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Aging Studies of VCE Dismantlement Returns

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Sonia E. Létant, Cynthia T. Alviso, Mark Pearson, Rebecca Albo, Ward Small, Thomas S. Wilson, Sarah C. Chinn, and Robert S. Maxwell

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1.1 Introduction

VCE is an ethylene/vinyl acetate/vinyl alcohol terpolymer binder for filled elastomers (Figure 1) which is designed to accept high filler loadings. Filled elastomer parts consist of the binder (VCE), a curing agent (Hylene MP, diphenol-4,4'-methylenebis(phenylcarbamate)), a processing aid (LS, lithium stearate), and filler particles (typically 70% fraction by weight). The curing of the filled elastomer parts occurs from the heat-activated reaction between the hydroxyl groups of VCE with the Hylene MP curing agent, resulting in a cross-linked network (Figure 2). The final vinyl acetate content is typically between 34.9 and 37.9%, while the vinyl alcohol content is typically between 1.27 and 1.78%.

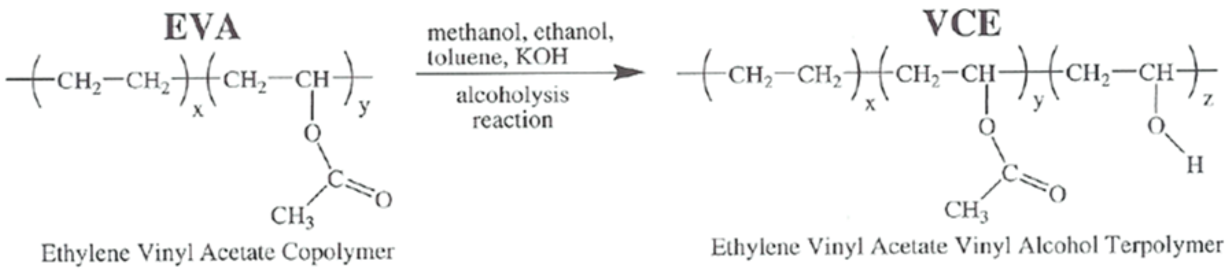

Figure 1: Base-catalyzed alcoholysis reaction of EVA copolymer yielding VCE [3]. Typical VCE composition is 34.9-37.9% vinyl acetate, and 1.27-1.78% hydroxyl.

Surveillance data for this material is both scarce and scattered, complicating the assessment of any aging trends in systems. In addition, most of the initial surveillance efforts focused on mechanical properties such as hardness and tensile strength, and chemical information is therefore lacking.

Material characterization and aging studies had been performed on previous formulations of the VCE material [1-2] but the Ethylene Vinyl Acetate (EVA) starting copolymer is no longer commercially available. New formulations with replacement EVA materials are currently being established and will require characterization as well as updated aging models [3, 4].

The initial work conducted in FY09 focused on the effects of gamma radiation up to 25 MR on the chemical and structural properties of filled and unfilled VCE material synthesized, milled, molded and cured by the Kansas City Plant (KCP) using WR-qualified processes (see KCP-613-6051). The work performed in FY10 focused on the effects of temperatures up to 150°C on the VCE material produced by KCP, and on additional measurements on samples exposed to gamma radiation. A comprehensive data integration was also performed in order to generate a mechanistic understanding of degradation mechanisms in the cross-linked VCE material, which sparked a collaboration with David Plant and Mark Read at AWE, who were using Density Functional Theory (DFT) to calculate the lowest energy configurations of a similar polymer used in the UK, as well as corresponding IR spectra.

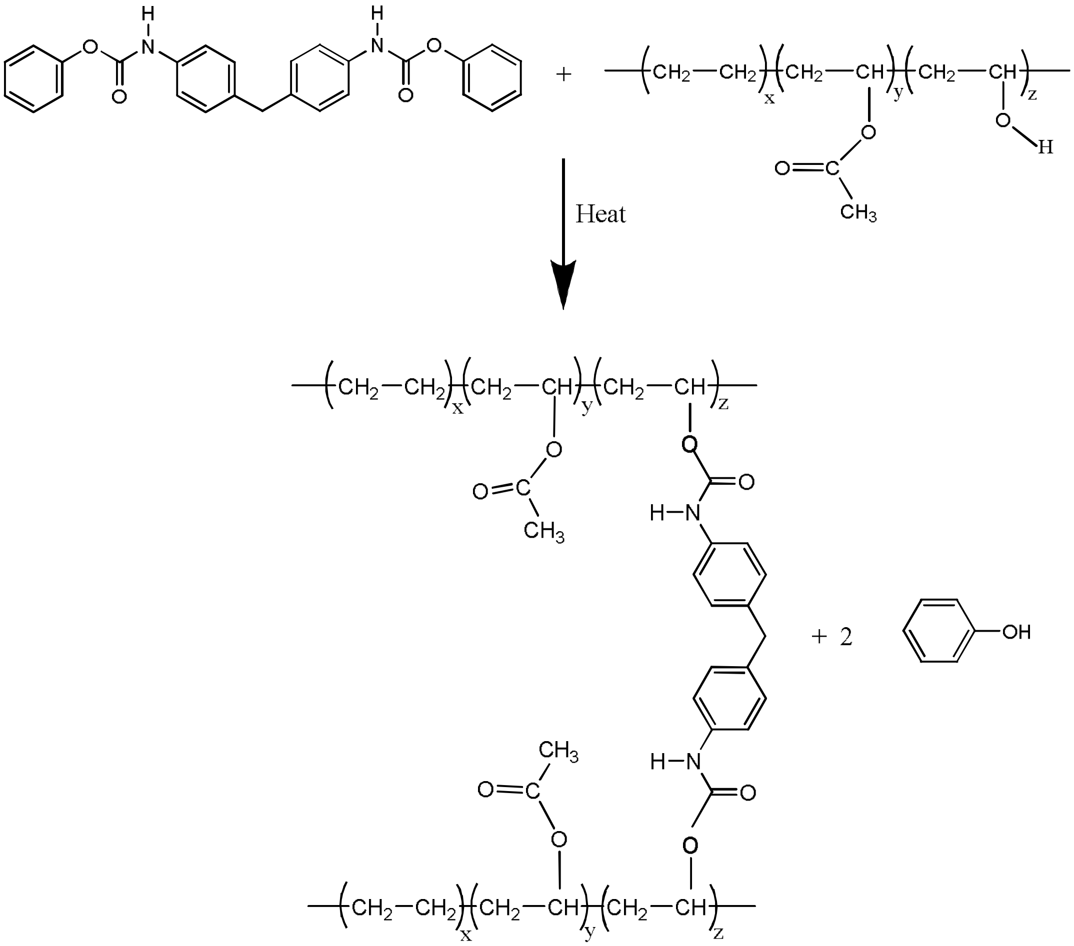

Figure 2: Curing reaction between VCE and Hylene MP [3].

Data acquired in FY09-10 showed a red shift of the material’s UV-visible absorption, the outgassing of acetic acid, and attenuated IR deformation modes upon exposure to increased levels of gamma radiation or increased temperatures, consistent with the de-acetylation model in which acetic acid is abstracted from the vinyl acetate group via a molecular rearrangement involving the displacement of a hydrogen atom from the ethylene backbone toward the acetyl group, and the propagation of the mechanism to adjacent vinyl acetate groups, forming polyenes in the polymer backbone [5, 6]. A set of VCE cluster fragments were constructed with varying degrees of de-acetylation to model possible molecular structures present in the pristine and then thermally- and/or radiologically- treated cross-linked polymer material. The goal of these calculations was to create representative molecular fragments matching the structures of the VCE material, and to predict electronic properties of the material at various stages of the de-acetylation process. We demonstrated the feasibility of DFT calculations on polymer fragments with sizes exceeding 200 atoms, and illustrated their accuracy by comparing predicted structural and spectroscopic properties with experimental measurements. The geometry-optimized structure of cross-linked VCE modeled using DFT (see Figure 3 for the structure of the distorted Hylene cross-linker within the constrained geometry-optimized structure of the de-acetylated VCE elastomer) yielded IR spectra enabling a mode by mode vibrational analysis of the fragments' structures, which were found to be in good qualitative agreement with the experimental IR spectra. UV-visible absorption spectra were also calculated using time-dependent DFT and the ALDA method for the partially de-acetylated and fully de-acetylated cross-linked VCE polymer fragments. The degree of C=C double bond conjugation resulting in the formation of chromophores was investigated for polyenes with n=5 and n=3. The n=5 de-acetylated structure and the associated absorption spectra resulted in a peak intensity centered at 395 nm, consistent with the experimentally measured value of 375 nm after thermal treatment (Figure 4 describes the de-acetylation mechanism and provides corresponding VCE structures). Finally, we demonstrated that DFT constitutes a unique tool to probe how changes in molecular structure relate to experimental observables by showing how conjugated double bonds in the EVA-OH chains distort the cross-linker, information which is only indirectly encompassed in the experimental and theoretical IR spectra [7].

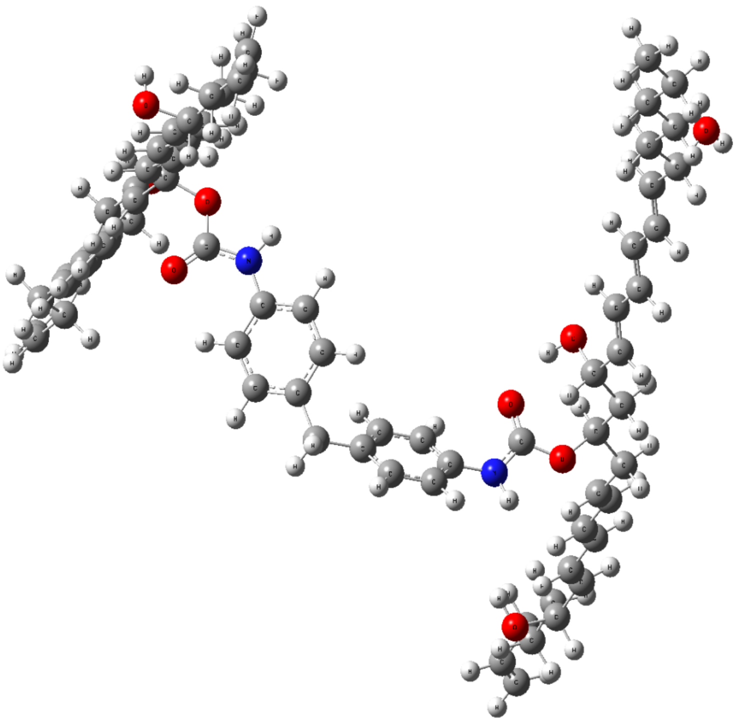

Figure 3. Molecular structure of the distorted Hylene cross-linker within the constrained geometry-optimized structure of the de-acetylated VCE elastomer [7].

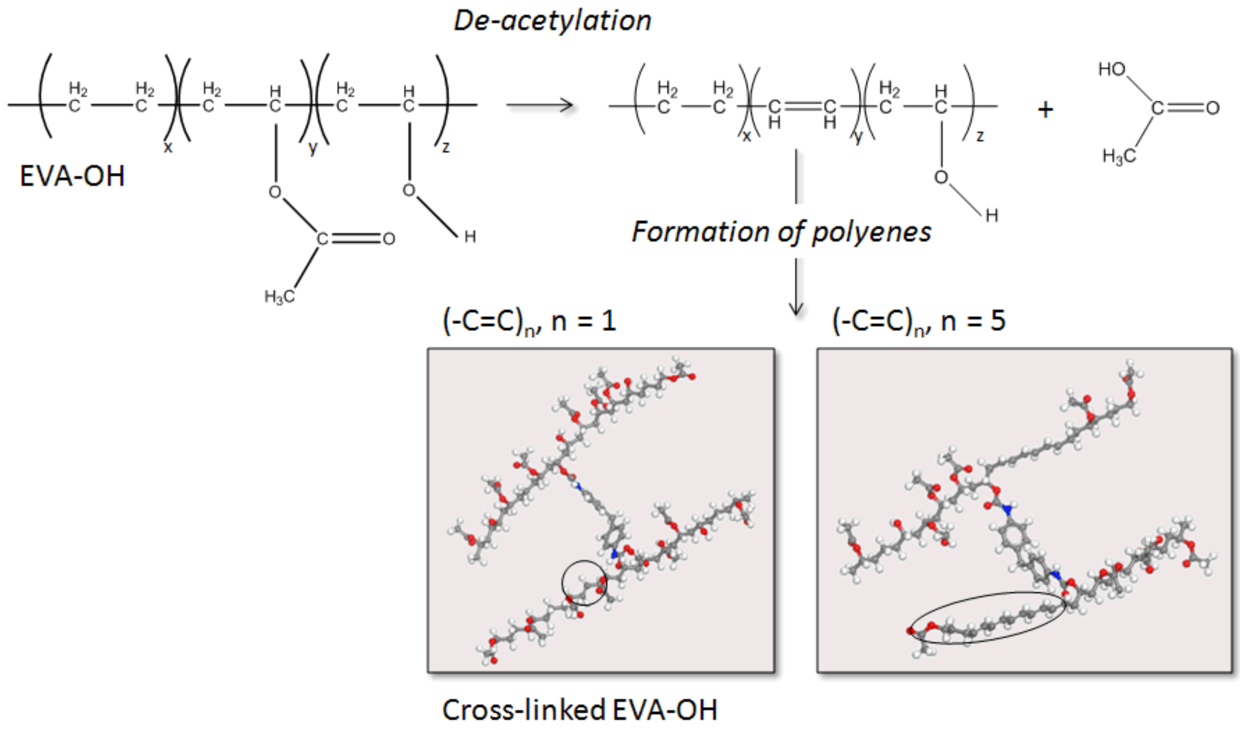

Figure 4. De-acetylation mechanism of cross-linked VCE, and corresponding DFT molecular structures.

The next step was to acquire VCE part returns to address the question of the material's lifetime into a system. This report summarizes results obtained on 37 year old VCE dismantlement parts analyzed using structural and chemical methods including Tensile Testing, TGA, IR spectroscopy, SPME-GC-MS, and pyro-GC-MS.

1.2 Experimental Approach

1.2.1 Sample Preparation

Pristine VCE samples were synthesized via alcoholysis of EVA in the presence of sodium hydroxide. The material used in this study was custom-synthesized at Honeywell Federal Manufacturing & Technologies, Kansas City, MO, with a vinyl alcohol content of 1.5% and a vinyl acetate content of 35%. After blending with 10% diphenol-4-4',-methylenebis(phenylcarbamate) and 1-2% lithium stearate (used as a lubricant) on a 2-roll mill, the VCE material was injected in molds and cured at 179°C for 30 min, resulting in the cross-linked network shown in Figure 2. Phenol released during the cross-linking reaction was removed using a thermal post-cure treatment at 120°C for 5 hr. VCE sheets with a diameter of 11" and a thickness of 0.030" were checked for uniformity using X-ray radiography and packaged with desiccant and heat-sealed sleeves prior to shipping to LLNL.

Eight 37 year old VCE dismantlement returns were also acquired from Pantex and cut into strips upon receipt. Visual inspection showed good overall integrity of the parts. Upon further examination, we realized that all parts were uniformly coated with Sylgard on each side. Parts were therefore analyzed as received, as well as after the removal of the Sylgard coatings with a razor blade, followed by inspection under the optical microscope.

1.2.2 Tensile Testing

Mechanical measurements were performed on an Instron (Model 5500-R) using a 10 lb load cell equipped with pneumatic grips. Test samples were cut from the pristine VCE or dismantlement returns to ASTM D-638 Type V dogbones using a punch. Materials were assumed to have a nominal thickness of 30 mils (0.762 mm). Testing was performed using a grip separation of 25.4 mm, which was used as the gage length for all calculations. For each sample, 5 replicates were tested to failure at a crosshead speed of 0.5 in/minute.

1.2.3 Thermo-Gravimetric Analysis

TGA experiments were performed on a Perkin Elmer TGA-7, under a flow of argon gas of 20 mL/min. Approximately 3 mg of each sample were heated from 50ºC to 900ºC with a ramp rate of 10 C /min and the change in weight percent was plotted as a function of temperature.

1.2.4 Solid Phase Micro-Extraction / Gas Chromatography / Mass Spectrometry

Replicate VCE samples (20-30 mg each) were placed in 20 mL SPME headspace glass vials, and sealed under nitrogen with crimp caps and septa (20 mm, Teflon/blue silicone, level 4, MicroLiter Analytical Supplies Inc., Suwanee, GA). Samples remained at 70°C for two weeks to maximize the volatilization of degradation signatures for observation by SPME sampling, while retaining room temperature samples and blanks to serve as controls.

Samples were analyzed by SPME-GC-MS using an automated GC-MS system (GC model 6890 and MS model 5973, both from Agilent Technologies Inc., Santa Clara, CA) with the following conditions: 85 µm Carboxen/Polydimethylsiloxane SPME fiber (Sigma-Aldrich Inc., St. Louis, MO), conditioned between samples for 5 min at 260°C. Each vial headspace was sampled at 50°C for 20 min and injected into the GC for 1 min at 250°C. The GC was set for 'splitless' injection and purged for 0.5 min with a constant 1.0 mL/min flow of helium. The column used for these experiments was designed for volatile analysis (30 m, 0.25 mm ID, 1.4 µm film, DB-624, Agilent Technologies Inc., Santa Clara, CA). Each 20 min run had the following temperature profile: 40°C hold for 1.05 min, 23.41°C /min ramp to 260°C, and 260°C hold for 6.81 min. The MS scanned the mass range from 35-450 m/z at a rate of 1.81 scans/s without filament delay. Materials outgassing from the VCE samples were identified by comparison of their mass spectra to the NIST 2.0 Library (2008).

1.2.5 Pyrolysis / Gas Chromatography / Mass Spectrometry

All pyrolysis studies were carried out with a CDS Analytical 5150 Pyro-probe coupled to an Agilent 7890 GC using an Agilent 5973N quadrupole MSD for detection of the analytes. Replicate samples from each VCE part (~0.150-0.200 mg) were accurately weighed into quartz sample tubes, and loaded into the Pt filament coil of the pyro-probe apparatus. Samples were held at an initial temperature of 60°C for 0.5 min, and then pyrolysed at a ballistic heating rate from 60 to 1000^{0}C under a purge flow of helium for a total pyrolysis time of 2.0 min. The pyrolysates were continually transferred from the pyro-probe apparatus to the GC inlet using an inert transfer line at 180°C with a 20:1 split flow for the total pyrolysis runtime. The column used for the analysis was an HP-PLOT U (30 m x 0.32 mm i.d. x 10 µm i.f.) analytical column under constant flow of 3.0 mL/min with helium carrier gas. The initial GC oven temperature was set at 40°C for 2.0 min and then ramped at 10°C/min to 180°C and held for 1.0 min at the final temperature for a total analysis time of 17.0 min. The MS ion source and quadrupole were held at 230°C and 150°C, respectively. Total ion chromatograms of the pyrolysis products were collected for each run. The NIST 2.0 Library (2008) was used for any mass spectra library searches.

1.2.6 Infra-red Spectroscopy

Infra-red spectra were acquired using a Bruker Hyperion spectrometer fitted with a 20X Attenuated Total Reflectance (ATR) objective, and a pressure setting of 3 (out of 5). All the spectra presented in this report were acquired using the same settings. A minimum of two replicate samples were analyzed for each set of experimental conditions and representative spectra are presented (there were generally no statistical differences between replicate spectra).

1.3 Results and Discussion

Visual inspection of 37 year old VCE shields obtained from dismantlement showed good material integrity. No cracks or tears were observed on any of the parts. The shields were uniformly coated with Sylgard on each side, as can be seen on a representative part cross-section image presented in Figure 5.

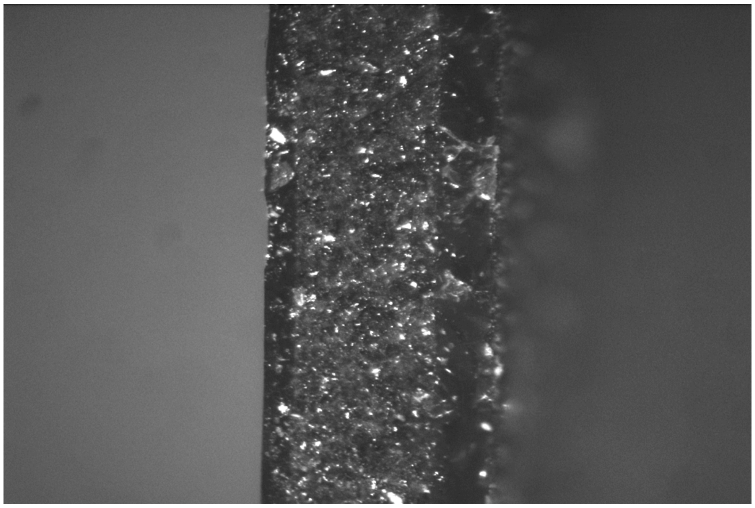

Figure 5. Optical cross-section of a 37 year old VCE shield.

Mechanical testing was conducted on parts as received, while chemical testing was conducted on parts both prior and after removal of the Sylgard coatings using a razor blade (after removal of the coatings, parts were inspected with an optical microscope to insure adequate removal of the coatings).

1.3.1 Tensile Testing

Tensile testing was conducted on 8 VCE shields using experimental conditions described in the Experimental Approach. Results summarized in Table 1 show the elongation at break and tensile stress at break for the eight VCE shields (5 replicates were analyzed for each shield and the average values are reported), and the corresponding Cycle 5 (C5) surveillance values. Typical standard deviations on these measurements were 0.02 lbf on the maximum load, 3% on the elongation at break, and 2 psi on the tensile stress at break. The data shows no statistical difference in elongation at break between the VCE part returns and the C5 value, and a slight enhancement in tensile stress at break for the VCE part returns over the C5 values, confirming the good mechanical integrity of the parts observed upon visual inspection. It should be stressed that mechanical testing is key for these parts since any breach in uniformity/integrity of the shield would interfere with the part performance.

Table 1. Summary of mechanical testing performed on eight 37 year old VCE shields, compared to Cycle 5 (C5) surveillance values.

VCE parts	Maximum Load (lbf)	Elongation at break (%)	Tensile stress at break (psi)
1	2.8	48.2	261.7
2	2.8	47.7	259.1
3	3.0	52.9	286.3
4	3.1	56.1	287.6
5	2.8	53.5	272.9
6	2.5	50.3	238.7
7	3.0	53.9	273.5
8	2.7	43.9	254.7
Cycle 5 Surveillance	**n/a**	**56 ± 19**	**210 ± 31**

1.3.2 Thermo-Gravimetric Analysis

TGA experiments were conducted on 8 VCE shields using experimental conditions described in the Experimental Approach. Parts were first analyzed as received, with the Sylgard coatings. Figure 6 shows a picture of pristine VCE synthesized at KCP (left) and VCE parts (right) after performing TGA experiments. Residuals from the VCE layer can be seen in black, while residuals from the Sylgard coatings can be seen in white. In a separate experiment, coatings were then removed and parts were re-analyzed, and compared to pristine VCE material synthesized at KCP.

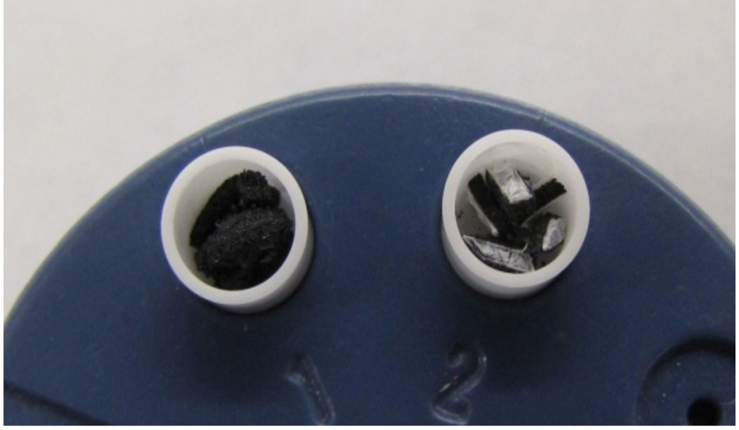

Figure 6. Image of VCE parts taken after TGA analysis. The sample holder on the left contained pristine VCE parts synthesized at KCP, while the container on the right contained 37 year old VCE part returns.

Figure 7 shows representative TGA results for 1 VCE shield (the other 7 parts lead to similar results). Two transitions are observed: the thermal scission of the acetate group starting around 280°C, followed by the thermal degradation of the hydrocarbon backbone of the polymer starting around 400°C. The filler content in the material can be extracted from the TGA curve from the residual mass after final thermal degradation. Results show that the filler content in the VCE material provided by KCP was ~74%, which matches information provided by Dr. Eastwood, who synthesized this VCE material. The filler content in the VCE part, after removal of the Sylgard coatings, was higher by ~7%. The thermal scission of the acetate group seen on the TGA curve also provides a means to assess the vinyl acetate content in the VCE material. Results show a vinyl acetate content in the pristine VCE around 33%, which again matches information provided by Dr. Eastwood. The vinyl acetate content measured in the VCE shields post dismantlement was only 22%. Such a low number strongly suggests the loss of vinyl acetate via the outgassing of acetic acid, and can also explain the abnormally higher filler content observed in the parts (if the total mass of the part decreased due to acetic acid outgassing, the mass fraction of the filler material is then artificially increased in TGA measurements).

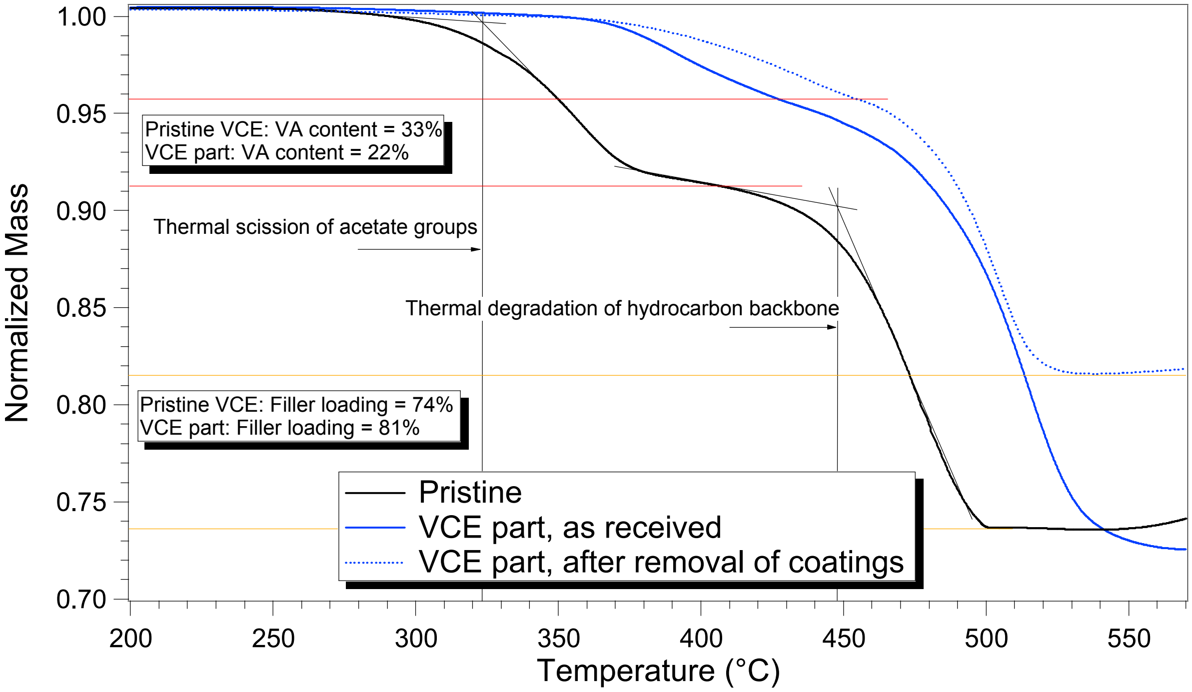

Figure 7. TGA spectra of: pristine VCE synthesized at KCP, 37 year old VCE dismantlement return (as received), and 37 year old VCE dismantlement return, after removal of the Sylgard coatings.

1.3.3 Solid Phase Micro-Extraction / Gas Chromatography / Mass Spectrometry

SPME-GC-MS analysis was conducted on 8 VCE shields using experimental conditions described in the Experimental Approach. Results summarized in Figure 8 show very different outgassing patterns for the VCE dismantlement returns relative to the pristine VCE material synthesized at KCP. Results from 4 different VCE parts are superimposed in Figure 8, illustrating the part to part reproducibility of the analysis.

SPME-GC-MS peaks from the pristine VCE material indicate the outgassing of: silanol, acetic acid, butanoic acid, propanoic acid, and phenol (ranked according to their retention times). The main peak, identified as acetic acid according to the NIST 02 mass spectrometry library, was confirmed by performing SPME-GS-MS on a vial spiked with acetic acid (identical retention times were obtained) and attributed to the thermal scission of the vinyl acetate group. Propanoic and butanoic acids, detected in low abundance, are attributed to fragments of the lithium stearate processing aid used at a level of 1-2% by weight, or to oxidized fragments from the polymer's alkyl chains. Phenol, also detected in low abundance, is a degradation product of the cross-linking agent (see Figure 2) used in the synthesis of VCE, resulting from thermal unblocking of urethane. Finally, the presence of low concentrations of silanol may be attributed to outgassing of residues from silicone used for mold release during the curing of the VCE samples, or to residues from the Carboxen/Polydimethylsiloxane SPME fiber, which are the only sources of silicon in the system.

In contrast to pristine VCE, peaks observed on the VCE part returns, after removal of the Sylgard coatings, were all attributed to cyclic siloxanes, which may be attributed to Sylgard residues on the material surface, and/or to the SPME fiber. Although parts were scrapped with a razor blade, and the sides of the sample were exposed, no acetic acid outgassing was detected after 2 weeks of storage at 70°C. Despite the fact that the SPME method is not quantitative, these results indicate a lower fraction of vinyl acetate in the dismantlement returns, consistent with the TGA results presented above.

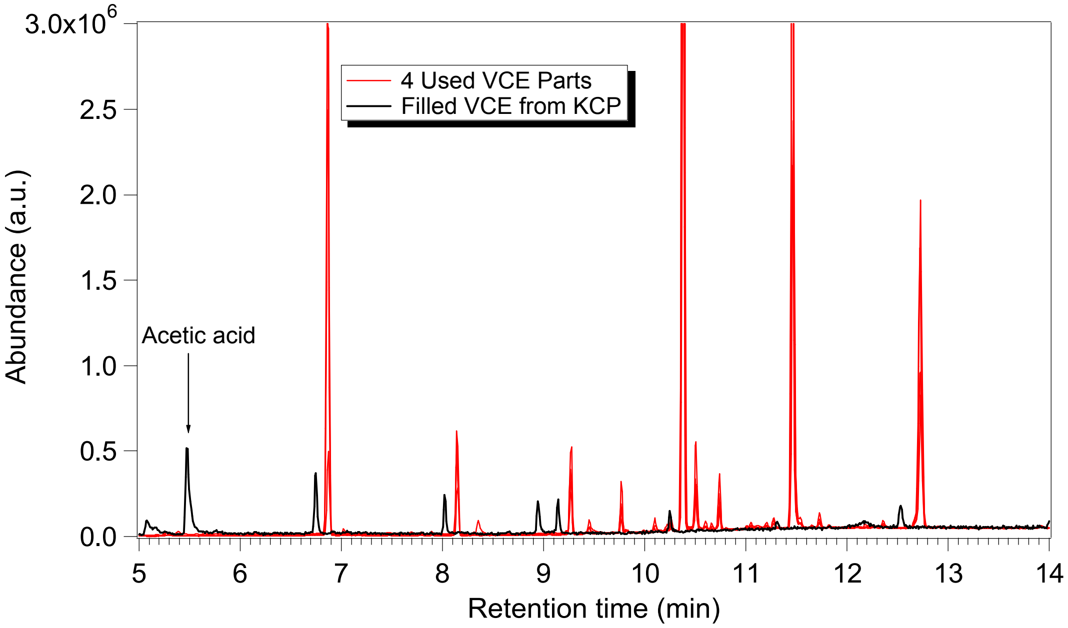

Figure 8. SPME-GC-MS analysis of: pristine VCE synthesized at KCP, and four 37 year old VCE dismantlement returns after removal of Sylgard coatings.

1.3.4 Pyrolysis / Gas Chromatography / Mass Spectrometry

Pyro-GC-MS analysis focusing on low molecular weight species was conducted on 8 VCE shields using experimental conditions described in the Experimental Approach. This method is complementary to the SPME-GC-MS method since samples are heated up to pyrolysis. Results summarized in Figure 9 show different outgassing patterns for the VCE dismantlement returns, relative to pristine VCE material synthesized at KCP. Results from only one VCE part is shown in Figure 9 for clarity, but all 8 eight parts generated similar outgassing patterns. For pristine VCE, the main outgassing peak was acetic acid, similar to data obtained by SPME-GC-MS. Additional peaks showed the outgassing of alkenes including ethane, propene, butane, pentene and hexene, which can be produced by the pyrolysis of alkyl acetate [8]. The absence of acetic acid evolution measured by SPME-GC-MS on VCE part returns was also confirmed by pyro-GC-MS, and points toward an absence (or lower concentration) of vinyl acetate in the parts.

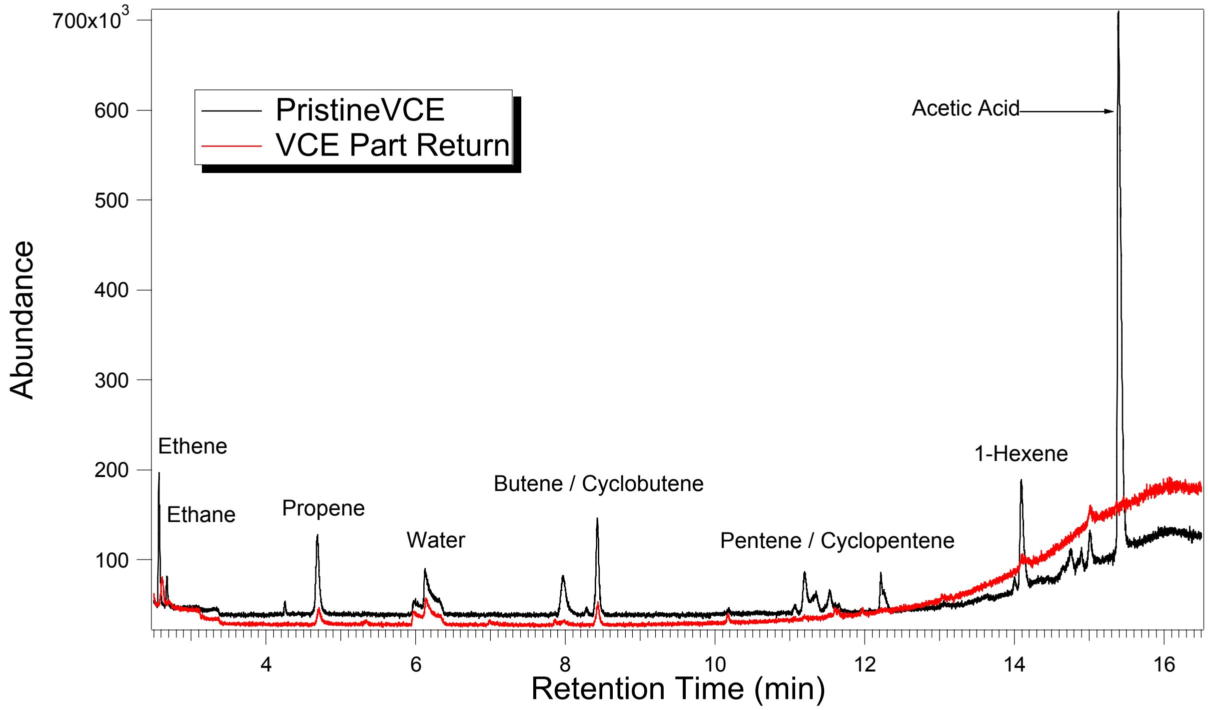

Figure 9. Pyro-GC-MS analysis of: pristine VCE synthesized at KCP, and four 37 year old VCE dismantlement returns after removal of Sylgard coatings.

1.3.5 Infra-red Spectroscopy

IR spectroscopy was conducted on 8 VCE shields using experimental conditions described in the Experimental Approach. Results summarized in Figure 10 show IR spectra of pristine VCE synthesized at KCP, as well as spectra from 4 representative VCE dismantlement returns. Similar to SPME-GC-MS analysis, IR showed very good sample to sample reproducibility, but results significantly different for the parts and the pristine VCE reference.

Peaks are indexed as follows: (2919, 2850 cm^{-1}) deformation modes from methylene backbone, (1735 cm^{-1}) carbonyl stretch, (1462, 1371 cm^{-1}) methylene deformations, (1238 cm^{-1}) C-O stretch from acetate group, (1085 cm^{-1}) C-O stretch from alcohol group, (1019 cm^{-1}) C-O stretch for polymer/acetate bond, (845-804cm^{-1}) aromatic bends, (719 cm^{-1}) methylene deformations, and (608 cm^{-1}) C-O bends from acetate group.

ATR is a surface analysis method and therefore, it does not provide reliable information on the chemical composition of the bulk material if the surface of the sample is not representative of the inner sample volume. In our case, since Sylgard coatings had to be peeled off from the parts, it is very possible that residues remained behind, therefore changing the surface composition of the samples. Nevertheless, it should be noted that the IR peak at 1735 cm^{-1} attributed to the vinyl acetate carbonyl stretch is completely absent from the spectra recorded on VCE parts. Although not a definitive result by itself, this observation corroborates results from TGA, SPME-GC-MS, and pyro-GC-MS analysis presented above, trending toward evidence of a lower vinyl acetate content in the VCE parts, relative to the pristine material synthesized by KCP.

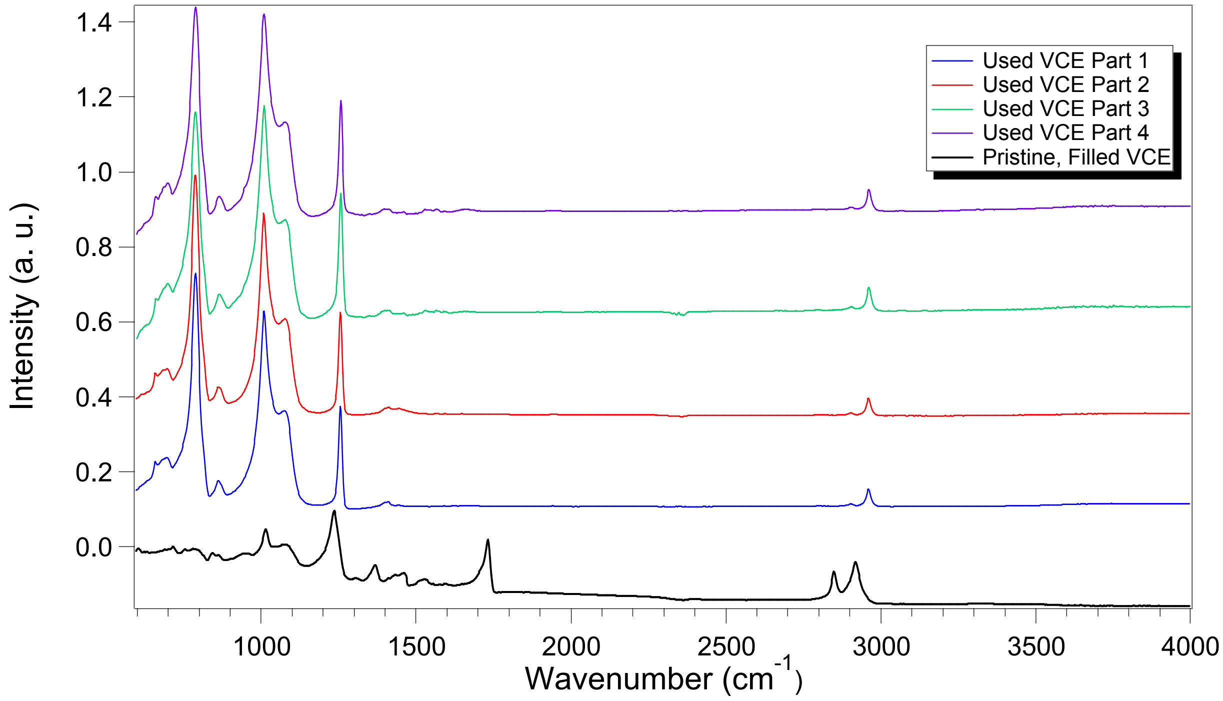

Figure 10. IR spectra of: pristine VCE synthesized at KCP, and four 37 year old VCE dismantlement returns after removal of Sylgard coatings.

1.3.6 Discussion

Results obtained on VCE dismantlement parts show good mechanical integrity of the parts, but also point toward a significant loss of acetic acid via de-acetylation mechanisms outlined in the FY10 report, and in our publication [7] (also see Figure 4). Visual inspection, combined with mechanical testing of the shields showed stable mechanical properties upon 37 years of service in a system. Based on these results, VCE shields are expected to effectively fulfill their role, yet a potential concern is linked to the outgassing of acetic acid. Since work conducted this year was performed on dismantlement parts, storage conditions were mostly unknown. The outgassing of acetic acid could have therefore taken place in the system, or during post-dismantlement storage at KCP. If losses occurred during storage, there is no concern for the systems, and our concept of using acetic acid as a degradation signature for VCE shields was validated. If losses occurred in the system, concerns related to the compatibility of components surrounding the shield with acetic acid would have to be explored with appropriate core-stack experiments.

1.4 Conclusions

Eight 37 year old VCE dismantlement parts were analyzed using structural and chemical methods including Tensile Testing, TGA, IR spectroscopy, SPME-GC-MS, and pyro-GC-MS. Tensile testing showed no statistical change in elongation at break, and a slight increase in tensile stress at break of the parts, compared to C5 surveillance data, which demonstrates the mechanical integrity of the parts after 37 years of service in systems. Parts were found to be coated with Sylgard on each side, complicating their chemical analysis. TGA, IR spectroscopy, SPME-GC-MS, and pyro-GC-MS analysis was therefore conducted both prior and after removal of the Sylgard coatings and results showed marked differences as a function of original EVA source, consistently indicating a lower vinyl acetate content in the parts (a ~10% mass loss associated with acetic acid outgassing was identified by TGA and no acetic acid was detected in SPME-GC-MS and Pyro-G-MS analysis of the parts). While there is little doubt that acetic acid was outgassed from these parts, it is not yet clear whether the outgassing took place in the system or during post-dismantlement storage. Surveillance returns, stored in controlled laboratory conditions will be analyzed in FY12 to address this question.

FY12 work will focus on the analysis of VCE shields from a different system. Parts will be returning from surveillance units, instead of dismantlement units, therefore allowing for controlled storage conditions. Additional chemical analysis will be performed in an effort to quantify losses in acetic acid identified in VCE shields, including solid state NMR, and vinyl acetate titration using the saponification method (KCP method 9981058).

1.5 References

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