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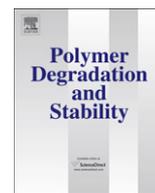
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Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

EPR and Mössbauer characterization of RTV polysiloxane foams and their constituents

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ARTICLE INFO

Article history:

Received 3 March 2008

Received in revised form 28 April 2008

Accepted 30 April 2008

Available online 8 May 2008

Keywords:

EPR

Mössbauer

RTV foams

Aging mechanisms

ABSTRACT

We have used electron paramagnetic resonance (EPR) and ⁵⁷Fe Mössbauer spectroscopies to investigate potential aging mechanisms in filled RTV polysiloxane foams, diatomaceous earth, and their other constituents. Intense, broad EPR resonances in the RTV foams were recorded at room temperature as a function of microwave power. These signals were shown to come from the diatomaceous earth filler (Celite[®] 350) in the RTV foams. ⁵⁷Fe Mössbauer measurements for neat Celite[®] 350 showed the presence of iron compounds in the form of lepidocrocite. Further EPR measurements showed that the intense, broad signals from Celite[®] 350 and the RTV foams were due to lepidocrocite that has been annealed to 175 °C and is in an excited state. EPR measurements of annealed samples of Celite[®] 350 also indicated that structural (chemisorbed) water is not easily released by the lepidocrocite. Therefore, the presence of intermediate forms of iron oxides in Celite[®] 350 and RTV foams indicates that water is not active in these materials.

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1. Introduction

Chemical degradation of room temperature vulcanized (RTV) siloxane filled foams is an important issue since it can strongly affect mechanical properties and long-term service of these materials. In particular, RTV foams, like all polymeric materials are subject to degradation as a result of aging and environmental conditions. Although RTV foams generally show low reactivity with oxygen, sunlight, and most chemicals, hydrolysis of these foams in closed systems with trace amounts of water is a potential concern [1]. For instance, it has been shown that hydrolysis and oxidation affect the oxidation state of tin octoate catalyst and subsequently the aging of RTV foams [2]. Furthermore, Zeldin et al. [3] have proposed that low molecular weight fragments can build up in the rubber network due to hydrolysis, and the presence of iron oxides can further promote scission in the siloxane chain [4]. While polysiloxanes are not hygroscopic, fillers used to reinforce polysiloxanes can absorb water. Rutherford and Coons [5] observed that RTV polysiloxane foam containing diatomaceous earth filler showed a dual-mode water sorption behavior that included a fast, Henry's law mode and a slow model that required months to

equilibrate with the ambient moisture level. They found that the diatomaceous earth was responsible for the slow mode.

We are especially interested in fully characterizing RTV siloxane foams to better elucidate the many factors that can influence their practical lifetimes. The RTV siloxane foams of interest include Dow Corning S5370 and three similar replacement foams with different amounts of cross-linker. RTV foams are cured by condensation reactions between silanols on hydroxyl-terminated polydimethylsiloxane and diphenylmethylsilanol and silanes on polymethylhydrogensilane, with evolution of hydrogen [6,7]. Cross-links are also formed by condensation between silanols and tetrapropylorthosilicate, with evolution of *n*-propyl alcohol. The condensation reactions are catalyzed by stannous-2-ethylhexanoate (tin octoate). In addition, these foams are filled with 15 wt% of diatomaceous earth. This filler has a large particle size (of the order of one micrometer) and provides bulk to the polymer. The present study aims to investigate the filler in detail through the use of electron paramagnetic resonance (EPR) and Mössbauer spectroscopies (MS).

2. Equipment and materials

2.1. Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) measurements were made on a Bruker EleXsys E-500 X-band spectrometer operating at

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Table 1
The constituents of the various RTV silicone foams by weight percent

Ingredient	S5370	LK3626	SX358	SX462
Low MW PDMS	12	16.5	17.19	12
Med MW PDMS	–	13.87	14.45	15.5
High MW PDMS	60	41.63	43.36	46.5
PMHS	6	6	3	4
DPMS	5	5	5	5
TPS	2	2	2	2
DE	15	15	15	15
	Celite [®] 315 ^a	Celite [®] 350	Celite [®] 350	Celite [®] 350

The abbreviations in the table are polydimethylsiloxane hydroxyl-terminated (PDMS), polymethylhydrosiloxane (PMHS), diphenylmethylsilane (DPMS), tetrapropylorthosilicate (TPS), and diatomaceous earth (DE). In addition, the commercial product used as the DE filler is given.

^a Equivalent to Celite[®] 350.

100 kHz field modulation and 4 G amplitude. All EPR measurements were made at room temperature in Suprasil EPR tubes that had been evacuated to 10^{-4} Torr and placed in the maximum magnetic field of the TE₀₁₁ microwave cavity.

2.2. Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectroscopy (MS) was performed at temperatures down to (4 K) using an integral cryostat and spectrometer. Mössbauer spectra were taken in transmission geometry using a ⁵⁷CoRh source of approximately 5 mCi activity and recorded in a standard 512 channels conventional constant acceleration spectrometer in the velocity range up to ± 10 mm/s. Velocity calibration was performed against a 12 μ m thick α -Fe foil. All spectra were fitted to Lorentzian line shapes with a constrained non-linear least-squares program. For simplicity, the magnetic fitting program generally assumes a “thin absorber,” unpolarized, and a single Fe site, with or without a quadrupole field present. Isomer shifts were referred to α -Fe at 298 K.

2.3. Samples

RTV foams investigated included 5-year-old S5370 foams and a set of candidate replacement foams. Foams were synthesized by mixing at room temperature a resin to 5 wt% stannous-2-ethylhexanoate. The resin composition for the replacement foams varied

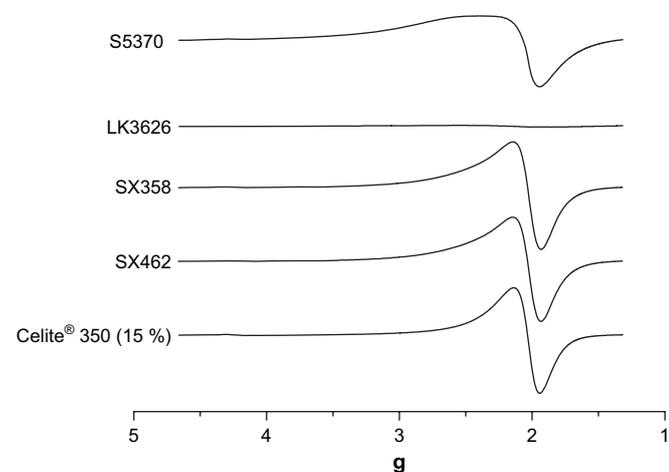


Fig. 1. EPR spectra of the RTV silicone foams and Celite[®] 350. The spectra have been transformed to display intensity vs. *g* value for easy comparison. The intensity of the Celite[®] 350 spectra was reduced 85% to correspond to its abundance in the various foams.

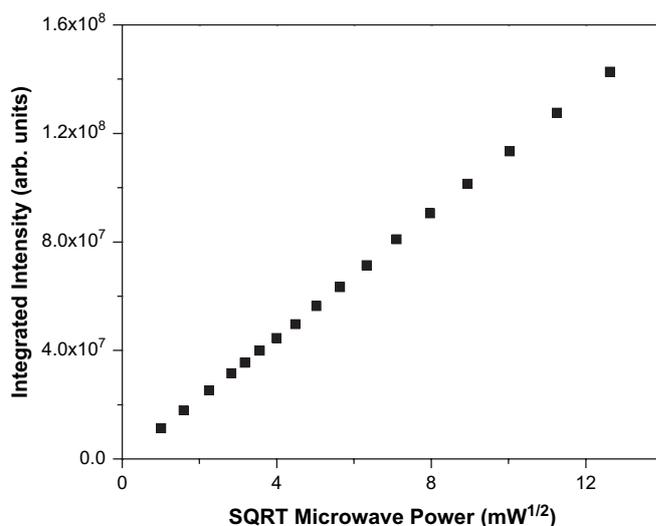


Fig. 2. EPR microwave power series for SX462 (RTV foam).

slightly to give foams with different amounts of cross-links. The weight percentages of polydimethylsiloxane (PDMS), polymethylhydrogensilane (PMHS), diphenylmethylsilanol (DPMS), tetrapropylorthosilicate (TPS), and diatomaceous earth (DE) for the S5370 formulation as reported by Baker [7] as well as the formulations of the three candidate replacements, SX358, SX462 and LK3626 are given in Table 1. In this study, we have also synthesized LK3626 foams without diatomaceous earth. Dow Corning S5370 foams were post-cured by heating at 120 °C in air for 1.5 h, whereas SX358, SX462 and LK3626 were post-cured by heating at 115–121 °C in air for 3 h. The post-cure procedure for the new foams was slightly different, but this was not believed to have caused any significant change in the diatomaceous earth filler. The 5-year-old S5370 sample had been stored under ambient laboratory conditions prior to this study.

Samples of Celite[®] 350 were obtained from the Celite Corporation of Lompoc, CA. Celite[®] 350 is mined from deposits of marine diatoms, calcined to be used as a functional filler, and comes as a fine, pink to buff powder. A chemical analysis supplied by the Celite Corporation found that the diatomaceous earth was dominated by silica (92.8%) with a significant amount of aluminum oxide (3.3%) and small amounts of water, iron oxide (hematite), calcium oxide, magnesium oxide, and other materials. Experimental results obtained for RTV foams and Celite[®] 350 samples were compared

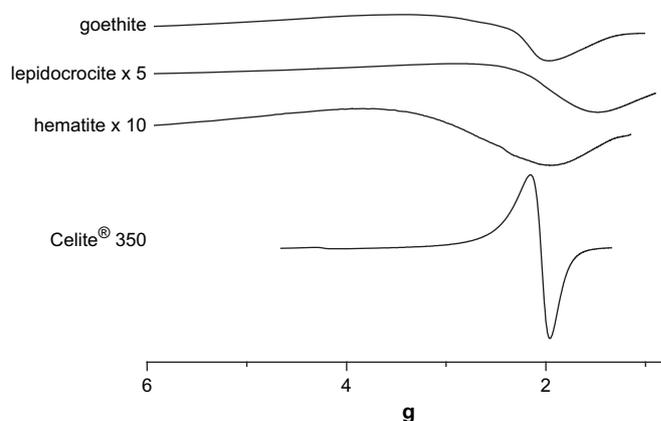


Fig. 3. EPR spectra of goethite, lepidocrocite, hematite, and Celite[®] 350. The spectra have been transformed to display intensity vs. *g* value for easy comparison.

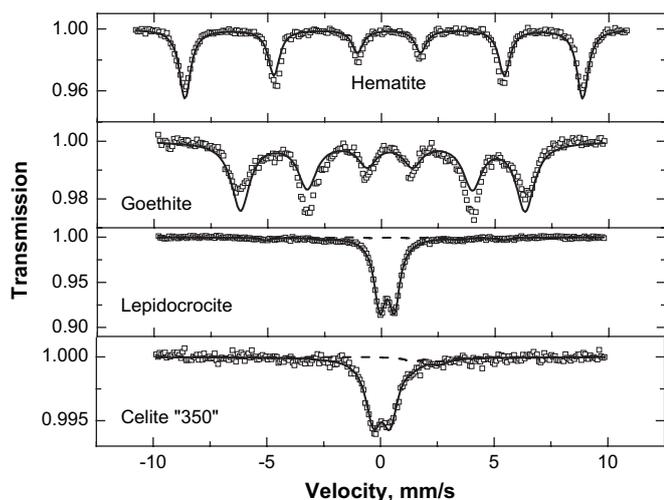


Fig. 4. Mössbauer spectra of hematite, goethite, lepidocrocite, and Celite® 350. The graph shows the raw data (open squares) and the best-fits for the primary phase (solid line), secondary phase (dashed line).

with various iron oxides. Several high purity powdered iron oxides (α -FeOOH or goethite, γ -FeOOH or lepidocrocite, and Fe₂O₃ or hematite) were purchased from Alpha Aesar and analyzed as received. Some iron oxides were step-annealed in air to monitor the change in the EPR and Mössbauer signals.

3. Results and discussion

3.1. The RTV silicone foams and Celite® 350

The EPR of the RTV foams and Celite® 350 are shown in Fig. 1. The figure shows that the EPR signals from the foams are derived from the diatomaceous earth filler. No EPR signal was detected for unfilled LK3626 foam, which is chemically similar to the other three foams, but it contained no diatomaceous earth. Differences in the g values and linewidths observed for the pristine foams (SX358 and SX462) and the 5-year-old S5370 could be due to the different preparation conditions for the diatomaceous earth fillers used (the two fillers are nominally the same but were heated differently). Interestingly, the spectra from pristine SX358, SX462, and Celite®

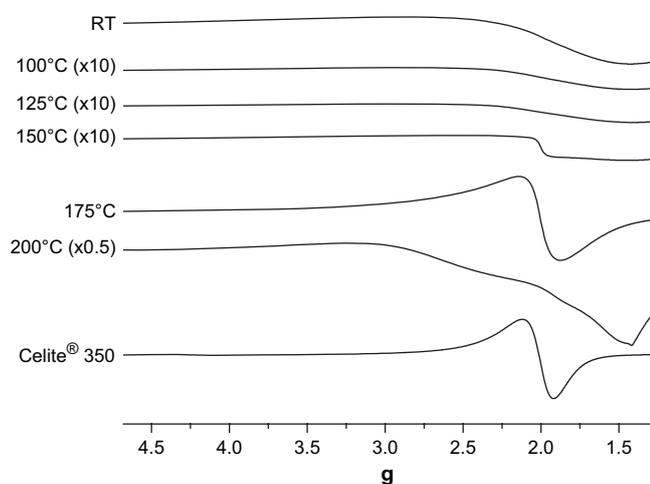


Fig. 5. EPR spectra, measured at room temperature, of lepidocrocite that has been step-annealed to the specified temperature. The EPR spectrum of Celite® 350 has also been shown for comparison.

Table 2

Parameters of the EPR spectra in Fig. 6 (the principle g value and peak-to-peak linewidth (ΔH_{pp}) are given)

T °C	Lepidocrocite	
	g value	ΔH_{pp} (G)
RT	1.914	2495
100	1.994	2487
125	1.998	2573
150	2.002	1994
175	2.008	454
200	2.034	2753

350 (scaled by 15%) are almost identical in principle g value, linewidth, and intensity indicating that the EPR signals in these foams arise from unaltered Celite® 350. We were unsuccessful to obtain ⁵⁷Fe Mössbauer signal for the RTV foams due to the low ⁵⁷Fe content.

Further analysis indicates that multiple inorganic species are responsible for the EPR signals seen in Fig. 1. The spectra from the foams and diatomaceous earth filler cannot be fit with a single Lorentzian, Gaussian, or Voigt lineshape, which indicates that the signals do not arise from one species. The inorganic nature of the species is indicated by Fig. 2 that shows no saturation effects with increasing microwave power for SX462 [8]. Considering the inorganic nature, the broad linewidths, and the chemical analysis of Celite® 350, the most likely source materials for the observed EPR signals are iron oxides and/or hydroxides.

3.2. Iron oxides and hydroxides

The most likely candidates for the source of the EPR signals from Celite® 350 and foams are iron oxides, and the chemical analysis of Celite® 350 assumes that all iron oxides are in the form of hematite which is the most stable iron oxide. While the EPR signals of iron oxides and hydroxides have not been well documented, Guskos et al. [9] studied hematite, goethite, and magnetite (Fe₃O₄). Guskos et al. found EPR signals near $g = 2$, indicating nearly free electrons, with peak-to-peak linewidths greater than 800 G, but these linewidths are too broad to be responsible for the EPR signals we have measured from Celite® 350. Not being certain of the chemical composition of Celite® 350, though, we investigated the properties of two iron hydroxides (goethite and lepidocrocite) and an iron oxide (hematite).

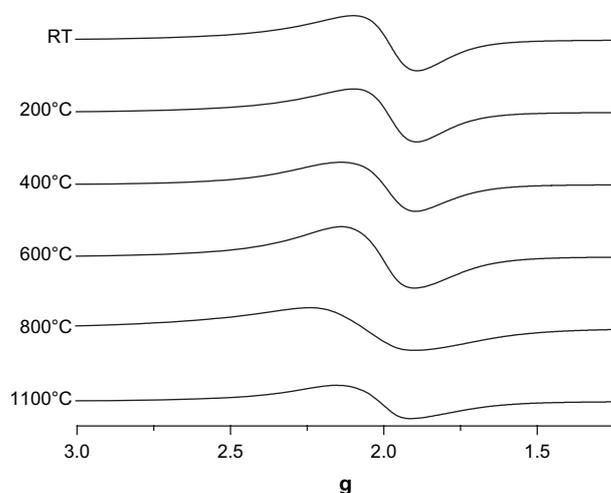


Fig. 6. Selected EPR spectra, measured at room temperature, of Celite® 350 that has been step-annealed to the specified temperature.

We first measured the EPR signals from pure samples of goethite, lepidocrocite, and hematite. The EPR spectra from these samples along with Celite[®] 350 are shown in Fig. 3. These spectra clearly demonstrate that the EPR signal from diatomaceous earth cannot simply be a convolution of the EPR signals from iron hydroxides and/or oxides as the *g* and peak-to-peak linewidth values are not similar.

The ⁵⁷Fe Mössbauer spectra of hematite, goethite, lepidocrocite, and Celite[®] 350 are shown in Fig. 4. Unlike the EPR spectra, the Mössbauer spectra indicate that lepidocrocite is the primary iron oxide present in Celite[®] 350. Both hematite and goethite show a single phase consisting of a six-line spectrum and the quadrupole splittings are negative for both spectra. On the other hand, both Celite[®] 350 and lepidocrocite Mössbauer spectra at room temperature are dominated by a quadrupole doublet with a quadrupole splitting of similar magnitude. Celite[®] 350 shows a weak quadrupole doublet “impurity” phase while lepidocrocite shows a weak six-line (magnetic) spectrum as a secondary phase (see also Fig. 7). We conclude that lepidocrocite appears to be the dominant iron compound in this diatomaceous earth, but it may also contain partially dehydroxylated lepidocrocite that has been altered (e.g., annealing).

3.3. Transformation of iron oxides and hydroxides

The iron oxide system consists of many phases that can interconvert with hematite being the most stable phase [10]. Two transformation processes of interest to this paper are goethite to hematite and lepidocrocite to hematite via maghemite (γ -Fe₂O₃). All of these transformations take place via either thermal or mechanical dehydroxylation. Celite[®] 350 is known to have been calcined to remove excess water from the filler, and the behavior of the iron hydroxides therefore directly relates to the presence or absence of water in the foams and/or fillers.

The iron hydroxide goethite was first step-annealed (the samples were held at each temperature for 1 h), and the EPR spectra were recorded after heating to each successive temperature. The measured *g* values varied slightly around a mean value during the annealing process but no definite shift occurred, and the peak-to-peak linewidth decreased by only approximately 17%. Thus, annealed goethite is not responsible for the EPR signal from Celite[®] 350.

The Mössbauer spectra of annealed goethite samples show that the samples have transformed to hematite. The isomer shifts and quadrupole splittings are similar for all of the annealed samples,

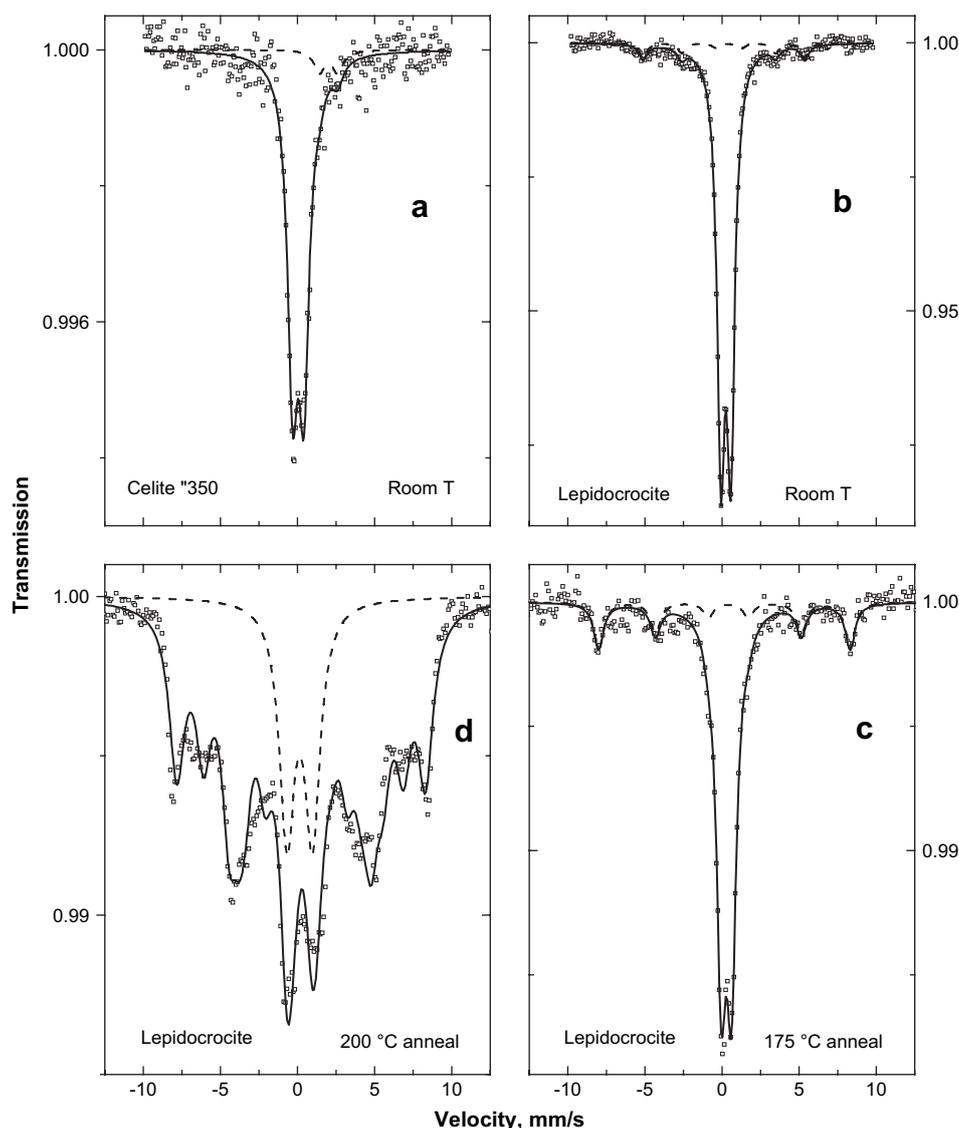


Fig. 7. Mössbauer spectra of lepidocrocite that has been step-annealed to the specified temperature. The Mössbauer spectrum of Celite[®] 350 is also shown for comparison.

but the effective internal magnetic fields clearly show that annealing goethite has transformed the sample to hematite as would be expected [10]. However, the Mössbauer spectrum of Celite[®] 350 is clearly not due to goethite that has been annealed as would be expected from the EPR data.

In order to investigate the thermal transformation of lepidocrocite, we step-annealed samples of lepidocrocite in increments of 25 °C from 100 to 200 °C (the samples were held at each temperature for 1 h). The EPR spectra measured after step annealing are shown in Fig. 5 (along with the EPR spectra for Celite[®] 350) and Table 2 summarizes the parameters of the spectra. Little change is seen in the EPR spectra for annealing up to 125 °C, but the EPR signals become more intense, the *g* value shifts to higher values, and the peak-to-peak linewidth is significantly reduced upon annealing to 150 °C. Then, after annealing lepidocrocite to 175 °C, the EPR spectra shifted dramatically. The spectra show only a slight positive shift in *g* value, but there was a dramatic increase in intensity (the EPR spectra after annealing to 175 °C was recorded at a significantly lower gain) and the peak-to-peak linewidth was reduced by approximately 82% as compared to the EPR spectra of the room temperature sample. Further annealing to 200 °C produced more significant changes in the EPR spectra, but Fig. 5 clearly shows that the EPR spectra of Celite[®] 350 is due to lepidocrocite that has been annealed to approximately 175 °C. The identification of lepidocrocite as the iron compound in Celite[®] 350 can be expected to apply for the RTV foams as well.

The fact that the EPR spectra of Celite[®] 350 is due to lepidocrocite that has been heated to 175 °C is significant when considering the potential for hydrolysis in the diatomaceous earth and RTV foams. Gehring et al. [11] attributed the change in lepidocrocite EPR to an excited state of the hydroxide when the FeO₆ octahedra reorients before transformation to maghemite. Therefore, dehydroxylation of the lepidocrocite has begun but is not complete (the process is completed upon annealing to approximately 220 °C [12]) and structural water is still present in the diatomaceous earth.

The results become even more important upon measuring the EPR spectra of Celite[®] 350 samples that have been step-annealed, the results of which are shown in Fig. 6. The *g* values shift to slightly higher values and the peak-to-peak linewidths are slightly broader with increasing temperature, but the spectra do not indicate that significant dehydroxylation of the lepidocrocite in Celite[®] 350 has taken place (i.e., lepidocrocite has not transformed to maghemite or hematite). These results strongly imply that the lepidocrocite in the diatomaceous earth filler of RTV foams cannot be thermally dehydroxylated, and therefore water is continually present in the system. These results may also indicate that water is strongly bound to the iron complex and it is unlikely to leave to hydrolyze something else.

The results for Mössbauer spectroscopy are not as conclusive. The Mössbauer spectra after step annealing of lepidocrocite are shown in Fig. 7. Very little change is seen in the isomer shift or the magnitude of the quadrupole splittings when lepidocrocite is annealed to 150 and 175 °C. Evidence of other phases (probably iron oxides) is seen upon annealing to 200 °C, and the quadrupole splitting of the lepidocrocite is perturbed. These results are consistent with previous findings [13]. The spectra certainly show that Celite[®] 350 does not contain lepidocrocite that has been heated to 200 °C (or above), and the spectrum of lepidocrocite annealed at or below 175 °C is at least qualitatively consistent with the Mössbauer spectrum of Celite[®] 350.

4. Conclusions

We have identified some of the iron compounds that are present in diatomaceous earth and in RTV polysiloxane foams by using EPR and Mössbauer spectroscopy. EPR spectroscopy first revealed that the broad intense signals in the RTV foams were due to the diatomaceous earth filler Celite[®] 350. Although the product specifications indicated that hematite (α -Fe₂O₃) was the chemical species of iron in Celite[®] 350, our results showed that hematite was not responsible for the observed EPR signals. However, Mössbauer spectroscopy indicated that lepidocrocite (γ -FeOOH) was consistent with the spectra from Celite[®] 350. Further measurements showed that the observed EPR signals from Celite[®] 350 could be attributed to lepidocrocite that had been annealed to 175 °C, and Mössbauer measurements are consistent with this conclusion.

The conclusion that RTV polysiloxane foams contain lepidocrocite that has been heated to 175 °C is of interest for aging processes in the foams. By being annealed to this temperature, the lepidocrocite has begun to release structural water but the process is not complete. More importantly, further annealing of Celite[®] 350 did not result in significant changes in the EPR signal indicating that either the structural water in lepidocrocite cannot be easily driven off in this material or more likely, the hydroxylated silica (opal) dominates the water equilibration. The possibility remains that Celite[®] 350 could slowly desorb water and therefore account for the bulk water desorption process seen by Rutherford and Coons [5], but the present study indicates that the lepidocrocite oxides in the diatomaceous earth are a marker for the water content rather than directly participating in this process.

References

- [1] Patel M, Skinner AR. Thermal aging studies on room-temperature vulcanized polysiloxane rubbers. *Polymer Degradation and Stability* 2001;73:399–402.
- [2] Labouriau A, Taylor D, Stephens TS, Pasternak M. Mössbauer and NMR characterization of tin octoate: neat and residues in RTV foams. *Polymer Degradation and Stability* 2006;91:1896–902.
- [3] Zeldin M, Bo-Rong Q, Choi SJ. Mechanism of thermal depolymerization of trimethylsiloxy-terminated polydimethylsiloxane. *Journal of Polymer Science Polymer Chemistry Edition* 1983;21:1361–9.
- [4] Yang ACM. Filler-induced softening effect in thermally aged polydimethylsiloxane elastomers. *Polymer* 1993;35:3206–11.
- [5] Rutherford SW, Coons JE. Water sorption in silicone foam containing diatomaceous earth. *Journal of Colloid and Interface Science* 2007;306:228–40.
- [6] Dallimore GR, Milligan RJ. RTV silicone foam for spacecraft electronic assemblies. *SAMPE Journal* 1982;18:8–13.
- [7] Baker GK. A history of silicone stress cushions in the weapons complex. Topical Report BDX-613-6344. Honeywell Federal Manufacturing and Technologies; June 2000. p. 1–37.
- [8] Poole CP. Electron spin resonance: a comprehensive treatise on experimental techniques. 2nd ed. Mineola, NY: Dover; 1983.
- [9] Guskos N, Papadopoulos GJ, Likodimos V, Patapis S, Yarmis D, Przepiera K, et al. Photoacoustic, EPR and electrical conductivity investigations of three synthetic mineral pigments: hematite, goethite, and magnetite. *Materials Research Bulletin* 2002;37:1051–61.
- [10] Cornell RM, Schwertmann U. The iron oxides. Weinheim, Germany: Wiley-VCH; 2003.
- [11] Gehring AU, Karthein R, Reller A. Activated state in the lepidocrocite structure during thermal treatment. *Naturwissenschaften* 1990;77:177–9.
- [12] Gehring AU, Hofmeister AM. The transformation of lepidocrocite during heating: a magnetic and spectroscopic study. *Clays and Clay Minerals* 1994;42:409–15.
- [13] Mitov I, Paneva D, Kunev B. Comparative study of the thermal decomposition of iron oxyhydroxides. *Thermochimica Acta* 2002;386:179–88.