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RADIATION-INDUCED CROSSLINKING OF SILICONE

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Abstract - Silicone is an important material used in demanding applications as implant for breast enlargement or augmentation mammaplasty, low temperature applications and eletronic ones. Presence of olygomers and catalysis residues can be a concern. This work proposes to study the use of a catalysis -free system as a way of crosslinking. One medical-grade silicone was evaluated. The crosslinking was performed by ionizing radiation and physical-chemical properties were assessed. It was achieved high gel content (>90%) at dose of 25kGy, determined by gel fraction measurement. Swelling measurements showed a trend for stabilization of crosslinking degree by 75 kGy. DMTA measurements showed that crystallization was impaired by the crosslinking reaction.

Introduction

Silicone is an important elastomer but its radiation chemistry has deserved very little attention from polymer scientists, as its curing system is already an established art. As a consequence the studies of irradiation of silicone are concerned with its radio-resistance connected with sterilization[1,2] or its use in nuclear facilities. In this work, it was studied the crosslinking of medical grade silicone by ionizing radiation. The resulting network was characterized by DTMA, as well as gel fraction and swelling degree.

Experimental

Plastic syringes filled with Dow Corning biomedical grade silicone were irradiated in ^{60}Co source at 5, 10, 25, 50 and 75kGy doses. Crosslinked silicone cylinders rods were cut in slices with mass and dimensions according to type of test to be done. Gel fraction and swelling assays were made utilizing analytical grade toluene.

Dynamic mechanical thermo-analysis (DMTA).

Stress-strain oscillation measurements were performed using a three bending point deformation mode, at frequency of 2 Hz with a dynamic mechanical thermoanalyzer NETZCH mod. DMA 242, in the linear viscoelastic region. The investigate samples thickness of 1.5 and 1.0 mm were cooled to –150 °C and heated under a strain-controlled sinusoidal tensile loading to 100 °C with a heating rate of 5°C/min. The maximum dynamic force used was 1 N with the amplitude of 30 μm. The viscoelastic properties, such as, the storage modulus (E') and the mechanical loss factor, damping (tan d = E"/ E'), were recorded as a function of temperature.

Swelling assay

Samples were immersed into analytical grade toluene and weighed at regular intervals until swelling equilibrium was reached.

Gel fraction assay

Samples were weighed and submitted to sol fraction extraction in a Soxhlet system with analytical grade toluene for 40h. After this period the samples were dried and their mass determined. Gel fraction was calculated as: % Gel fraction = wt. of dried gel after extraction / wt. of dry gel x 100.

Results and Discussion (Times New Roman 10, bold)

The results of gel fractions of silicone irradiated at different doses of gamma radiation are presented in table 1. Figure 1 show the graphical representation of table 1, i.e., the gel fraction curve as a function of irradiation dose. From table 1, it is possible to observe that silicone is an easily crosslinkable polymer. At 5 kGy of total dose the gel fraction is already 54%. High gel content, over 90%, is achieved at a sterilization dose of 25 kGy, however, the rate of increase slow down considerably at higher doses as shown in table 1 comparing the gel fraction at 50 and 75 kGy. It shows a clear trend to stabilize at 95% of gel fraction.

Table 1. Gel Fraction Assay Results of irradiated silicone in different doses.

Irradiation dose (kGy)	Gel fraction
2,5	Not measured
5	0.5442
10	0.8098
15	0.8434
25	0.9125
50	0.9421
75	0.9500

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The amount of gel does not inform us about the network features at higher doses, ie, over 5 kGy. Swelling data is necessary to have an insight on the network features.

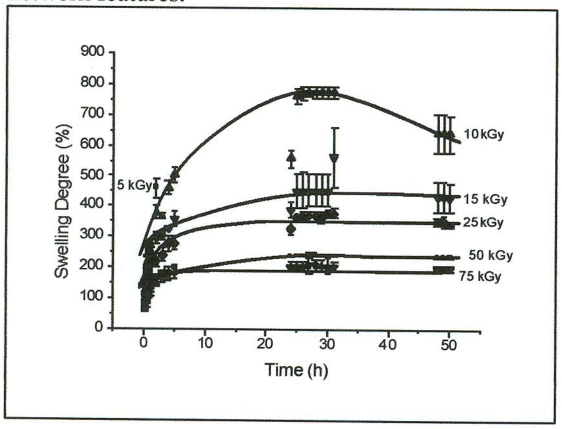

Figure 1– Swelling assay curves of silicone irradiated under 5, 10, 15, 25, 50 and 75kGy doses.

Figure 1 shows the swelling degree of the radiation-crosslinked silicone samples as a function of time and dose. It is possible to see that the samples irradiated with 5 kGy did not support the swelling procedure and fall apart after 2 hours of immersion in toluene. The sample crosslinked with 10 kGy showed an unusual behaviour, i.e., a reduction of swelling degree after 30 hours. This can be explained by the extraction of the sol fraction and consequent difference in mass of swollen sample. The same phenomena can be observed in minor proportion for the 15 kGy sample and only very slightly for the sample 25 kGy and over as the gel content approaches 100%.

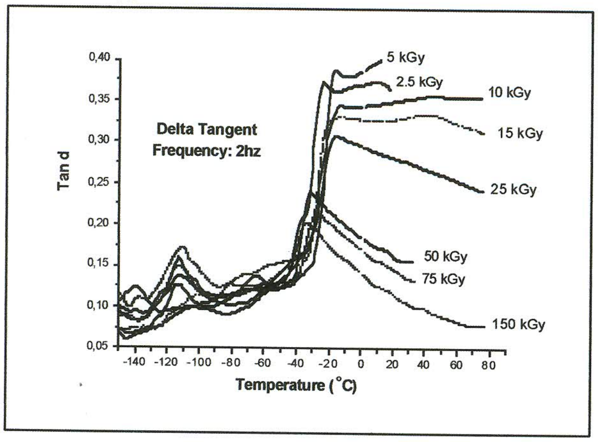

Figure 2. TDMA of Silicone irradiated under different doses

From figure 2, it is possible to see that the degree of swelling at 75 kGy showed only a small decrease as compared with the degree at 50 kGy. It is possible to suppose that the rigidity of the network is making more and more difficult to promote the crosslinking reaction. DTMA assays were used to evaluate the thermo-mechanical characteristics of the network. It is easy to distinguish two groups of curves. In the first group are the weakly crosslinked samples, i.e., the samples from 2.5 to 15 kGy. In the second group are the strongly crosslinked samples, i.e. the samples from 50 to 150 KGy. The 25 kGy sample is on the middle showing an intermediary behavior.

It is known that the glass transition temperature of silicone is in the range of -120°C and the melting is in the range of -40°C. Figure 2 shows that the weakly crosslinked samples have small amplitude peaks for glass transitions and large ones for the melting transition. It was evident from figure 4 that the crystallization was reduced due to crosslinking and amorphous region was increased. This decrease in crystalinity agrees very well with previous work of Stevenson et al[3]. It is related to the increase in crosslinking density as measured by swelling degree. It can be concluded that higher the crosslinking density lower the mobility of silicone segments and so crystallization is impaired.

Conclusion

Radiation-crosslinking proved to be an useful process to produce well-established silicone networks at low dose in the absence of any catalyst system.

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