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HANSER

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Trouble-Free Sterilization

Silicone Elastomers

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Special reprint

A needle-free valve for infusion tubes: silicone valves made from newly developed liquid silicone rubber are radiation resistant and can be readily sterilized with ionizing radiation. (photo: Wacker Chemie AG, with the kind permission of B Braun Melsungen AG)

Trouble-Free Sterilization

Silicone Elastomers. Using a new liquid silicone rubber, silicone valves for medical technology can now be manufactured whose valve slits will not recombine chemically or "heal" even when subjected to intensive radiation sterilization. Production is possible without the use of additional auxiliaries.

CHRISTOPH BRIEHN

In medical product applications, all potential risks to hygiene must be precluded. This is why, for instance, medical equipment that is intended for single use and may come in contact with bodily fluids is sterilized in its packaging. Exposure to ionizing radiation has become the established key sterilization method for single-use products. Most frequent is sterilization with gamma radiation, but irradiation with high-speed electrons (beta radiation) is also gaining in importance.

Sterilization usually requires radiation doses between 25 and 50 kGy. These doses are so high that silicone elastomers start to undergo chemical changes when subjected to such conditions. In most cases, the resulting changes in characteristics are minor and without significance for the application.

However, caution must be exercised with regard to silicone valves that have to guarantee the precise dosing of medication and other liquids, such as valves used in insulin pumps and needle-free infusion systems, or for enteral or parenteral nutrition. In this case, there is a risk that the valve slits will partially or completely heal up during radiation sterilization, increasing the opening pressure of the valve. This can impair dosing precision or even result in complete failure of the valve, and thus in the breakdown of the sterilized equipment.

To prevent this unwelcome healing of valve slits, silicone valve manufacturers have often resorted to an additional auxiliary that separates the slit edges from one another chemically or physically. Frequently, an oil or a particulate release agent is used as an auxiliary that is either directly mixed into the silicone rubber or applied to the slit edges using a stamping tool.

This measure is a costly one for manufacturers of silicone valves, for several reasons: the releasing treatment adds more stages to the production process and the use of release agents also increases the risk of contamination of valves and the work environment that could necessitate costly follow-up treatment measures. Another factor is the material cost of the release agent used which, especially in the case of an oil, can be significant.

The new liquid silicone rubber developed by Wacker Chemie AG, Munich, Germany, marketed under the name Silpuran 6610/40, has made such problems a thing of the past. The new product allows the manufacture of biocompatible silicone valves, whose slits – even without the use of release agents – do not heal at radiation doses of up to 75 kGy.

Ionizing Radiation Induces Post-curing

It has been known since the 1950s that the mechanical properties of silicone elastomers can change under the influence of ionizing radiation. Both the gamma radiation and high-speed electrons initiate

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the formation of free radicals from the cross-linked polysiloxane molecules. As a result, the elastomer network degrades, while at the same time, free-radical reactions are triggered that create new linkages between the polymer chains.

Irradiation thus leads to a reorganization of the network. In this process, the network-building reactions predominate so that the polymer chains are more strongly cross-linked after irradiation than they were before – irradiation increases the density of the network. **Figure 1** shows examples of reaction paths leading to such radiation-induced crosslinking.

In addition, irradiation also affects the interaction between fillers and the silicone polymer. The reorganization of the network and the changed bonding of the fillers affect the mechanical properties of the silicone elastomer. Overall, this makes the silicone elastomer brittle, characterized by increased hardness and a rise in the elasticity module, as well as reduced elongation at break, tensile strength and tear strength.

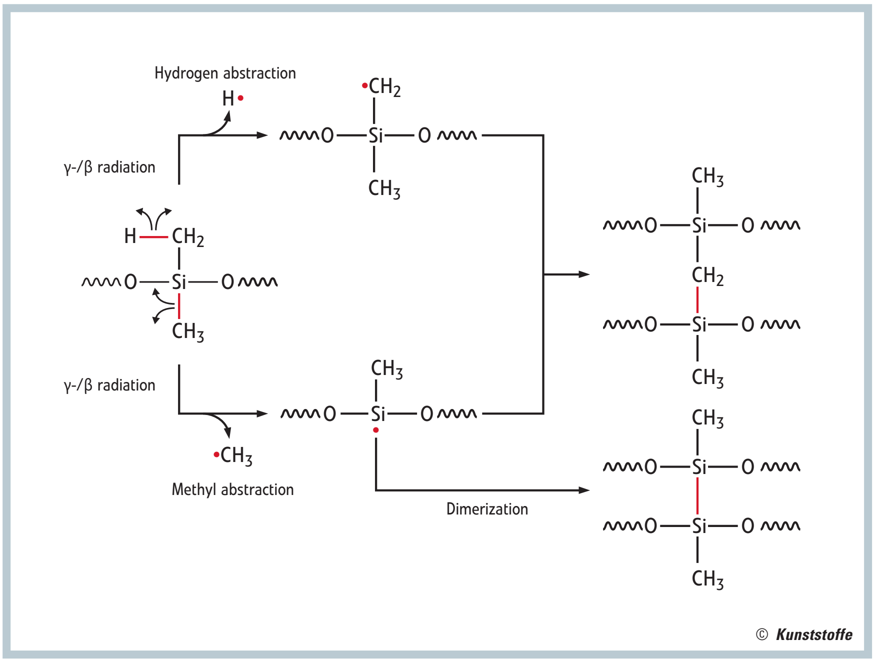

Fig. 1. Beta or gamma irradiation triggers a reorganization of the network in the silicone elastomer through free-radical reactions. The diagram shows two important reactions that cause radiation-induced crosslinking of the rubber (sources and photos: Wacker Chemie)

Radiation-induced free-radical reactions also take place on the surface of a silicone elastomer. If, for example, free radicals from two adjoining surfaces recombine, linkages are created between polymer molecules from both surfaces. The result is that the surfaces heal. Due to this, cuts in silicone surfaces can close up. The unwelcome closing-up of valve slits during radiation sterilization is also the result of such a healing process.

The higher the intensity of radiation applied and the longer the irradiation period, the greater the likelihood that the slits cut into any given silicone elastomer will partially or completely close up. However, whether and to what extent irradiation with gamma or beta rays will lead to a reorganization of the polymer network and to the closing-up of valve slits depends not only on the radiation dose, but also on the nature of the irradiated silicone elastomer. This makes it possible to influence the susceptibility of the vulcanizate to radiation-induced changes through the formulation of the silicone rubber used for the vulcanization.

Fig. 2. Laboratory non-healing effect test. At left: test sheet of standard silicone rubber with slit fully closed over. At right: test sheet of Silpuran 6610/40 with open slit

A New Formulation for a Non-healing Effect

The newly developed liquid silicone rubber Silpuran 6610/40 is based on a specialized formulation concept that gives the

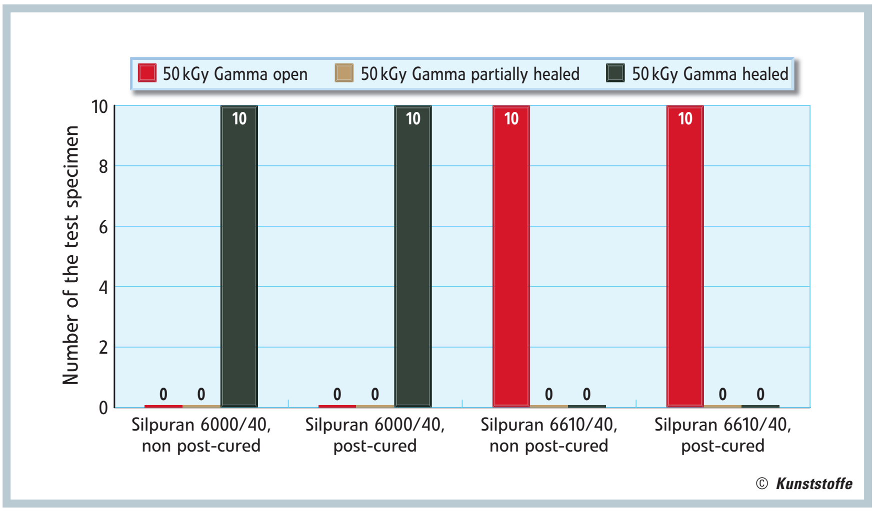

Fig. 3. Gamma irradiation test result (50 kGy). The chart shows the number of slits that are open, partially healed and fully healed; ten test sheets were evaluated in each case (post-curing: 4 h at 200 °C). Several tests were performed using both beta and gamma radiation at doses of 25, 50 and 75 kGy, all of which yielded similar results

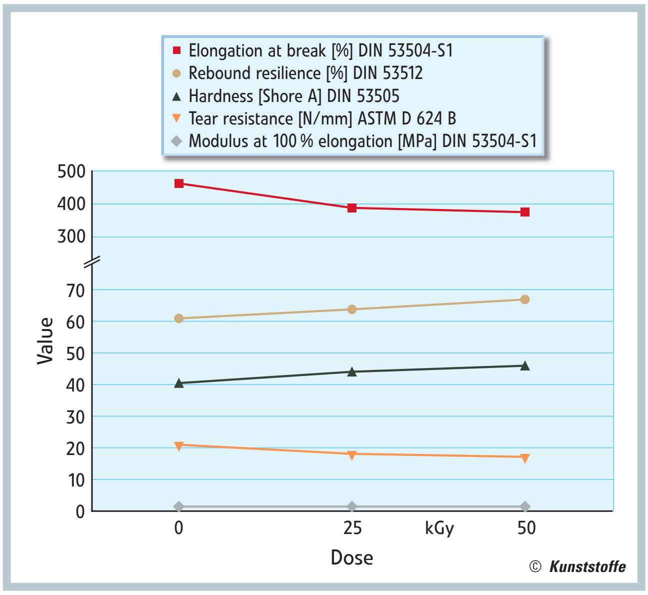

Fig. 4. Mechanical properties as a function of the absorbed dose of gamma radiation (Silpuran 6610/40 test sample, post-curing: 4 h at 200 °C)

vulcanizate a non-healing effect. Because of this effect, slit edges in this silicone elastomer remain separated from one another even when treated with ionizing radiation. Even when exposed to radiation doses far above those usually applied in sterilization, the valve slits do not close up. No additional release agent is required in the valve production process to achieve this.

The effect was examined in a simple laboratory test. This involved making test sheets from the new liquid silicone rubber, slitting them with a scalpel and treating them with gamma or beta radiation. To examine whether the slits remained open or had healed, the irradiated sheets were bent slightly, and the condition of the slits was assessed visually (**Fig. 2**). Test sheets made from a standard liquid silicone rubber, treated in the same way, were used as controls.

Figure 3 shows the test results. In contrast to the test sheets made from the control material, the slits in the vulcanizate of the new rubber grade remained open in each case at radiation doses of up to 50 kGy, regardless of whether gamma or beta radiation was applied to the test samples. The results also show that the slits can be made before the vulcanizate is post-cured. The influence of ionizing radiation on the mechanical properties of post-cured vulcanizates of the new liquid silicone rubber was also tested. The measurements show that changes in mechanical properties at radiation doses up to 50 kGy remain moderate (**Fig. 4**).

Like all products of the Silpuran range, the vulcanizates of the new liquid silicone rubber grade are biocompatible according to selected ISO 10993 and USP Class VI tests. In the ISO 10993 test, the post-cured vulcanizate was examined for cytotoxicity and pyrogenicity, as well as for its sensitizing properties. The USP Class VI testing included tests relating to acute systemic toxicity, intracutaneous toxicity and short-term implantation.

Wacker also has special measures in place to ensure optimum purity of its Silpuran silicone products, which are specially designed for use in medical technology. For example, the new liquid silicone rubber grade is filtered and inspected visually. Filling takes place in a class 8 cleanroom in compliance with ISO 4644 to prevent contamination of the liquid rubber with floating particles.

Conclusion

The property profile of the new liquid silicone rubber grade is predestined for large-scale production of dosing valves for medical equipment. Such valves are biocompatible and can be sterilized without problems through exposure to gamma or beta radiation.

The new type of rubber opens the door to the fast and clean production of biocompatible injection-molded silicone slit valves. Valve slits can be inserted before post-curing using a punching tool or a slit knife, and it is even possible to create them directly during injection molding with a suitable mold. In addition, silicone processors do not have to use an additional release agent during the process and, therefore, do not have to accept the risk of contamination associated with the application of release agents.

Manufacturers of medical equipment also benefit in that they get a silicone valve that is free of potential release agent contamination. They also have the certainty that their equipment will not fail because valve slits heal up after sterilization, i. e., fewer rejects are produced. Physicians and patients also profit from the new silicone because they can be sure that doses of medication and nutrient solutions are always administered with consistently high accuracy. ■

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