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Title: The Effects of Temperature, Aging, and Plasticizer Content on VCE

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The Effects of Temperature, Aging, and Plasticizer Content on VCE

Introduction

Ethylene vinyl acetate vinyl alcohol (VCE) is a terpolymer. It is commonly used as a binder for highly filled elastomeric materials (2). Because of its use, it is important that it is studied extensively to ascertain the possible risks. It is crucial to know how VCE is affected by temperature, aging and how plasticizers may affect this polymer. Aging can be tested experimentally by using different temperatures and heating rates and times. If the VCE breaks down or reacts it could be detrimental to the application and there could be safety concerns. The starting copolymer in the synthesis of VCE is ethylene vinyl acetate (EVA) (Figure 1).

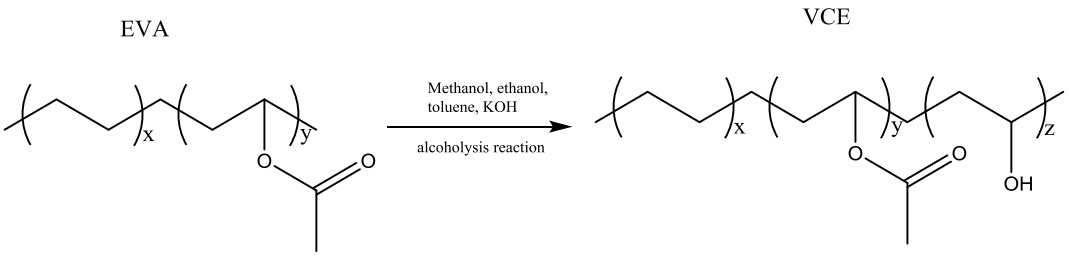


Figure 1: The synthesis of VCE.

After VCE has been synthesized using this method, it is considered uncured. A curing agent, Hylene, can be used to cure VCE (Figure 2). Cured VCE is what is used for most applications so it was more heavily tested but the differences between cured and uncured VCE were also noted.

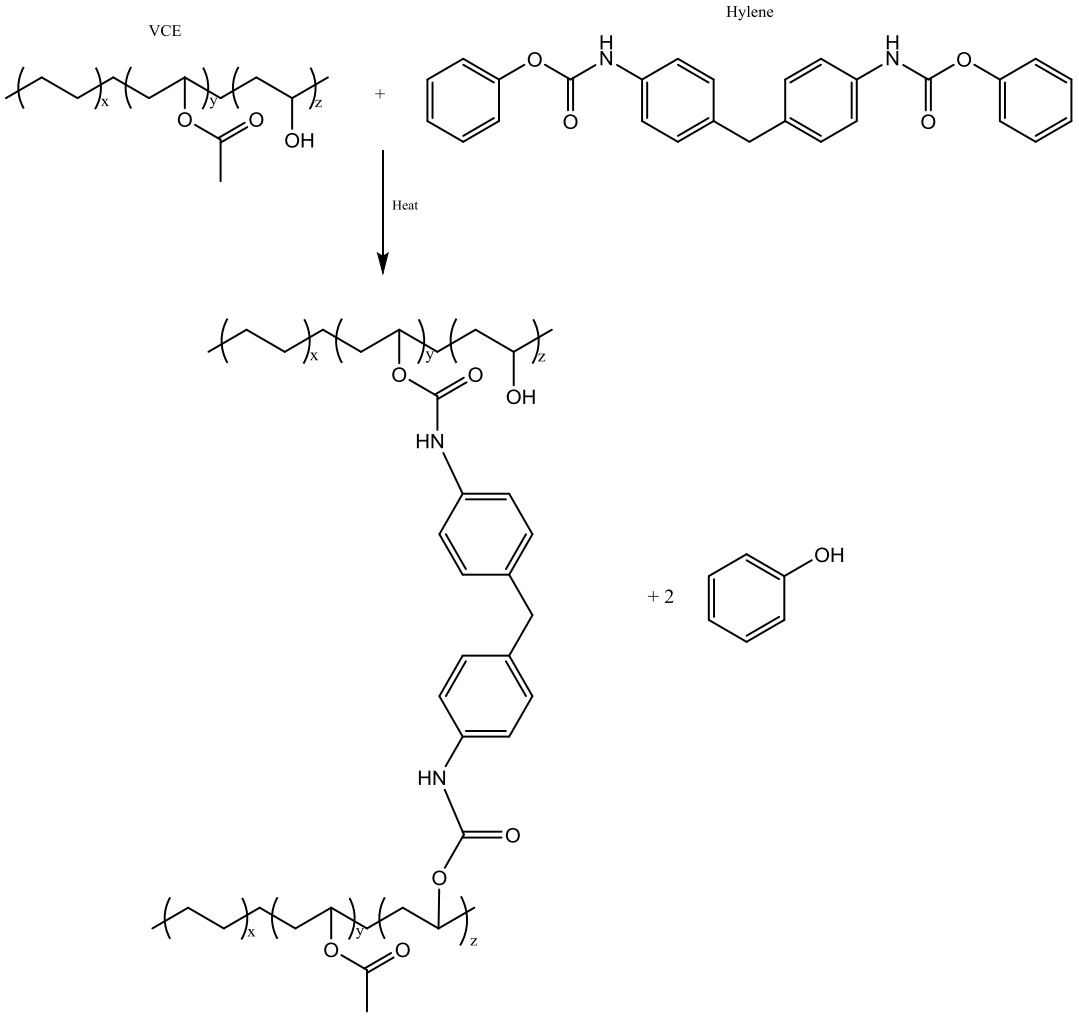


Figure 2: Synthesis of cured VCE by way of Hylene as a curing agent.

As mentioned above it was of interest to see what effect plasticizers had on the VCE. A nitroplasticizer (NP) was used to study this effect. Different concentrations of VCE were used (50%, 75%, 90%, and 100%) for this study. By testing different percentages of VCE with varying amounts of NP, it can be seen if both VCE and NP have an effect or if just one or the other does.

It is also important to test how aging can have an effect on VCE and NP. To test the aging process, samples were heated for different amounts of time and at different temperatures. Depending on the results obtained, the aging studies might continue on.

Experimental

FTIR

The starting material (EVA), uncured VCE, and cured VCE samples were tested on a Vertex 80v FTIR from Bruker. A background was obtained before the measurements and

subtracted out using the software. A diamond ATR attachment was used for all of the samples and the sidearm was used to add pressure while the measurement was being taken.

Different concentrations of cured VCE were also tested using the same FTIR. 50%, 75%, 90%, and 100%VCE were all studied. The 100% VCE samples are a clear color while the 50%, 75%, and 90% VCE are black because of the added filler.

Different concentrations of NP were added to the differing percentages of VCE and also tested using the FTIR. The concentrations of NP went from 0 to 40%. 40% NP was fully saturated for 100%VCE samples. For some of the higher concentrations of NP, a kim-wipe was used to wipe the sample before running the test because there may be excess NP present on the outside of the sample. This was done to prevent over-saturating the detector. All of the VCE samples were temperature treated at 70°C when adding the plasticizer.

Aged samples of NP were also tested. These samples were also run using the ATR attachment by just placing a drop of the NP on the diamond detector. First, a concentrated sample of NP that was not aged was run as a baseline. From there, samples with different heating rates and heating times were tested and compared. The NP was kept in a small vial and then put into a secondary container to be heated. Some of the secondary containers contained water vapor which may interact with the samples. NP samples were left at room temperature for 3 months or heated at 50°C, 70°C, or 90°C. These samples will need to be analyzed again at 6, 9 and 12 months to continue on with the project.

XRD

To test how plasticizer would affect the crystallinity of VCE, X-ray diffraction was performed. The XRD that was used is a Siemens D5000. The sample holder that was used is a plastic polymeric material. The background was subtracted in all of the measurements using the software. Carbon tape was used to attach the samples to the XRD sample holder so that they did not move during the testing and so they were the same height throughout. All of the samples were run at the same parameters so that the data could be easily comparable. The step size was very small to increase the resolution. Since VCE is an amorphous polymer, it was also important to have a large time per step to get a good signal to noise ratio. XRD results have been published before and they show a large wide peak from 10-30 degrees and a smaller wide peak from 35-50 degrees (1).

To test how temperature will affect the crystallinity and the overall structure of the VCE, two samples were tested; a 100% VCE sample that was heated at 38°C overnight and a sample that was heated at 55°C overnight. The effect of temperature and plasticizer content were also measured. A sample of 100% VCE with 40% NP was heated at 38°C overnight and another sample was heated at 55°C overnight.

Results-Discussion:

FTIR

The FTIR spectra of the EVA, uncured VCE, and cured VCE samples are as expected given the known chemical structure of each molecule. Most of the peaks were the same for EVA, uncured VCE, and cured VCE, except for uncured VCE had a peak around 3200cm^{-1} which is attributed to the OH bond that it contains. Figure 3 shows the three spectra on the same axis as a comparison. Both uncured and cured VCE have some noise on the spectra around 2250-2000cm^{-1}. This is attributed to the diamond ATR attachment used and the atmosphere that may have been present.

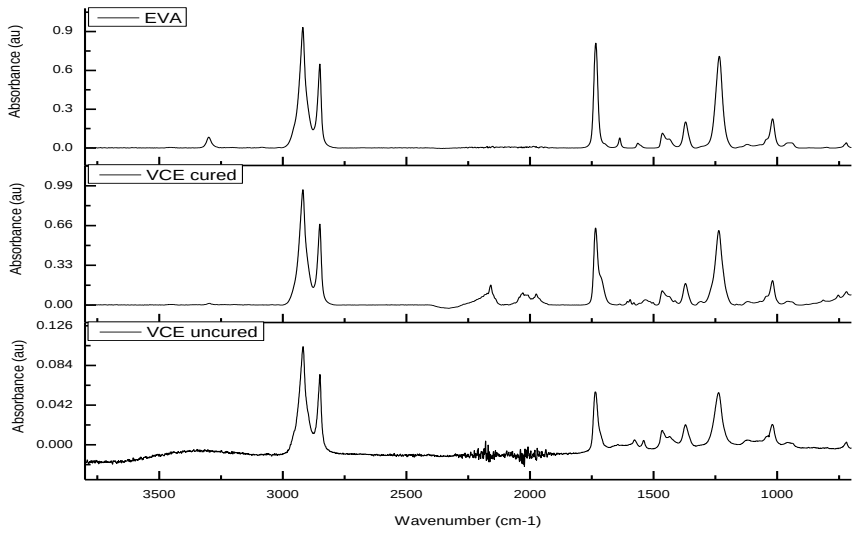


Figure 3: FTIR spectra of EVA, uncured VCE, and cured VCE.

The peaks for 50%, 75%, 90%, and 100% VCE are the same as the cured VCE sample. There was no notable difference in between the different concentrations of VCE. All of the spectra look very similar. This was expected because the filler present should not have much of an effect on the FTIR spectra.

Different percentages of VCE were tested with varying amounts of NP. This data was used to determine if the concentration of NP has different effects on different samples of VCE. Table 1 shows what peaks should be present because of the NP that was added. Figure 4 shows 50% and 90% VCE with varying amounts of NP ranging from high to low. The 75%VCE and the 100%VCE spectra were omitted because they were very similar to the other graphs. When NP is added to the samples; the FTIR spectra changes. The main change is the NO_2 peak around 1590-1570cm^{-1}. This peak increases with increasing NP content. As can be seen in Figure 4, once a large amount of NP is added and the sample becomes saturated, the NP peak is very

strong. The COCC peak from 1150-1050cm^{-1} also dramatically changes with NP concentration. Once the sample is fully saturated with NP the peak is a different shape than the less concentrated samples and is much stronger. This trend can be seen in all of the VCE samples (50%, 75%, 90%, and 100%).

FTIR Peaks Due to NP	
Wavenumber (cm^{-1})	Peak (Functional Group Vibration)
1590-1570	NO_2 stretch (asymmetric)
1350-1300	NO_2 stretch (symmetric)
970-900	N-O stretch (aliphatic)

Table 1: FTIR peaks that are due to the NP present in the samples

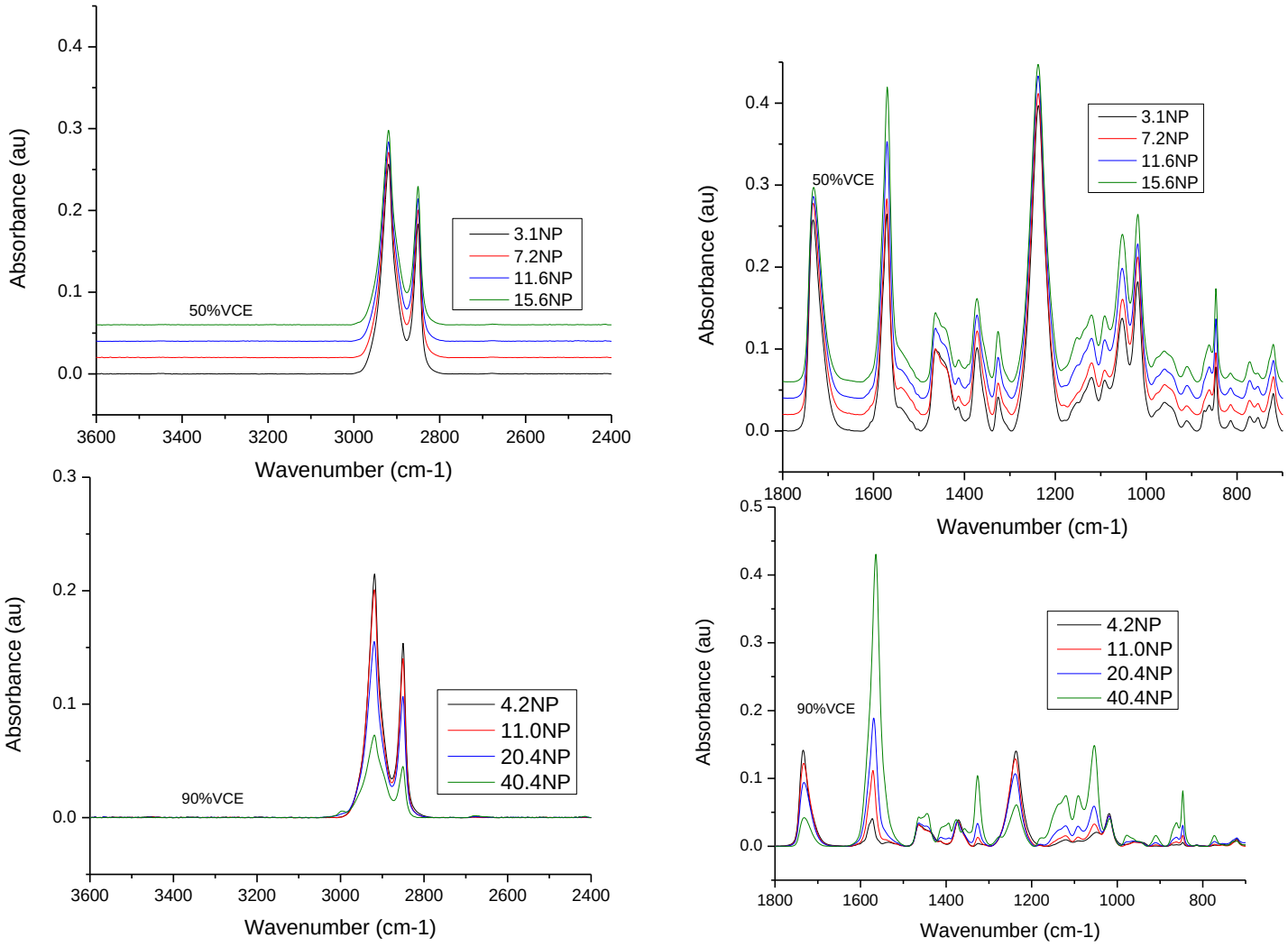


Figure 4: 50%VCE and 90%VCE with varying percentages of NP.

A correlation curve was made so that the concentration of NP could be back calculated and a trend could be identified between all of the samples. All of the VCE samples should have followed the same trend. Four different peaks were used for this calculation. The CH stretch from 3025-2775cm^{-1}, the NO_2 stretch from 1640-1495cm^{-1}, the CH acetate peak from 1390-1345cm^{-1}, and the CO acetate peak form 1300-1190cm^{-1}. Each of the peaks were divided by the NO_2 peak and graphed versus weight percentage of NP in the sample. The weight percentages of NP were normalized by the percentage of VCE in the sample so that they could be viewed on the same graph. The areas under the curve were calculated using Origin. All of the FTIR and XRD data was worked up and analyzed on Origin. Figure 5 shows the results. Most of the results follow the same trend. In the CH stretch/NO_2 graph, the 50%VCE does not align with the other concentrations of VCE. This could be due to the amount of filler present in the samples. In the other graphs this does not seem to be much of an issue. Because of the spectral differences between the highly concentrated NP samples and the difficulty at which they were measured; only concentrations of NP that were under 40% were shown. When the samples became too concentrated with NP they did not follow any trend. There are still some outliers in the data that do not seem to follow the trend, but overall the data correlates. These correlation curves could be beneficial in the future to determine the NP concentration in unknown samples of VCE.

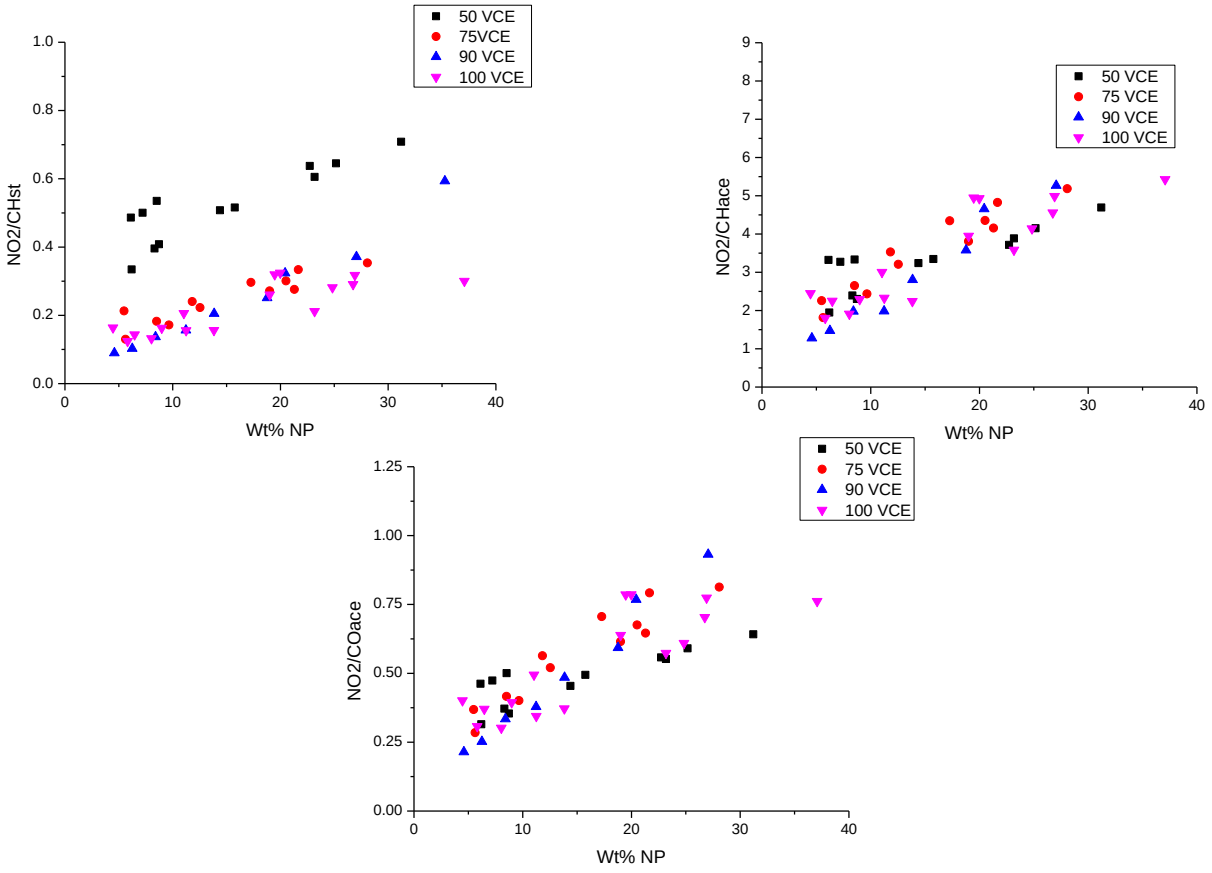
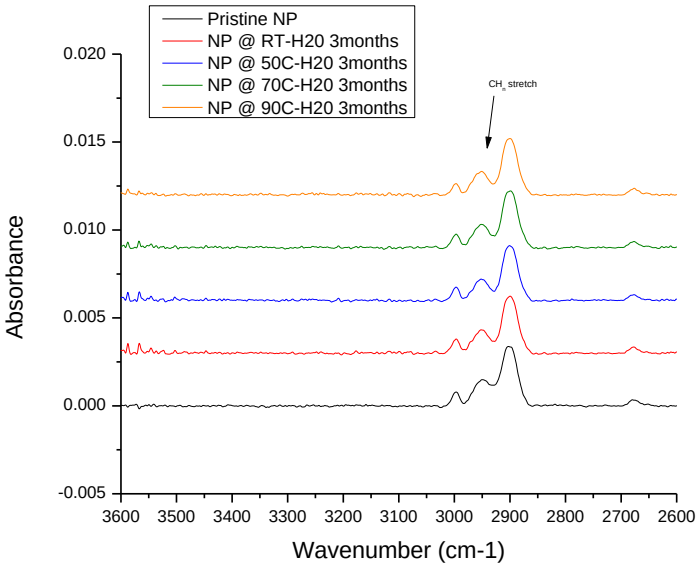
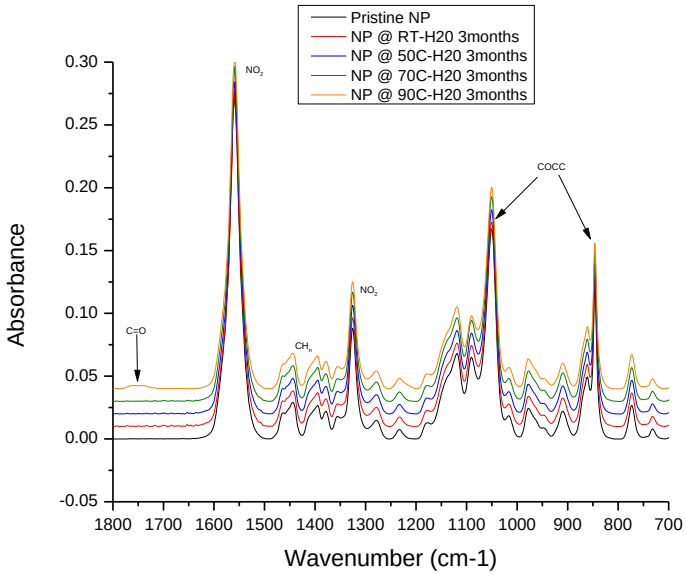


Figure 5: The correlation data between 50%, 75%, 90%, and 100% VCE with varying NP concentrations.

Samples of pure NP were heated in an oven at varying temperatures to determine the effect of aging on NP samples. Some NP samples had water vapor in the secondary container that they were heated in. This was studied to see if putting water vapor in a secondary container had any effect on the aging process. Figure 6 shows the FTIR spectra of all of the aged NP samples. The peaks for each sample are labeled and compared. The aged NP samples that were tested on the FTIR do not show much change. For the samples that we heated at 90°C for 3 months there is a slight peak around 1750cm^{-1} which could be attributed to a C=O bond (Figure 6). Other than that change, there are no differences. This means that the sample is not decomposing due to aging. This same result can be seen from the XRD where aging was also tested. This means that at the temperatures and time periods that the samples were in the oven to simulate the aging process there was little effect. This would agree with other studies have previously determined that thermal scission of the acetate group in VCE usually occurs around 280°C while degradation of the hydrocarbon backbone takes place around 400°C (2).





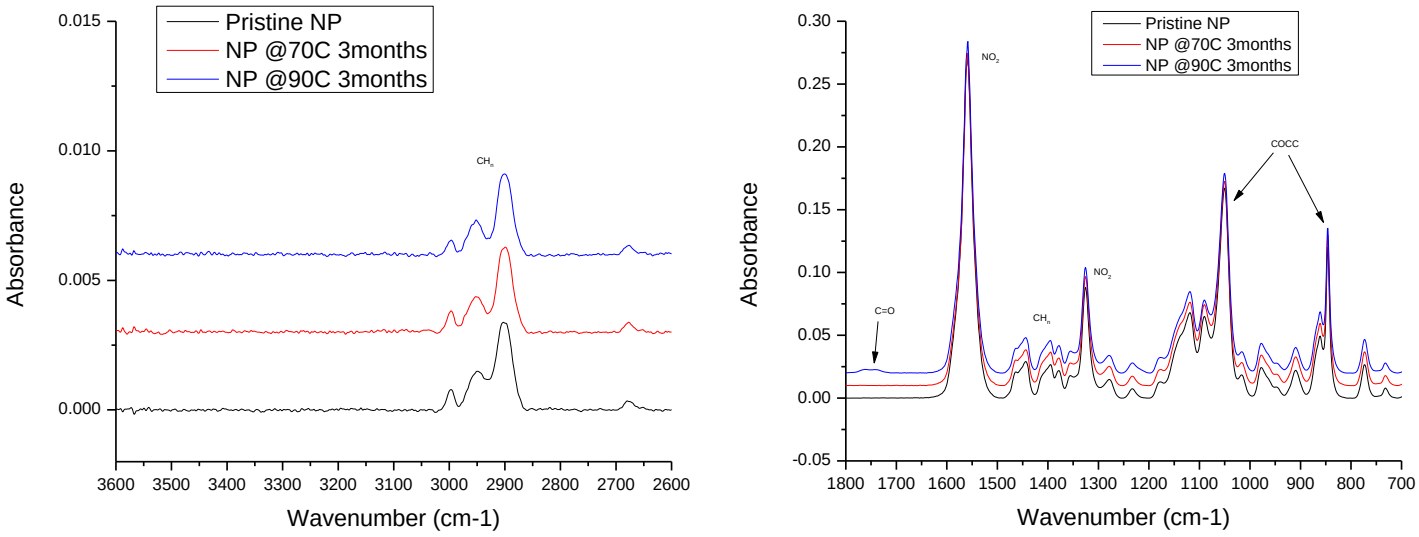


Figure 6: FTIR spectra of NP that has been put under different aging conditions.

XRD

Figure 7 shows the XRD data from the 100% VCE with two different concentrations of NP; 20% and 40%. The XRD data agrees with previously published results (1). The main difference is the small, sharp peak around 28 degrees that is seen in all of the samples. Further analysis would be needed for a determination of the peak to be made. With increasing amounts of plasticizer the intensity of the peaks decreases. This is expected because plasticizer causes polymers to become more amorphous. Since XRD studies the crystallinity of structures it is expected that the crystallinity decreases with increasing plasticizer concentration. This decrease in intensity and the widening of the peaks relate well to the NP concentration; 40% NP is broader and less intense.

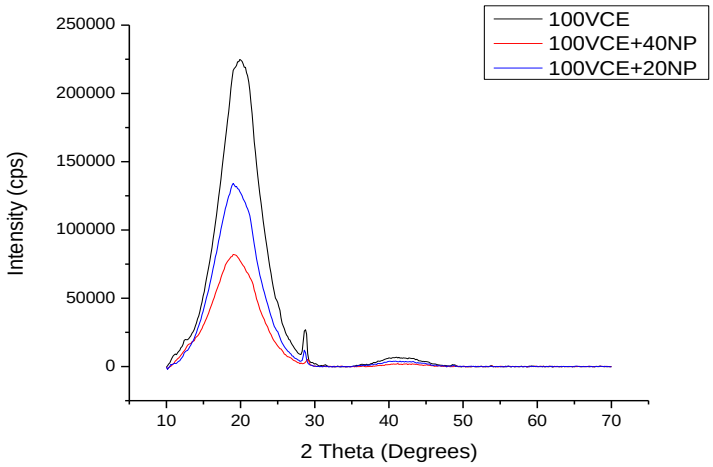


Figure 7: XRD spectrum of 100%VCE with varying amounts of NP.

100% VCE samples were also tested at 55°C and 38°C. These samples were heated overnight. There was no difference in the structure. Two 100% VCE samples that were fully saturated with NP were also tested. One was heated overnight at 38°C and the other at 55°C. There was no difference between the two samples. This agrees with the FTIR data that shows that the aging procedures had little effect on the samples.

Future Work:

Samples are currently being aged in the ovens. These samples will be tested every three months for at least one year. They will be analyzed on the FTIR and the XRD. These results will be compared to all different times and temperatures to determine when or if the VCE samples degrade. DSC and TGA may be used in the future to better understand the changes in the thermal properties of VCE. From these results it can be determined what applications VCE can be used for and how safe and stable they are.

References:

1. Letant, S., J. Herberg, et al. (2009). Aging Studies of Filled and Unfilled VCE, Lawrence Livermone National Laboratory.
2. Letant, S., C. Alviso, et al. (2011). Aging Studies of VCE Dismantlement Returns, Lawrence Livermore National Laboratory.