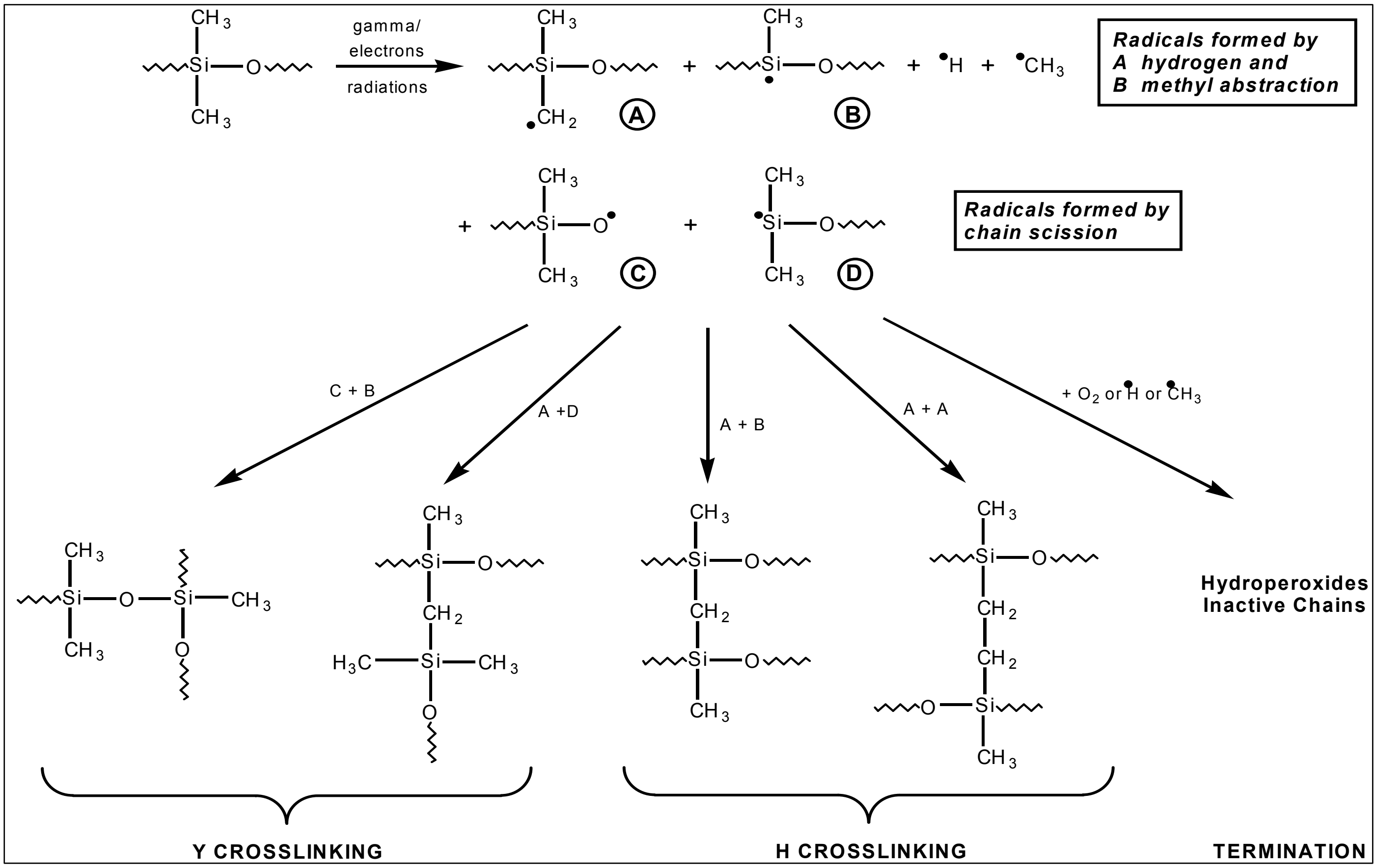
* Corresponding author
E-mail address: Danny.Ou@Saint-Gobain.com
Tel: 508-351-7179
Fax: 508-351-7805

1. Introduction

Silicone rubber is widely used in medical applications, where sterilizability is an essential requirement for all medical tools and devices that contact the body or bodily fluid. Medical components must be sterilized frequently and repeatedly by high level energy and/or chemical vapor in order to eliminate bacterial surface contamination. Such treatments may also affect the molecular structure of the silicone rubber, causing changes in the physical properties and performance of the material. Several studies on this topic have been reported; however, a systematic investigation has not been performed on the effect of standard sterilization procedures on commercial silicone rubbers commonly used in the medical industry. To date, most investigations have focused on the treatment of unfilled silicone polymer under ideal radiation conditions, the results of which cannot be directly correlated with the effect of realistic sterilization conditions on commercial medical components. This report may be used as a material selection tool for medical device designers, as well as a guide for selecting sterilization procedures that are compatible with specific silicone materials.

Three common sterilization techniques were applied to three commercially available silicone rubbers: gamma ionizing irradiation, electron-beam irradiation, and ethylene oxide (EtO) treatment. The effect of these sterilization methods on the mechanical properties of platinum cured liquid silicone rubber (LSR), platinum cured high consistency rubber (platinum cured HCR), and peroxide cured high consistency rubber (peroxide cured HCR) was investigated. The results provide a complete picture of the effect of sterilization on the physical properties of silicone rubbers typically used in the healthcare industry. This information is key to ensuring that, irrespective of repeated sterilization cycles, the functionality provided by the silicone part will be maintained throughout the lifecycle of the product.

Figure 1. Effect of gamma and electron radiations on silicone polymer chains.



2. Sterilization Techniques and Effect on Silicone Rubber

The most common methods used for sterilizing medical devices are autoclaving (steam sterilization), ethylene oxide (EtO) gas treatment, and gamma and electron-beam (e-beam) ionizing irradiation. [1] Steam sterilization is generally employed for reusable parts made of resistant polymer or metal. Disposable medical devices are typically sterilized using EtO gas, gamma or e-beam irradiation.

Gamma radiation is known to induce changes in the molecular architecture of silicone rubber, resulting in an increase in molecular weight and a decrease in elasticity. This effect is also observed in samples previously subjected to post-cure treatments. Radicals are generated by chain scission and/or methyl or hydrogen abstraction and are subsequently terminated via oxidation reactions or coupled to form longer chain branches, as shown in Figure 1. Although these two mechanisms compete against each other, crosslinking reactions dominate in silicone materials; higher dosages of gamma radiation and longer treatment cycles have been shown to result in higher crosslink densities. [2] An increase in polymer-filler interfacial interactions through crosslinking reactions is also observed. A recent review by Clarson et al. describes the behavior of various silicone polymers upon exposure to gamma radiation. [3]

The interaction of both gamma radiation and electrons with matter generates a shower of secondary electrons that initiate ionization and induce free radicals in the polymer. [4] As a result, gamma and electron irradiation produce scission and crosslinking reactions. Electron radiation also modifies the polymer-filler interface, thus contributing to the development of physical and chemical crosslinking in the rubber and resulting in a much higher durometer hardness and tensile modulus. [5] Although gamma radiation has approximately five times the penetration capability of e-beam radiation as illustrated in Figure 2, electron-beam sterilization can take less than 1 minute to reach the required dose, whereas gamma irradiation delivers the same sterilizing dose in several hours. [6] Due to the short radiation exposure time, the possibility of oxidative degradation (free radicals reacting with oxygen) may decrease in the case of e-beam sterilization if the procedure is performed in air. Ultimately two sterilization condition-dependent phenomena will affect the crosslink density of silicone resins: the atmosphere-dependent availability of unconsumed radicals that can participate in crosslinking reactions and the exposure time-dependent quantity of chain scission reactions that occur. [7] Overall, the effect of electron-beam and gamma sterilizations on the mechanical properties of silicone rubbers is expected to be similar.

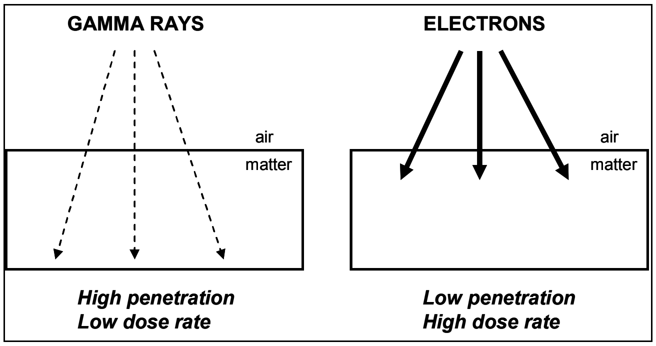


Figure 2. Interaction of gamma rays and electrons with matter.

Ambient temperature sterilization methods are sometimes preferred over conventional dry heat, irradiation, or autoclaving since high temperatures may result in the extraction of low molecular weight species from the sterilized material. One such method is ethylene oxide (EtO) gaseous sterilization. While EtO treatment is effective in eliminating bacteria at the surface of silicone parts, it can present potential toxicological issues if the gas is absorbed into and subsequently released from the component into tissue. Various studies have addressed this issue by quantifying the speed of absorption and desorption of EtO for silicones. [8,9] However, to the best of our knowledge, the effect of the EtO sterilization on the mechanical properties of silicone remains unknown.

3. Experimental

3.1. Materials

The liquid silicone rubber (LSR) used in this study was Elastosil® LR3003/50 and was obtained from Wacker. The platinum cured high consistency rubber (Platinum cured HCR) used in this study was Elastosil® R4000/50 and was obtained from Wacker. The peroxide cured high consistency rubber (Peroxide cured HCR) was HV3 622 base rubber and was obtained from Bayer. It was cured by Di-2,4-dichlorobenzoylperoxide with 1% loading.

3.2. Sterilization

Gamma exposure

Three levels of gamma irradiation experiments were performed in air on the three silicone rubbers by Steris Isomedix using ^{60}Co as radiation sources. The dosing levels of gamma radiation were 25 kGy, 50 kGy and 75 kGy.

E-beam exposure

Three levels of e-beam irradiation experiments were performed in air on the three silicone rubbers by STERIS Isomedix using 80 kW 5 Mev System electron beam. The dosing levels of gamma radiation were 10 kGy, 40 kGy and 80 kGy.

Ethylene Oxide (ETO) treatment

The three silicone rubbers were exposed to 100% ethylene oxide at room temperature in fully automated conveyor system in Steris Isomedix Spartanburg facility.

3.3. Mechanical Testing

Tensile, modulus, and elongation properties were evaluated on an Instron using ASTM D-412. Tear tests were performed on an Instron according to ASTM D-624. Hardness measurements were carried out on a shore A durometer, following the procedure of ASTM D-2240. Each data point reported on the plots presented in the next chapter is the average of 5 specimens from the same sample.

4. Results and Discussion

4.1. Effect of Gamma Irradiation

As the gamma radiation dose increases, the hardness and modulus of silicone rubber also increase since they are directly proportional to the crosslink density of the rubber. In this study, the hardness (increase by >10 shA after 75 kGy radiation) and the modulus (more than 200% increment after 75 kGy radiation) of the peroxide cured rubber were affected the most by gamma radiation compared to the hardness and modulus of the platinum cured LSR and HCR, as shown in Figures 3 and 4, respectively. This can be explained by the presence of radiation-sensitive oxygen-containing active species in peroxide cured silicone rubbers that promote the formation of free radicals, resulting in increased chain branching. The hardness and modulus of platinum cured LSR and HCRs increase slightly upon gamma radiation exposure, possibly due to unreacted SiH functionalities inducing further crosslinking. The slight initial drop (after 25 kGy gamma radiation) in the durometer hardness and the tensile modulus of the platinum cured HCR may be attributed to a disruption of the hydrogen bonds on the filler surface. [10] This behavior has also been observed by Patel et al. [11]

Unsurprisingly, gamma radiation reduced the tensile elongation of each of the three silicone rubbers tested, as illustrated in Figure 5. Property degradation of the peroxide cured rubber was more extensive, with up to 75% reduction in tensile elongation occurring after exposure to a 75 kGy dose of gamma radiation. Only 45% and 35% reductions in tensile elongation were observed at the same radiation dose for platinum cured LSR and HCR, respectively.

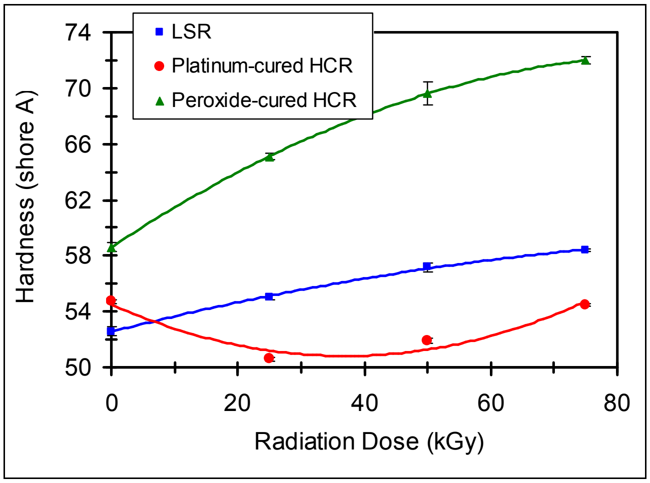


Figure 3. Effect of gamma radiation on durometer hardness of silicone rubbers.

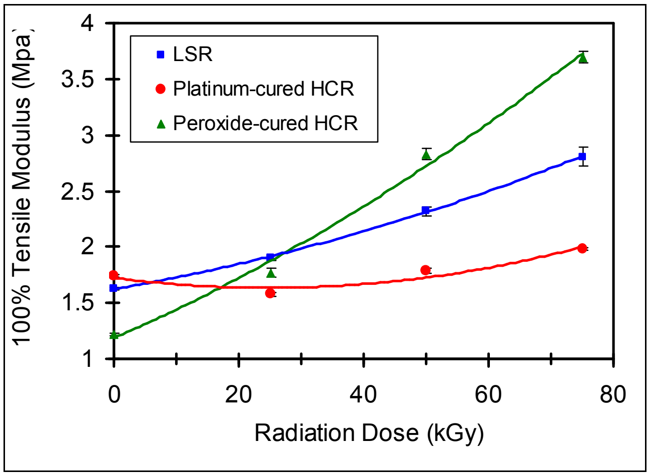


Figure 4. Effect of gamma radiation on tensile modulus of silicone rubbers.

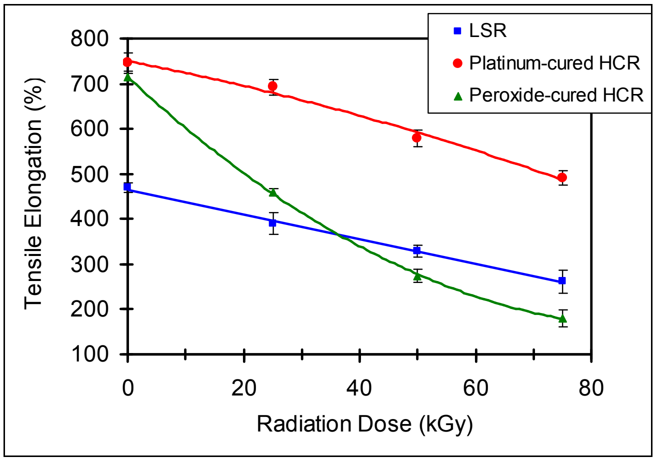


Figure 5. Effect of gamma radiation on tensile elongation of silicone rubbers.

The effect of gamma radiation on tensile strength is mostly due to the silicone rubber filler content and filler treatment, which is proprietary information for the commercially available materials evaluated during this study. For this reason, it is difficult to predict or rationally explain the trend of the data plotted in Figure 6. It was observed that gamma radiation had a minimal effect on the tensile strength of LSR and platinum cured HCR. In contrast, the tensile strength of the peroxide cured HCR was reduced by 50% after the sample was exposed to a75 kGy dose of radiation.

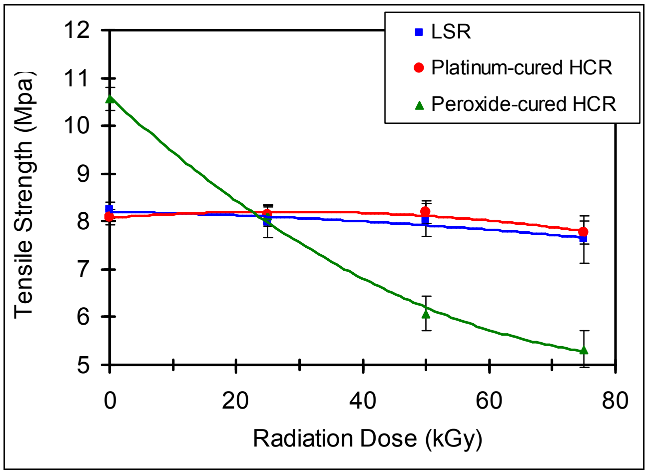


Figure 6. Effect of gamma radiation on tensile strength of silicone rubbers.

Tear strength is primarily affected by the arrangement of crosslinking, bimodality (ratio of short polymer chains to long chains) and the amount of crosslinker used for curing rather than by the crosslink density itself. It is also well-known that the tear properties of the silicone rubber are dictated by the level and type of filler used. [11] Again, information on the content and nature of fillers is not available for the materials evaluated in this study. However, it is known that the tear strength of platinum cured silicone rubbers is generally higher than that of peroxide cured HCR due to the nature of the crosslinks, as presented in Figure 7.

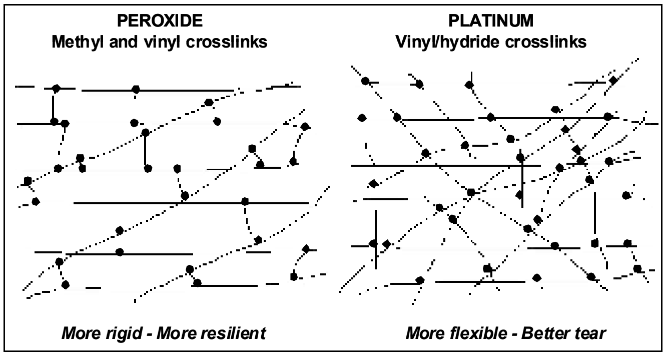


Figure 7. Nature of crosslinks obtained in peroxide vs. platinum cured HCR silicone rubber.

As shown in Figure 8, gamma radiation reduced the tear strength of all three silicone rubbers. The platinum cured HCR was the most resistant to gamma radiation; a 30% decrease of tear strength occurred when the platinum cured HCR was exposed to a 75 kGy dose of radiation, while the tear strength of the peroxide cured silicone exhibited a 45% reduction after the sample received the same dosage of radiation.

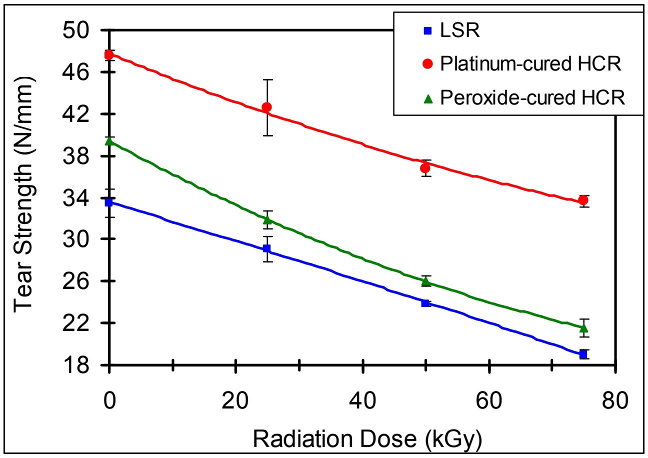


Figure 8. Effect of gamma radiation on tear strength of silicone rubbers.

4.2. Effect of E-beam Irradiation

Compared to gamma sterilization, e-beam irradiation had an analogous effect on the mechanical properties of the silicone rubbers, albeit slightly less pronounced. This difference may be attributed to the lower degree of penetration of the electrons into the silicone or to limited oxidative degradation due to the shorter exposure required for e-beam sterilization. E-beam radiation led to an increase in the durometer hardness and the tensile modulus of the rubbers, with a stronger effect on the properties of the peroxide cured HCR (increase of over 14 shore A and 160% in tensile modulus after 80 kGy dosing of e-beam radiation), as illustrated in Figures 9 and 10.

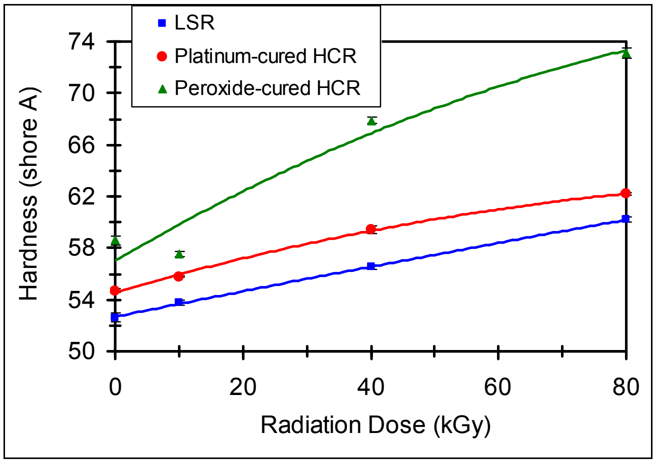


Figure 9. Effect of e-beam radiation on durometer hardness of silicone rubbers.

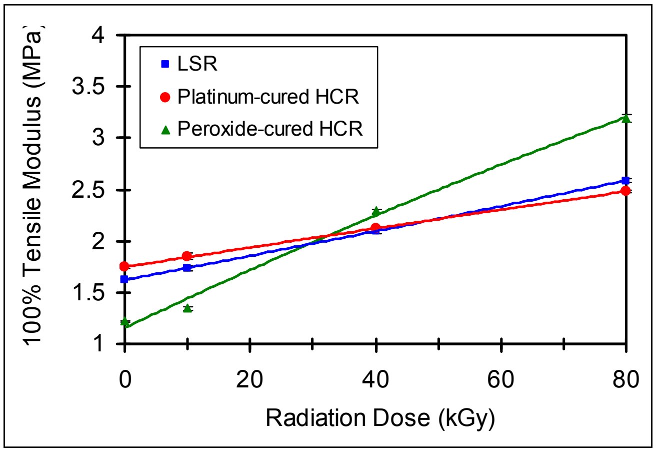


Figure 10. Effect of e-beam radiation on tensile modulus of silicone rubbers.

As shown in Figure 11, e-beam radiation reduced the tensile elongation of the three silicone rubbers. Property degradation was more extensive for the peroxide cured rubber, with up to a 62% reduction in tensile elongation occurring after the sample was exposed to an 80 kGy dose of e-beam radiation. After the same radiation dose, 33% and 39% reductions in tensile elongation were observed for the platinum cure LSR and HCR, respectively.

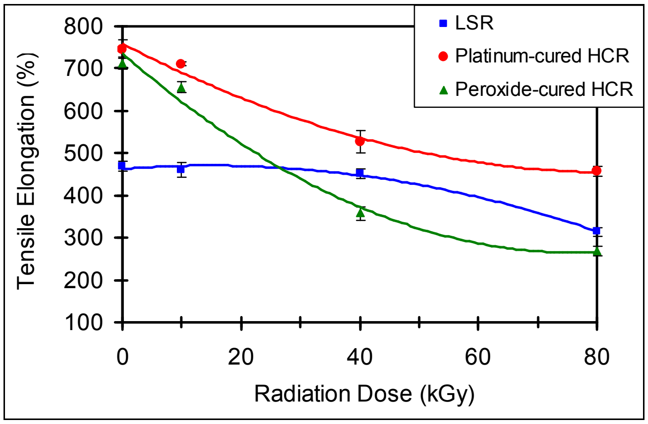


Figure11. Effect of e-beam radiation on tensile elongation of silicone rubbers.

E-beam radiation slightly increased the tensile strength of LSR and platinum cured HCR. However, it deteriorated the tensile strength of the peroxide cured HCR by up to 39%, as illustrated in Figure 12. A low level dose (10 kGy) had a minimal effect on the tear strength of all three silicone rubbers, while higher radiation doses led to substantial amounts of tear deterioration, as presented in Figure 13. A 35% to 40% reduction of tear strength was observed for all samples after exposure to an 80 kGy radiation dose of e-beam radiation.

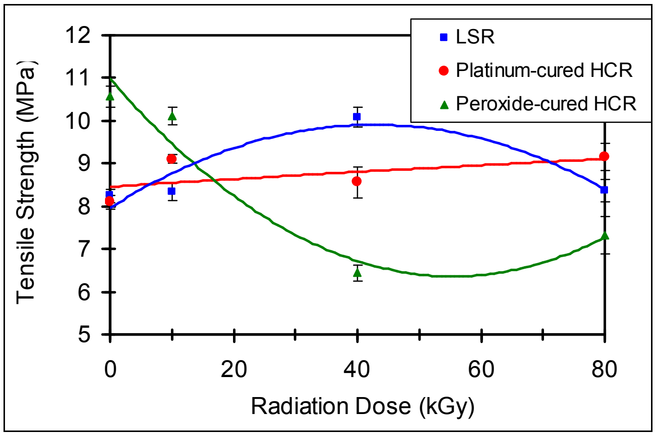


Figure 12. Effect of e-beam radiation on tensile strength of silicone rubbers.

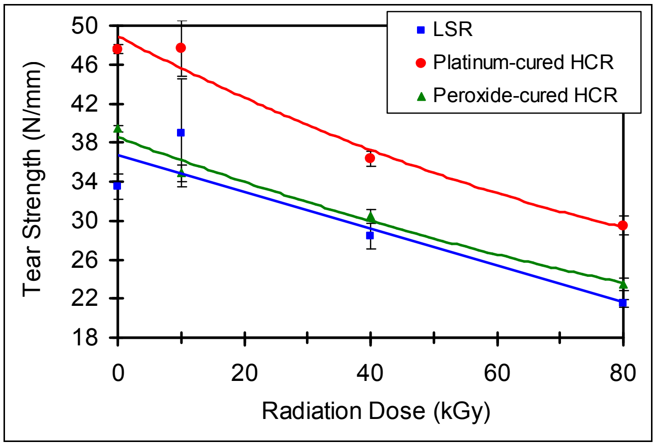


Figure 13. Effect of e-beam radiation on tear strength of silicone rubbers.

4.3. Effect of Ethylene Oxide Treatment

As shown in Figures 14, 15, and 16, EtO treatment had a negligible effect on the durometer hardness, the tensile modulus, and the tear strength of the three silicone rubbers. A 20% higher tensile elongation was measured for LSR after EtO treatment, as illustrated in Figure 17. In contrast, the effects of EtO treatment on the two HCRs were negligible and within the error limit of the test.

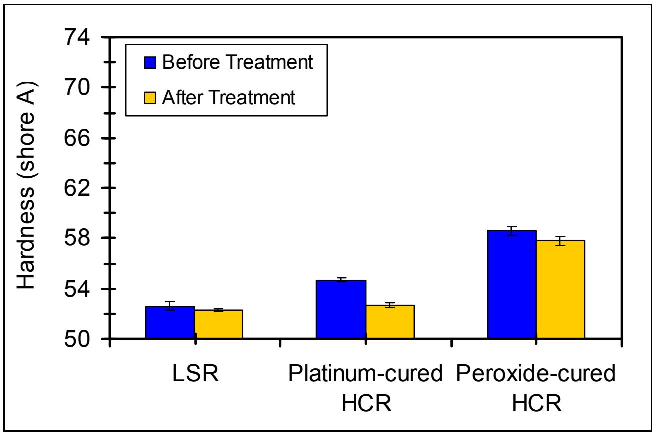


Figure 14. Effect of ETO treatment on durometer hardness of silicone rubbers.

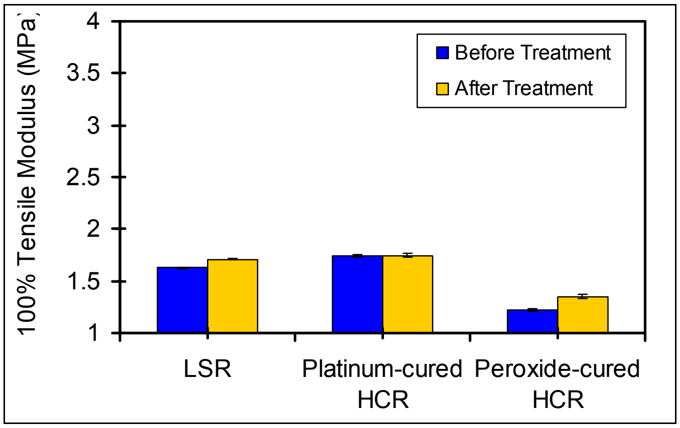


Figure 15. Effect of ETO treatment on tensile modulus of silicone rubbers.

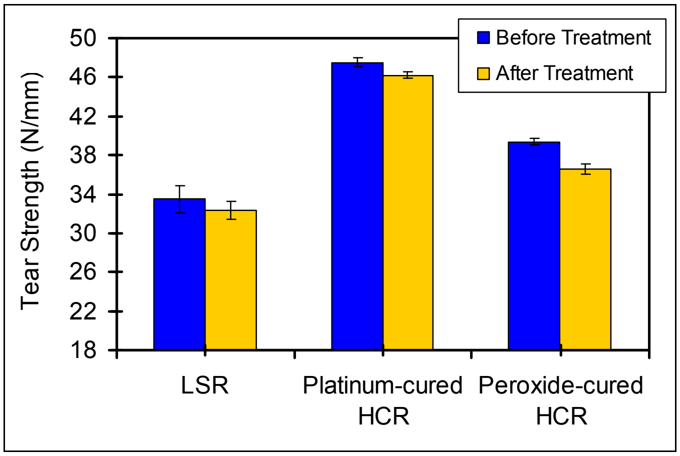


Figure 16. Effect of ETO treatment on tear strength of silicone rubbers.

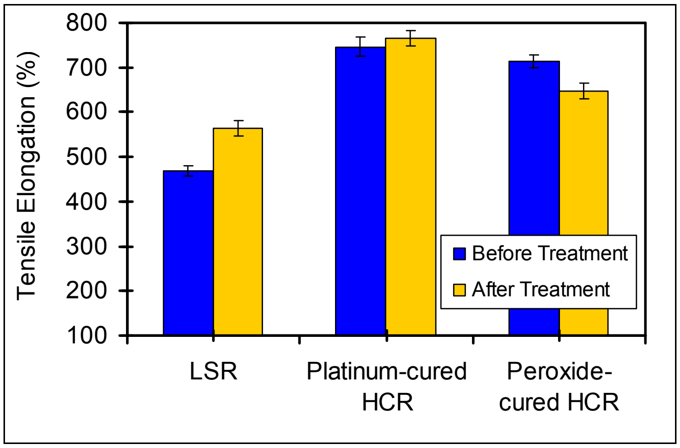


Figure 17. Effect of ETO treatment on tensile elongation of silicone rubbers.

As shown in Figure 18, the tensile strength of LSR increased by nearly one third following EtO treatment. Minor improvement in the tensile strength of the two HCRs was observed after EtO treatment. An improvement of 13% was observed for the platinum cured HCR after EtO treatment, which is just above the error limit of the measurement.

It is unclear why the EtO treatment had such a large effect on the tensile strength of LSR while the other LSR properties and the properties of the other two HCRs remained relatively unaffected. The proprietary filler loading content and filler surface treatment for LSR Elastosil® LR3003/50 from Wacker may be responsible for the observed trend.

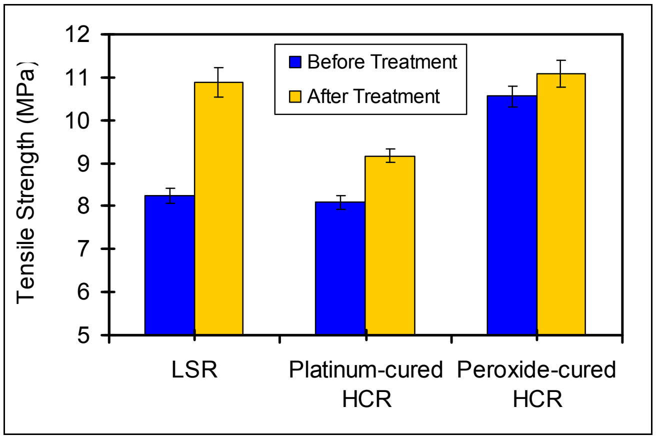


Figure 18. Effect of ETO treatment on tensile strength of silicone rubbers.

5. Conclusion

The effect of sterilization on three types of commercial silicone rubbers has been investigated. An increase of hardness durometer and tensile modulus was observed in peroxide cured HCR after high levels of gamma or e-beam radiation. Gamma and e-beam radiation also led to the reduction of tear strength of silicone rubber. Both gamma and e-beam sterilizations led to the deterioration of tensile elongation and tensile strength properties of the materials evaluated. The extent of deterioration is more pronounced in the case of peroxide cured HCR, with up to a 45% reduction of tensile strength and a 74% reduction of tensile elongation occurring. Given these data, we do not recommend the use of peroxide cured silicone rubber in any part or component that may be subjected to radiation-based sterilization procedures.

ETO treatment led to an improvement in tensile strength and tensile elongation of LSR. It had little to no effect on the mechanical properties of the HCRs studied. Overall, EtO sterilization did not have a significant negative effect on the properties commercial silicone rubbers. For this reason, we consider EtO treatment to be the preferred method of sterilization for silicone rubber-based medical components.

Acknowledgements

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