



Gamma irradiation and oxidative degradation of a silica-filled silicone elastomer



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ABSTRACT

The radiation oxidative degradation of a commonly used silica-filled silicone elastomer DC745 was investigated by a series of experimental techniques. This elastomer is known to be chemically and thermally stable, but insufficient data exist on its radiation resistance. In the present work, gamma doses up to 200 kGy were applied under air at room temperature and 1 Gy/s. Chemical changes due to radiation were investigated by NMR, FT-IR, resonance Raman, and mass spectroscopy. DSC and TGA experiments probed thermal transitions and thermal stability changes with exposure dose. SEM probed variations on the surface of the elastomer, and changes in the polymer network were investigated using solvent swelling methods. Electron paramagnetic resonance (EPR) was employed to detect and identify free radicals. Uniaxial compression load tests at variable temperatures were performed to assess changes in the material's mechanical response as a function of radiation dose. Results demonstrate that, with increasing exposure, DC745 undergoes changes in chemistry that lead to an increase in thermal stability and cross-link density, formation of free radical species, decrease in heat of fusion and increase in stiffness at low temperatures. Taken together, these results indicate that oxidative cross-linking is the dominant radiolysis mechanism that occurs when this material is exposed to gamma irradiation in air.

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1. Introduction

Siloxane polymers are used in numerous applications and are thus subjected to various environmental conditions that may adversely impact their performance and stability. In particular, it is important to understand changes in structure–property relationships that are triggered by exposure to harsh environments. For instance, ionizing radiation can greatly alter the molecular structure and thereby the macroscopic properties of polymers through ‘radiation chemistry’ mechanisms like chain scission, cross-linking and oxidation [1,2]. Consequently, understanding the molecular origin of these chemical and structural changes is important in order to predict the material's lifetime. Ideally, sensitive experimental methods would provide the means to fully determine the radiolysis mechanisms that trigger damage and limit long-term performance. However, due to the low sensitivity of many

experimental techniques, polymers are usually exposed to high gamma doses in order to create significant degradation in the material. This approach certainly allows for easier experimental detection of radiolysis induced damage, but it may also lead to promoting mechanisms that do not occur under lower dose and dose rate conditions.

In this work, we were interested in exposing a commercially available cross-linked and silica filled elastomer DC745 to moderate doses of gamma irradiation. Radiolysis in this material was previously investigated for samples exposed to doses up to 250 kGy under nitrogen atmosphere [3]. The authors employed NMR techniques to demonstrate that gamma exposure decreased polymer chain segmental dynamics, which was accompanied by a bimodal distribution of residual dipolar couplings. In the NMR time scale, topological constraints interfere with segmental re-orientations so that homonuclear dipolar couplings do not average to zero. The bimodal distribution was reasoned to be mainly associated with two distinct populations: cross-links in the polymer network and polymer–filler interactions. The two populations and the strength of

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their residual dipolar couplings were found to increase with radiation dose. DSC and solvent swelling experiments confirmed the NMR interpretation. The same research team also used NMR relaxation times and magnetic resonance imaging experiments to monitor the deformation and cross-linking in a DC745 material that was subjected to high compressive strain and gamma irradiation in a nitrogen environment [4,5]. The results of their experiments showed a strong decrease in NMR transverse relaxation time (T_2) with increase in the degree of cross-linking. In the present work, similar gamma doses were applied, but the material was irradiated in air instead of a nitrogen environment. It is well known that the atmosphere under which the polymer is irradiated has an effect on the nature of the chemical reactions that occur. Under inert atmosphere, radicals often tend to react to form cross-links, which increases the mechanical strength of the material. Similarly, under reactive atmosphere like air, oxygen reacts with free radicals and initiates oxidative degradation processes that can cause material hardening via oxidative cross-linking in parallel with scission reactions. At low temperatures, the presence of oxygen in the polymer or in the atmosphere may lead to formation of stable peroxides or hydroperoxides, which are likely to compete with cross-link reactions. Overall, oxygen is usually expected to increase the amount and/or rate of cross-linking and oxidative degradation of the polymer [6,7]. The balance between cross-linking and scission reactions, both under inert or oxidative conditions is normally material specific and hence of primary interest in polymer radiation chemistry studies.

During this work the material was exposed up to 200 kGy at RT, and a comprehensive set of experimental techniques was used to detect changes in chemical, physical and mechanical properties. Solid-state and liquid-state NMR, FT-IR, Raman and mass spectroscopy were performed to monitor chemical changes, detect evolved gases and radiolysis products. Thermal analyses (TGA and DSC) were performed to investigate changes in the thermal stability and degree of crystallinity. Solvent swelling experiments were used to gauge variations in the polymer network and cross-link density, whereas imaging techniques (SEM) probed changes to the surface and cross-sections of the polymer. Electron paramagnetic resonance provided information on any stable free radicals that remained in the polymer long after gamma exposure was concluded. Finally, mechanical tests were performed to monitor changes in the macroscopic elastic properties of the material.

2. Materials and methods

2.1. Material preparation

DC745 is a filled cross-linked copolymer that was obtained from Dow Corning as an uncured resin. It comprises a mixture of 38 wt% high surface area fumed silica and low surface area quartz blend with 62% reactive silicone resin. The silicone resin is composed of poly(dimethylsiloxane)-*co*-poly(methylphenylsiloxane) (PDMS-*co*-PMPS). NMR characterization of the uncured resin suggests that it contains about 98.5% dimethylsiloxane, 1.5% methylphenylsiloxane and a small amount of vinylsiloxane constituents that are converted to short chain (likely $N = 4$) alkyl cross-linking junctions during a free radical curing process. The resin is cured by thermal activation of an added peroxide initiator at 170 °C for 10 min. The resulting filled rubber material has a density of 1.2 g/cc. For the radiation experiments, cured DC745 samples were placed into sealed aluminum canisters in an air atmosphere. The canisters had a volume of 120 cc, and the samples occupied less than 10% of the total volume of the canister. The canisters were backfilled with dry air to about 750 torr. The average sample thickness was 0.32 cm. Samples were exposed at the gamma irradiation facility (GIF) at

Sandia National Laboratory in New Mexico using a Co-60 source (1.2 MeV). The samples were exposed at 1 Gy/s (100 rad/sec) to cumulative doses of 12.5, 50, and 200 kGy at room temperature (10 kGy is equivalent to 1 Mrad). In addition, a canister containing 3.2 g of DC745 was also exposed to 200 kGy at 0.25 Gy/s to evaluate evolved gases and estimate oxygen consumption. No changes in color due to gamma exposure were observed for any of the samples investigated in this work. We also analyzed the effects of gamma irradiation on the filler present in the resin. To separate the filler from the uncured resin, a toluene and ammonium hydroxide solution was prepared containing the uncured DC745. This solution was centrifuged to separate the solute from the solid phase. This solid phase was dried overnight at 100 °C and later analyzed by ^{29}Si MAS NMR, which established that it contained primarily inorganic material. The isolated filler was then exposed to 100 kGy at 1 Gy/s in air and examined by EPR to probe long-lived radicals.

2.2. Thermal analyses

TGA experiments were performed on a Thermal Instruments Q500. Approximately 5–10 mg of DC745 sample was placed in an aluminum TGA pan. DC745 thermo-gravimetry carried out in inert atmosphere showed a single weight loss step as commonly observed for PDMS [8]. DC745 samples were subject to a selection of five temperature ramp rates (from 0.5 °C/min to 20 °C/min) from room temperature to 600 °C under a nitrogen purge, with a flow rate of 10 ml/min. The range of ramp rates was chosen in order to calculate the respective activation energies for thermal decomposition for each sample type. Kinetic information was obtained using the method proposed by Flynn and Wall for well-resolved single step decompositions and first order kinetics [9,10]. The equation used was $E = -R \cdot (d \log \beta / d(1/T))$, where R is the gas constant, and β is the heating rate. DSC experiments were performed on a TA Instruments Q2000 DSC with a quench cooling accessory. Approximately 5–10 mg sample were sealed in a Tzero aluminum hermetic pan. Each sample experienced two cycles of cooling and heating; both cycles started at room temperature and ramped to a temperature of -150 °C, and then were heated to a temperature of 160 °C at 10 °C/min. An isothermal conditioning was performed for 15 min at -150 °C. The second cooling cycle was modulated at a rate of 5 °C/min. The first cooling and heating cycle was used to determine if any processing history was present, the second slow cooling and heating cycle was used to determine the baseline thermal characteristics. Both the temperature and heat of fusion were calibrated using the melting of high purity Indium. The pristine polymer was characterized by a melting temperature at -43.6 °C and a glass transition temperature at -120 °C.

2.3. Chemical analyses

Solid-state NMR experiments were performed using a Bruker Avance NMR spectrometer operating at 400.13 MHz for ^1H and a Bruker (4 mm) MAS probe spinning at 8 kHz. The external reference used was tetramethylsilane (TMS) and about 512 scans were acquired per experiment. Liquid-state ^1H NMR experiments were carried out using a Bruker Avance NMR spectrometer operating at 300.13 MHz; proton signals were referenced to internal deuterated chloroform (CDCl_3) (99.6% deuterated from Acros Organics). Extractable material was obtained by immersing 100 mg of DC745 in 1.5 g of CDCl_3 overnight. Extracts were analyzed by liquid-state ^1H NMR. The resonance Raman spectra were recorded on a Renishaw inVia micro resonance Raman spectroscopy system, using the TE air-cooled 576×400 CCD array in a confocal Raman system (wavelength: 514 nm). The incident laser power was kept at 7.37 mW and total accumulation times of 3 s were employed. The

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