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A. T. Chien, B. Balazs, J. LeMay

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Characterization of the Polymer-Filler Interface in γ-Irradiated Silica-Reinforced Polysiloxane Composites

Allen T. Chien, Bryan Balazs, and James LeMay
Chemistry and Materials Science Directorate,
Lawrence Livermore National Laboratory, Livermore, CA 94551

ABSTRACT

The changes in hydrogen bonding at the interface of silica-reinforced polysiloxane composites due to aging in gamma radiation environments were examined in this study. Solvent swelling was utilized to determine the individual contributions of the matrix polymer and polymer-filler interactions to the overall crosslink density. The results show how the polymer-filler hydrogen bonding dominates the overall crosslink density of the material. Air irradiated samples displayed decreased hydrogen bonding at the polymer-filler interface, while vacuum irradiation revealed the opposite effect.

INTRODUCTION

Silica-reinforced polysiloxane composites are of technological interest due to the significant reinforcement of the polymer through hydrogen bonding between the silicone polymer chains and the surface silanol groups on the silica filler surface. The properties of filled-polymer systems are governed by the individual components of the composite which include: polymer and filler composition, filler size and morphology, and strength of the interfacial bonding between the polymer and the filler phases.[1,2,3] Although the interactions and reinforcement mechanisms of silica-reinforced silicone systems have been extensively studied using variations in particle size, shape, and surface modification, there has been little work done regarding changes that may occur in these systems when they are subjected to high energy ionizing radiation.

A two-step swelling procedure developed by Polmanteer and Lentz has been used to accurately measure the crosslink density of silica-reinforced polysiloxane composites.[4] This procedure allows for the differentiation of the chemical crosslink density of the polymer matrix and the apparent crosslink density resulting from hydrogen bonding between the filler and polymer matrix. In this paper, we examine have applied solvent swelling to assess radiation-induced changes in crosslink density and polymer-filler interactions of silica-reinforced polysiloxane composites.

EXPERIMENTAL

The polymer used in this study was a random copolymer of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxanes. The percentages of each monomer unit in the base rubber were 90.7 wt. % PDMS, 9.0 wt. % PDPS, and 0.31 wt. % PVMS (NuSil Corp., Carpenteria, CA). This elastomer was compounded into a reinforced gum by milling with a mixture of 21.6 wt. % fumed silica (Cab-o-Sil M7D, Cabot Corporation, Tuscola, Il), 4.0 wt. % precipitated silica (Hi-Sil 233, PPG Industries Inc., Pittsburgh, Pa), and 6.8 wt. % ethoxy-endblocked siloxane processing aid (Y1587, Union Carbide Corp, Danbury, CT). After bin aging, this reinforced gum was formulated with the addition of a peroxide curing agent. The resulting system was studied as a 50% porous open cell material by mixing with 50 weight percent of 25-40 mesh prilled urea spheres (Sheritt-Gordon Mines Ltd., Canada) which were subsequently rinsed out with water after curing of the polymer. Samples were irradiated for various periods of time in a stainless steel container (volume ~ 2 *l*) exposed to a Co^{60} source (E_{avg}~1.2 MeV, 0.5 Mrad/hr). Vacuum samples were encapsulated in evacuated glass tubes (pressure ~$1x10^{-4}$ torr), while air-irradiated samples were left exposed to the air environment inside the container. All experiments were performed at the same dose rate.

The composite sample was first weighed for the initial dry weight and then submerged in 600 ml of toluene (Aldrich, Milwaukee, WI) in a sealed Teflon container while stirring. Periodically, the swollen weight of the sample was measured until an equilibrium weight was obtained. Once equilibrium had been established, 150 ml of concentrated ammonium hydroxide (28 wt. %, Aldrich, Milwaukee, WI)) was added directly to the toluene solution, the container was resealed, and stirring continued. Each sample was weighed periodically until equilibrium was reached with the toluene/ammonia mixture. The samples were then dried overnight under vacuum or under ambient conditions for seven days and reweighed for the final dry weight.

Molecular weight between crosslinks (M_x) was calculated using the French and Flory equations (equations 1 and 2 respectively) given below.[5,6] A correction was made for the weight gained due to the filling of the pore spaces with solvent. This weight was subtracted from the swollen weight before M_x was calculated. For each determination, we averaged the results of six samples from the same material lot.

$$c = \frac{S_P - \frac{S_e}{\phi_B}\left(\frac{I-F}{I}\right)}{S_p + S_s\left(\frac{S-F}{I}\right) - S_e\left(\frac{I-F}{I}\right)} \tag{1}$$

$$M_x = \frac{-\upsilon_1\rho_2\left(c^{1/3} - \frac{c}{2}\right)}{\ln(1-c) + c + \chi_1 c^2} \tag{2}$$

where c = Concentration or volume fraction of the swollen polymer
I = Initial weight
S = Swollen weight
F = Final dry weight
S_P = Initial specific volume
S_e = Extracted specific volume
S_S = Solvent specific volume
ϕ_B = Volume fraction of the filler
M_x = Number average molecular weight between crosslinks
ν_1 = Molar volume of toluene
ρ_2 = Polymer density
χ_1 = Flory-Huggins interaction parameter

RESULTS AND DISCUSSION

The crosslink densities of unirradiated samples were measured using the mixed toluene/ammonia immersion swelling process. The theoretical M_x was calculated to be approximately 27,700 Daltons assuming a 0.31 wt. % vinyl content. The average M_x that was determined for seven different lots of unirradiated material was 28,600 Daltons with a standard deviation of 4,800. This measured value is within 5% of the theoretical estimate. The percent relative standard deviation (RSD) from within one sampling group was approximately 0.14% indicating that the measurement technique is extremely precise. From the toluene-only swelling data, the polymer matrix contribution to the total crosslink density was approximately 33%. After disruption of the hydrogen bonding network at the polymer/filler interface through the addition of ammonia, the filler contribution to the total apparent crosslink density was determined to be approximately 67%. This result illustrates that the silica filler provides considerable reinforcement to the composite system.

A series of samples were gamma irradiated from 0.5 to 50 Mrads in either air or vacuum. Figure 1 illustrates the percent change in apparent M_x versus dose for the materials irradiated in both environments. An initial decrease in the crosslink density in air-irradiated as evidenced by the increase in M_x by 40% at doses from 0-5 Mrad. From 5-15 Mrad, the trend reverses and is characterized by a gradual increase in crosslink density as indicated by the monotonic decrease in M_x. At a dose of 50 Mrads, a drop in M_x of approximately 25% from that of the original material was observed. Samples irradiated under vacuum undergo an immediate increase in crosslink density with increasing radiation dose, followed by a plateau at around 25 Mrads. This behavior is opposite from the air irradiated samples. At doses of 10 Mrad or higher, samples irradiated under vacuum were noticeably less rubbery to the touch, consistent with a higher crosslink density.

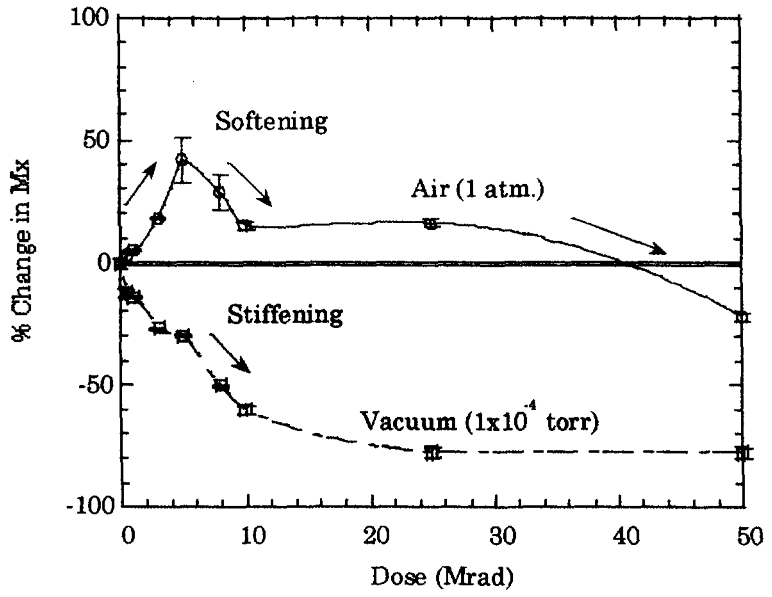

Figure 1. Plot of percent change in crosslink density versus dose of radiation for silicones in air and vacuum.

The ability to separate the contributions of the polymer and filler to crosslink density is a tremendous advantage of the toluene/ammonia swelling technique. Figure 2 shows a comparison of the individual contributions to total apparent crosslink density for both the polymer matrix and polymer-filler interactions for samples irradiated in air and in vacuum. The polymer matrix does not show much change in crosslink density at low doses in air (0-5 Mrad), but undergoes a gradual increase at higher doses. Samples irradiated under vacuum exhibit more pronounced changes in M_x versus. dose. The polymer matrix undergoes an increase in crosslink density under vacuum at lower doses (<1 Mrad) and to a much greater extent than those samples sealed in air. Presumably, the lack of oxygen prolongs the lifetime of radical species formed during irradiation, thus enhancing opportunities for crosslinks to form. In the case of the samples irradiated in air, the presence of oxygen likely promotes the formation of peroxides and hyperperoxides, which increases the rate of polymer scission and counters the effects of crosslinking.[7]

Figure 2b shows a reduction in the crosslink density attributed to the filler (air irradiation) which suggests a likely disruption of the hydrogen bonding at the polymer-filler interface. It is this reduction in interfacial hydrogen bonding that appears to drive the overall changes in the apparent M_x of the material. Vacuum-irradiated materials exhibit the opposite effect in that the polymer-filler interactions increased with dose followed by a leveling off at 10 Mrads. Possible reasons for this difference in hydrogen bonding include changes in surface water content, filler surface structure, and polymer matrix structure due to irradiation.

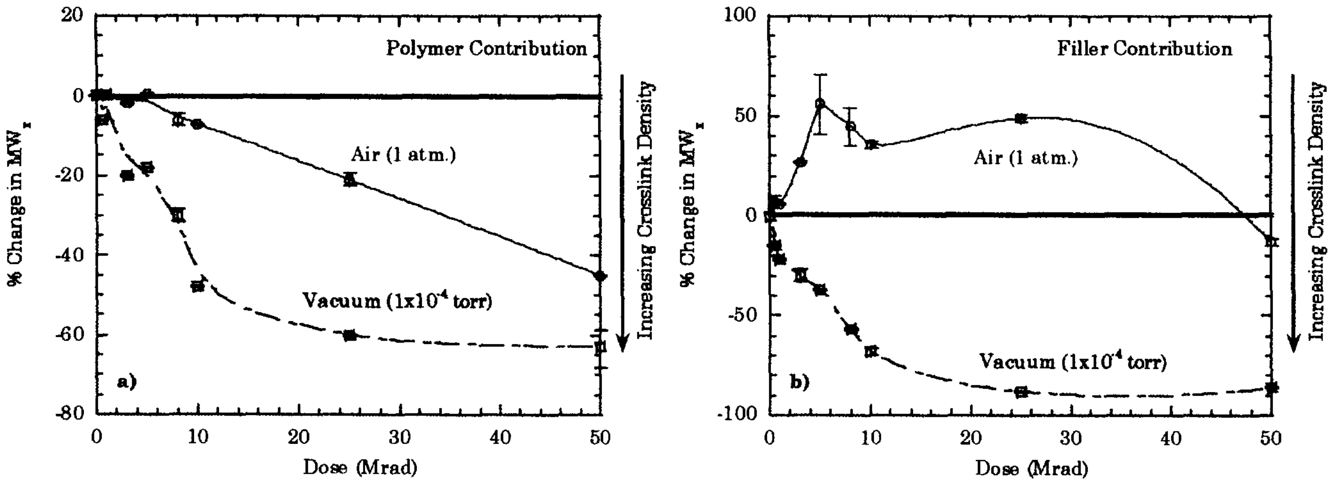

Figure 2. Plot of percent change in M_x versus dose of the individual contributions to total crosslink density of the foam comparing vacuum to air irradiation: (a) polymer matrix contribution and (b) filler contribution

Although there have been extensive studies on the changes in the defect structure, optical properties, and density of silica with radiation, few studies have examined the effects of radiation on the adsorption properties of silica surfaces and the interactions between polymer and fillers in polymer matrix composites. Tegieve *et al.* showed that gamma irradiation of silica under vacuum results in a strong dehydration of the surface as Si-OH and Si-H sites are ionized and water is removed.[8] It is possible that the resulting surface species may react with free radicals along the polymer backbone to create covalent bonds rather than hydrogen bonds and thus result in the reduction of hydrogen bonding observed between polymer and filler in our vacuum experiments. Another possibility is that changes in hydration or surface silanol density on silica may alter the extent of polymer-filler interactions.[9] Increasing amounts of adsorbed water or surface silanols have been observed to decrease the modulus in filled polymer systems through decreased polymer-filler and filler-filler interactions. Gamma irradiation has also been observed to change the density and surface area of silica particles depending upon whether hydrogen is present or not.[7,10]

CONCLUSIONS

Silica-reinforced polysiloxane composites exhibited considerable changes resulting from gamma radiation in both air and vacuum environments. Solvent swelling provided an excellent probe for the changes that occur at the polymer/filler interface which was found to dictate the changes in overall crosslink density. Samples irradiated in air showed initial softening due to the loss of hydrogen bonding at the interface between the polymer matrix and the filler. However, samples irradiated under vacuum stiffened upon irradiation due to an increase in polymer matrix crosslink density and hydrogen bonding at the polymer/filler interface. Further experiments are currently underway to advance our understanding on the mechanisms of hydrogen-bonding changes observed in the current work.

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