LA-UR-15-21679

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Intended for: Report

Issued: 2015-03-06

# Effect of Filler Concentration on Thermal Stability of Vinyl Copolymer Elastomer (VCE) Composites

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**Abstract:** To study the thermal stability of vinyl copolymer elastomer (VCE) in its composite form, systematic TGA characterizations were conducted in both non-isothermal and isothermal modes. The effects of filler concentration on the aging behaviors of the VCE/filler composites were investigated under nitroplasticizer (NP) environment. FTIR characterization was used to probe the structural changes in the VCE polymer before and after the thermal treatments. This study suggests that the filler concentration significantly deteriorates the thermal stability of NP at a moderate temperature (< 70 °C). The degradation of NP, in turn, accelerates the aging process of the VCE polymer in its composite form.

Key words: VCE, EVA, EVA-OH, Nitroplasticizer (NP), iso-thermal TGA, non-isothermal TGA, FTIR, thermal stability, DSC, thermal conductivity, desorption, diffusion

## 1. Introduction

Ethylene/vinyl acetate co-polymer (EVA) is widely used as coating, binder, and sealant materials due to their processibility (flexible, clear, and tough) and chemical stability. To further increase its thermal stability, ethylene/vinyl acetate/vinyl alcohol terpolymer (EVA-OH) was synthesized from EVA through an alcoholysis reaction[1]. The hydroxyl group was used to thermally react with a curing agent, such as Hylene MP - diphenol-4,4'-methylenebis(phenylcarbamate), to form a cross-linked vinyl copolymer elastomer (VCE), as shown in Figure 1[2-9]. Early studies have demonstrated that VCE does not appreciably degrade when the polymer is thermally exposed to air with and

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without moisture at the temperature below 100 °C[10]. However, in some applications, VCE is used as a binder to compound together with a large concentration of filler materials. Therefore, there is a large interfacial area between the polymer phase and filler particles. Due to the poor adhesion between polymer and filler particles, the appreciable amount of voids (> 20 v%) exists in the composite matrix[11]. Undesirable vapor and/or liquid phase will trap inside the voids, which ultimately changes the properties of VCE over a long period of time. In 2011, Letant et al. reported that the long-term aged VCE composite lost its vinyl acetate content appreciably. Although its mechanical integrity still meets its requirement, the polymer becomes rigid[4]. Furthermore, in some applications, the VCE composites are also exposed to acidic environment. For example, nitroplasticizer (NP) is commonly used in plastic-bonded explosive (PBX) formulations to improve the manufacture process[12-15]. One type of NP is an eutectic mixture of bis(2,2-dinitropropyl) acetal (BDNPA) and bis(2,2-dinitropropyl) formal (BDNPF) (50%/50%). Their molecular structures are also illustrated in Figure 1. When the VCE composite and PBX/NP materials were stored together, VCE slowly uptakes NP[16-18]. Our previous study confirms that the VCE polymer can uptake 340 mg/gram of NP at ambient conditions, and up to 420 mg/gram at 70 °C. As the filler concentration increases to 80 wt%, the VCE composites often uptake more NP than polymer itself because some free NP is able to trap in the voids of the VCE composites[19].

NP in its liquid form is thermally stable at the elevated temperature for a few months[19]. Due to the high boiling point (150 °C), the vapor pressure is typically very low at the ambient conditions[20, 21]. Pauler et al. proposed that NP may degrade through a non-radical reaction and generate HONO at the low temperature condition; and calculated the activation energy of the HONO formation to be <42 kJ/mol[22]. However, the activation energy of the NP degradation in a constituent aging study (CAS) of PBX 9501 was found to be as low as 28 kJ/mol[23]. The largely decreased activation energy suggests that the reactivity of NP in highly heterogeneous matrixes is higher than in its liquid form. Recently, we investigated the chemical stability of VCE when its composite was exposed to the NP vapor at 50 – 70 °C. The nine month exposure severely degrades the VCE polymer[11]. We conclude that the key factor causing the polymer degradation is due to the NP degradation. In reality, the VCE composite is typically aging at a temperature < 50 °C, but for an extensive period of time. The stability of NP and VCE at this mild condition is of importance. In this study, we will investigate the impacts of filler concentration and NP concentration on the thermal stability of the VCE polymer. Through this study, we hope to obtain scientific insights about the long-term aging behavior of the VCE composite at the mild temperature condition.

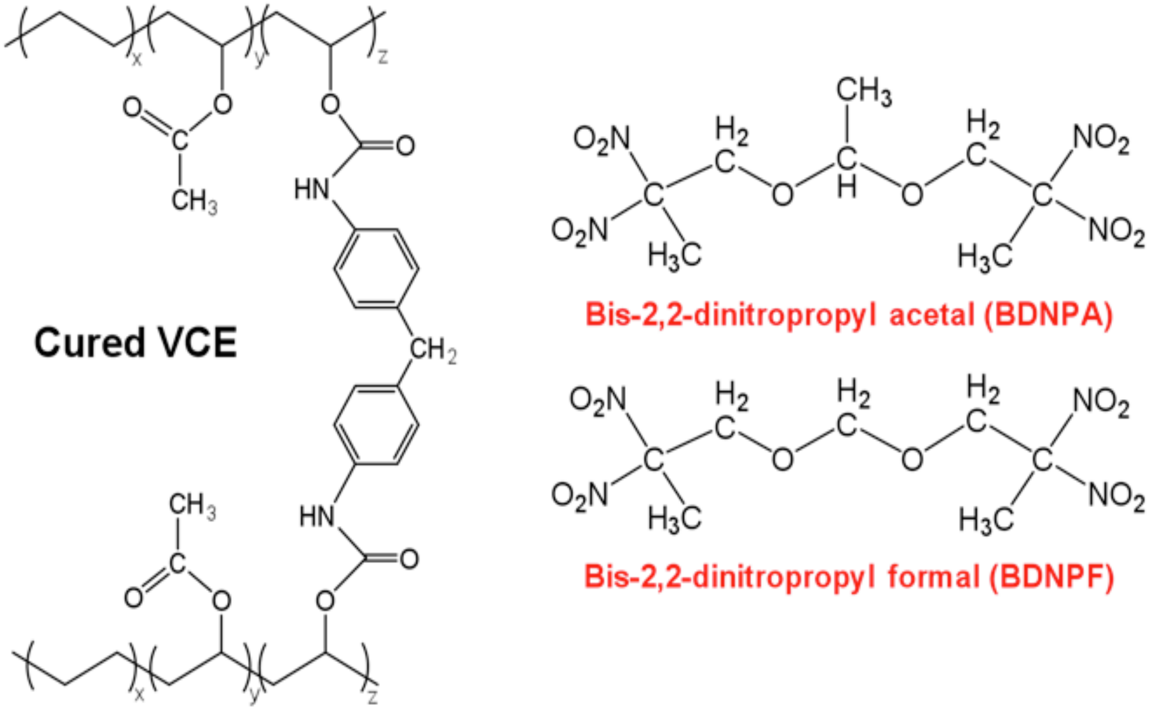

Figure 1. Molecular structures of cured VCE and NP mixtures.

## 2. Experimental

### 2.1 Materials

The flat sheets of VCE polymer and five VCE composites with different VCE concentrations (20, 30, 50, 75, and 90 wt%) were prepared at KCP. NP is obtained from Pantex. Detailed description about both VCE and NP can be found elsewhere[3, 8, 21, 24].

### 2.2. Sample Preparation and Aging Experiments

The disks of VCE and its composites (diameter of ~20 mm) were cut from the flat sheet. All samples were completely wetted and immersed inside NP at room temperature. By controlling the immersion time, we were able to control the NP concentration in the VCE composites. The NP concentration was determined by weight gain and TGA measurement.

For the aging study, the 20% VCE composites were pretreated with NP at different saturations (e.g. 0, ~4, and ~8 wt%), and then kept inside three sealed containers. Before the aging experiment, the containers were evacuated and back filled with nitrogen. This procedure was repeated three times to minimize the oxygen content inside the containers. Later, the containers were placed in 38, 55 and 70 °C ovens and aged for different times. The sample removal was conducted under the nitrogen environment.

## 2.3 Thermal Analysis

Thermal Instruments Q500 Thermogravimetric Analyzer (TGA) was used to analyze the thermal stability of NP and VCE samples. The samples were heated from ambient temperature to 600 °C at 5 °C/min with a nitrogen purge (10 ml/min). To examine the heating rate effect, some sample sets were heated at the heating rate ranging from 0.01 to 20 °C/min under nitrogen purge. To examine the isothermal behavior, some samples were heated at 50, 60, 70, 80, 90 or 100 °C over 4000 mins under nitrogen purge. Platinum pans were used in the TGA measurement.

## 2.4 Thermal Conductivity Measurement

Thermal conductivity was measured using a method based on modulated DSC. The approach is suitable for materials with thermal conductivities in the range of 0.1 to 1.5 $W\text{-}C^{-1}m^{-1}$[25]. The basis of the method is a comparison of the modulated heat flux signal of a sample of known geometry at high and low modulation frequencies. The ratio of those signals can be related to thermal conductivity. The experiment was conducted by ramping to the desired temperature and modulating the temperature at a fixed amplitude (0.5 °C). Two measurements were made at each temperature. The first is at a sufficiently long period such that no effect due to sample thermal conductivity was observed. For our experiments 120 sec was found to be sufficient. The second measurement was conducted at a short period, 15 sec. The measured heat flux amplitude was reduced relative to the long period measurement due to the thermal lag. The apparent heat capacity was calculated and used along with the specific heat measurement to calculate the thermal conductivity. An additional calibration measurement was made at each temperature prior to the conductivity measurement. This was done using a sapphire sample of known dimensions and conductivity and measuring the specific heat at each temperature.

### 2.5 FTIR Characterization

FTIR absorption data were obtained with a Nicolet 6700 FTIR bench operating in Attenuated Total Reflectance (ATR) mode. ATR accessory equipped with a germanium crystal. Data were collected using a Spectra-Tech Thunderdome. All data were taken with a resolution of 4 $cm^{-1}$, and represent the average of 120 scans. Typically, 3 replicate samples were analyzed for each set of experimental conditions. The representative spectra are presented.

## 3. Results and Discussion

### *3.1 Effect of Filler Concentration on Thermal Stabilities of NP and VCE*

In the previous study[19], TGA results indicated that the pristine VCE has two decomposition temperatures (referred to as $DT_{VCE}$s). At the heating rate of 5 °C/min, the first $DT_{VCE}$ (~335.4 °C) is associated with the vinyl acetate group decomposition while the second one (~451.6 °C) is due to the thermal decomposition of all hydrocarbon functional groups. At temperature above 500 °C, VCE completely decomposes with the total weight loss of ~98.82%. The residual weight (<1.2%) may be un-decomposed materials from lithium stearate, which was added during the VCE/filler compounding process[3]. At the same heating rate, liquid NP decomposes at ~233 °C. Interestingly, the previous study also suggests that the addition of filler in the VCE composite depresses the decomposition temperature of NP (referred to as $DT_{NP}$), but does not impact the $DT_{VCE}$s significantly[19]. In this study, we systematically study the filler effect on the reduced $DT_{NP}$. Figures 2(a) and (b) present the TGA results of 100% VCE and 20%/80% VCE/filler composite containing different amounts of NP, respectively. When the filler concentration increases from 0 to 80 wt% in the composites, more than 40 °C decease in $DT_{NP}$ is observed compared to the $DT_{NP}$ of liquid NP (at 233 °C). Clearly, the filler addition in the VCE composite significantly changes the thermal stability of NP, but does not change $DT_{VCE}$s. To understand these results, we need to investigate the effect of filler particles on the thermal conductivities of its VCE composites.

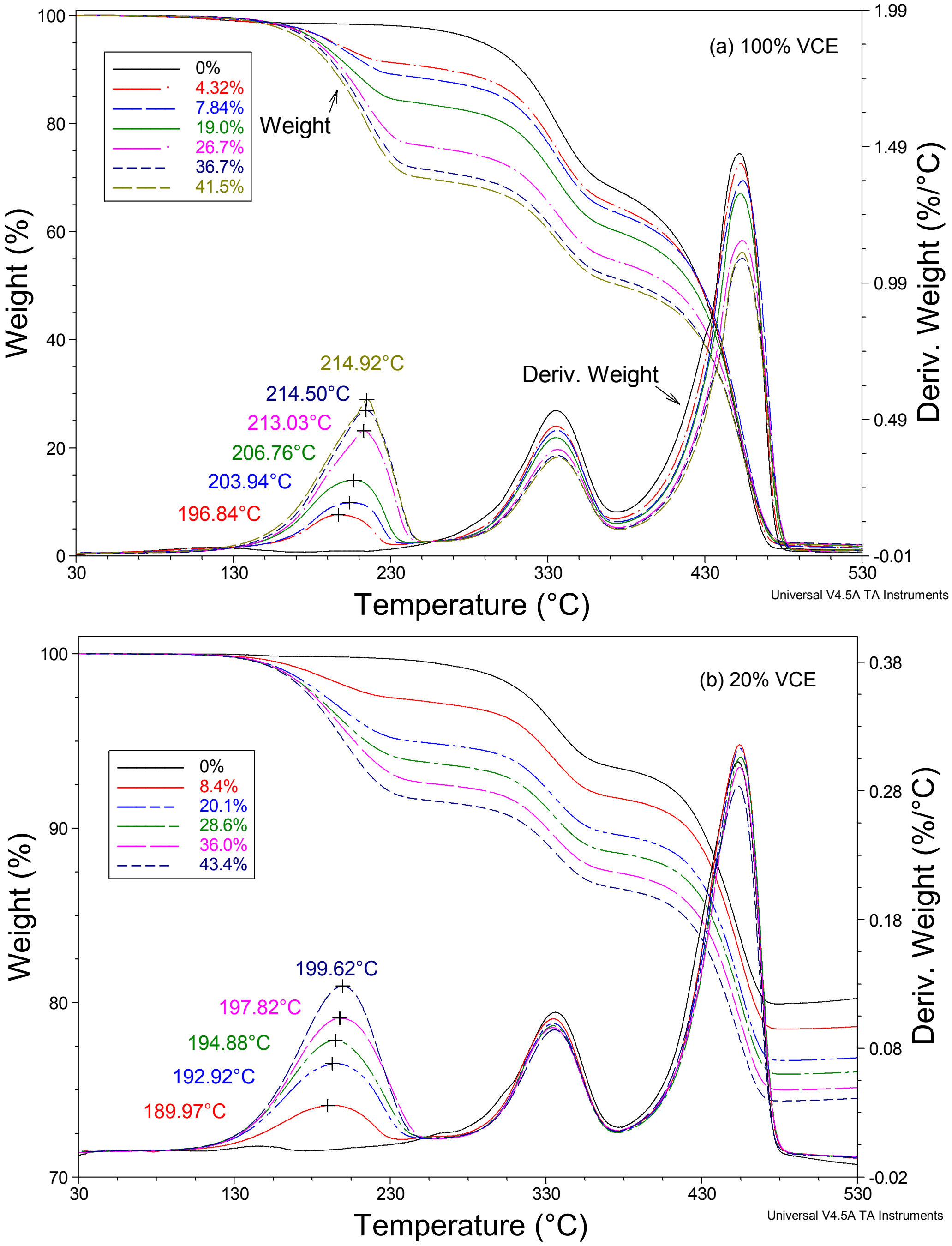

Figure 2. Effect of NP concentration on the TGA results of (a) 100% VCE and (b) 20% VCE/filler composites (all NP concentration was normalized based on the VCE concentration. The heating rate was 5 °C/min).

In Figure 3, we compare the thermal conductivities of the VCE, VCE/filler composite, and VCE/filler/NP composite. The thermal conductivities of NP and filler in the temperature range of 30 – 150 °C are 0.8 – 1.2 and >25 W/m-K, respectively. Among these three components, the VCE polymer has the lowest thermal conductivity (0.1 – 0.2 W/m-K). Interestingly, although the filler particles are 100 times more conductive than the VCE polymer, the filler addition into the VCE matrix does not alter the thermal conductivity of the composites. We believe that this insignificant impact is mainly due to the poor adhesion between filler particles and polymer matrix. We also acknowledge that many factors, such as filler volume fraction, particle size and distribution, etc. can play the roles as well[26, 27]. Even though filler particles and VCE were mechanically compressed together, the lack of chemical affinity results in the poor adhesion between the filler particles and polymer, which results in the large volume fraction of the voids in the VCE composites (> 20%)[19]. Theoretically, the thermal resistance is caused by phonon scattering[28]. These voids provide perfect space for phonon scattering between the filler and polymer domain, and diminish the filler impact on the thermal conductivity of the composite, as shown in Figure 4(left).

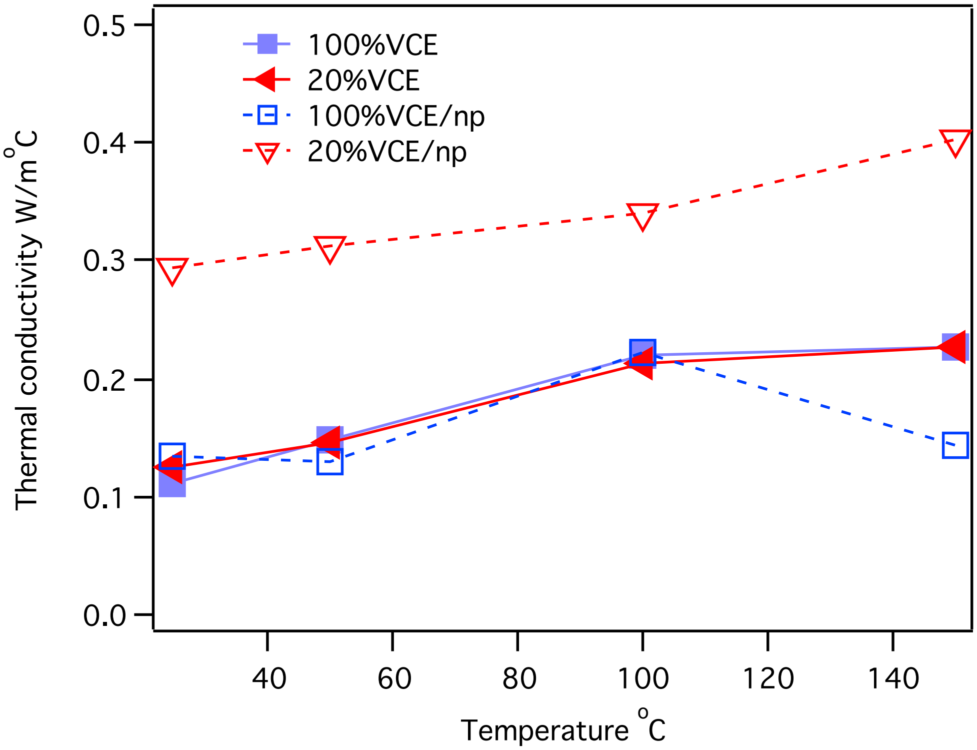

Figure 3. The thermal conductivities of the VCE polymer and 20% VCE composites (solid lines), and the thermal conductivities the VCE polymer and 20% VCE composites saturated with NP (dash lines).

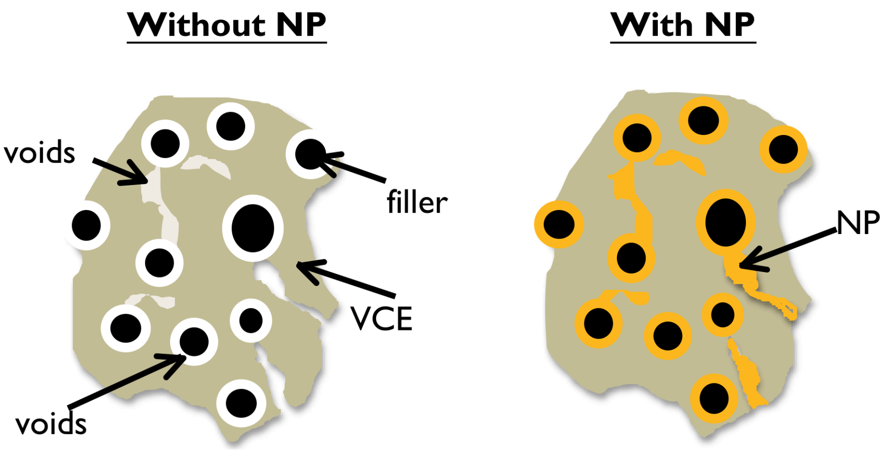

Figure 4. Illustration the matrix of the VCE/filler (left) and VCE/filler/NP (right) composites.

Now, we try to understand why the filler addition greatly reduces $DT_{NP}$. To better illustrate the effect of the filler addition on the $DT_{NP}$s, we compare the $DT_{NP}$s obtained from 5 sets of the VCE composites with different polymer concentrations in Table 1. As the filler concentration increases from 0 to 50%, the impact of the filler concentration is not appreciable. However, as the filler concentration further increases to 70 and 80%, the $DT_{NP}$ decreases more than 10 °C. As we point out, the filler addition creates the voids in the VCE domain. Some free NP can trap inside the voids, as shown in Figure 4(right). The intimate contact among NP, filler particles, and polymer results in the significant increase in the overall thermal conductivity of the VCE composites. Therefore, the composite saturated with NP gives more than 2 times higher thermal conductivity than the composite without NP, as shown in Figure 3. The enhanced thermal conductivity improves the heat transfer property, which, in turn, increases the NP evaporation rate, and decreases $DT_{NP}$.

Table 2. The effect of filler concentration on $DT_{NP}$ in the VCE composites which were fully saturated with NP.

| VCE concentration (wt%) | Filler concentration (wt%) | $DT_{NP}$ (°C) |
|---|---|---|
| 100 | 0 | 214.9 |
| 75 | 25 | 216.5 |
| 50 | 50 | 218.0 |
| 30 | 70 | 199.8 |
| 20 | 80 | 199.6 |

The other important observation is that NP decomposes at ~216 °C when NP is dissipated in the VCE composite, which is more than 18 °C lower than that of NP in its liquid form (at 233 °C). The reduced $DT_{NP}$ indicates that the interaction strength between the NP and VCE molecules is less than that among NP molecules. This observation is consistent with the positive sorption heat (~2.2 kJ/mol) found in our previous work[19]. In summary, the amount of filler addition greatly decreases the stability of NP when NP is dissipated in the VCE/filler composites.

### *3.2 Effect of Heating Rate*

When polymers naturally age in the weapon applications, they are essentially exposed to thermal conditions with seasonal temperature fluctuation – mostly equivalent to the isothermal condition with a zero heating rate. It typically takes many years to see the aging sign. In the laboratory, to make the aging study more feasible, it is often carried out in an accelerated mode. To do so, the thermal analysis is commonly used to survey the thermal properties of the polymers, which is often conducted under a non-isothermal mode with various heating rates. However, it is well known that the thermal stability of a polymer greatly depends on the aging conditions. Therefore, the aging behavior of a polymer found from the accelerated aging often does not apply to that found at the natural aging condition. In this section, we examine the heating rate effect on the thermal stability of NP and VCE polymer. For the simplicity of the discussion, we will focus the discussion on two samples – the VCE polymer and the VCE/filler composite which only contains 20 wt% of VCE. Both samples were fully saturated with NP prior to the thermal measurements.

Figure 5 presents their TGA results. When the heating rate decreases from 20 to 0.1 °C/min, the $DT_{VCE}$s decrease more than 90 °C. At the 0.2 °C/min, the new peak emerges at 218.5 °C. As the rate further decreases to 0.1 °C/min, this new peak decreases to 211.6 °C. Similarly, as the rate decreases from 20 to 0.1 °C/min, the $DT_{NP}$ decreases from ~240 to 123.8 °C. At 0.1 °C/min, TGA detects a weight lose as low as 70 °C, which confirms the detectable vaporization of liquid NP occurring at 70 °C[17].

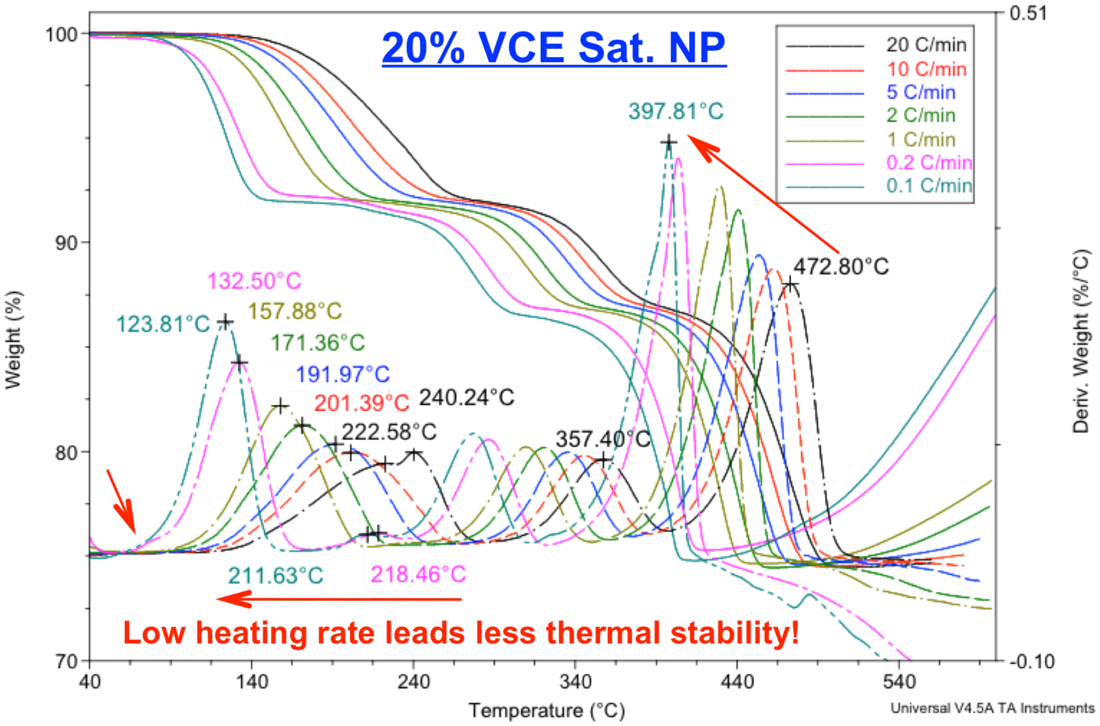

Figure 5. Effect of heating rate on $DT_{NP}$ and $DT_{VCE}$ of the VCE/filler/NP composites.

Figures 6(a) and (b) show the effect of the heating rate and filler concentration on the $DT_{NP}$ and 1st $DT_{VCE}$, respectively. In the same plots, we extrapolate the DTs to the extremely low heating rate by assuming the same decomposition mechanism applied over the entire range. If this assumption is true, the $DT_{NP}$ would have been as low as 45 °C in the 20% VCE composites and the 1st $DT_{VCE}$ as low as 170 °C. While the filler addition appreciably decreases the NP stability, it does not alter the VCE stability. Nevertheless, the heating rate significantly changes the thermal stability of both NP and polymers.

The above studies demonstrate that the heating rate significantly changes the kinetics of the NP evaporation/decomposition behaviors. At the low heating rate, the vaporized NP and emerged VCE peak at the low temperature potentially alter the degradation mechanism from the ones observed at the non-isothermal condition. To investigate the possible changes, we next examine the thermal stability of NP and VCE under the isothermal condition at temperature lower than 100 °C.

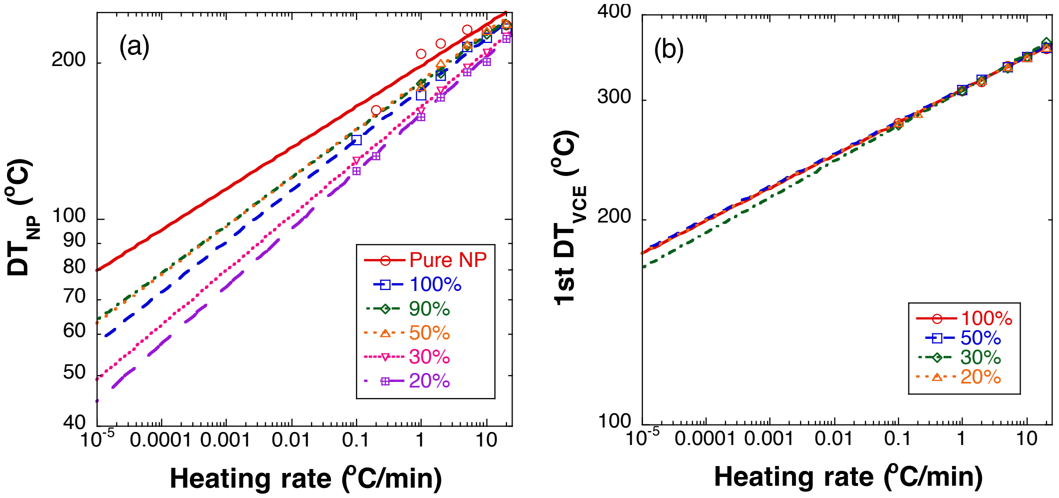

Figure 6. Effect of VCE concentration on the correlation between heating rate and DT$_{NP}$ of pure NP, VCE and VCE/filler composites (a) and the correlation between heating rate and the 1$^{st}$ DT$_{VCE}$ of the VCE sample and VCE/filler composites (b).

### *3.3 Isotherms of VCE and VCE Composites Saturated with NP*

Figures 7(a) and (b) present the isotherms conducted at different temperatures for the VCE polymer and the 20% VCE/filler composite, respectively. Both VCE and its composites were saturated with NP prior to the test. For the same measurement, the pristine VCE shows <0.05% of weight loss at 100 °C and <0.01% at 70 °C. Therefore, for the VCE/NP samples, it is reasonable to assume that the weight loss at <100 °C is solely due to the NP evaporation unless chemical degradation occurs. This study serves two purposes: 1) to investigate the NP desorption process, and 2) to examine the thermal stability of the NP and VCE under isothermal conditions. First, we discuss the NP desorption process. If we used the 1$^{st}$ order decay model to fit the TGA isothermal results, we can estimate the evaporation rate of NP from the VCE samples by using Eq. (1)[29]:

$$\ln\left(\frac{W_t - W_f}{W_i - W_f}\right) = -kt + C \quad , \qquad (1)$$

where $W_t$ is the sample weight at time $t$ (sec), $W_i$ is the initial weight, $W_f$ is the weight of VCE and filler, and $k$ is the first order rate constant of evaporation (1/sec). The calculated results are shown in Figures 8(a) and (b) for the 100% VCE/NP samples and 20% VCE/filler/NP composites, respectively. The 100%VCE/NP samples follow the 1$^{st}$ order decay well over the entire experimental course, which suggests that the NP desorption process obeys Fick's diffusion law. Under the isothermal conditions, the NP molecules diffuse out and evaporate from the surface of the matrix into the vapor phase, and result in the weight loss.

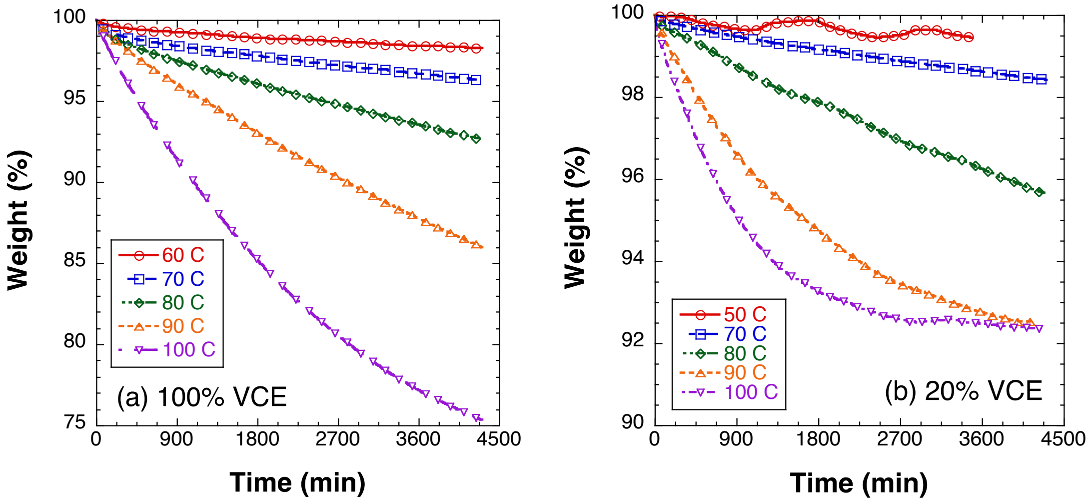

Figure 7. The isothermal TGA results of VCE/NP (a) and 20%VCE/NP composites (b). The weight loss is calculated based on the sample weight. At the beginning of the runs, the NP concentration was 40.5 wt% in VCE and 7.98 wt% in the 20% VCE composite, respectively. At 50 °C, the weight loss was so small that the fluctuation of surrounding temperature was detected.

However, for the 20% VCE composites, the calculated results verses time follow the 1st order decay model only when the samples were heated below 90 °C. Above 90 °C, their traces of the weight loss depart from the 1$^{st}$ order decay at the later portion of the run, which suggests that something other than NP vaporization occurs. Nevertheless, if we assume that the early portion of the weight loss is solely due to the NP evaporation, and the desorption process obeys Fick's diffusion, we can estimate the diffusivity ($D$) of the NP desorption from the matrix using Eq. (2) [29, 30]:

$$D = k(\frac{2l}{\pi})^2 \quad , \qquad (2)$$

where $l$ (cm) is the thickness of the sample. Since the sample was loaded onto the TGA pan, the NP molecules could only migrate from the one-side of the sample. Therefore, the single-sided theory is used to calculate the evaporation rates and diffusivities of NP[29, 30]. These results are summarized in Table 2. In this table, we also include the results obtained from the 50% and 30% VCE composites. As temperature increases, both NP evaporation rate and diffusivity increase – owing the increased mobility of the

NP molecules and polymer chain segments at the elevated temperatures. In addition to the temperature effect, for the VCE/filler composites, the increased interfacial area and enhanced thermal conductivity also accelerate the NP transport properties, and result in the increased diffusivity.

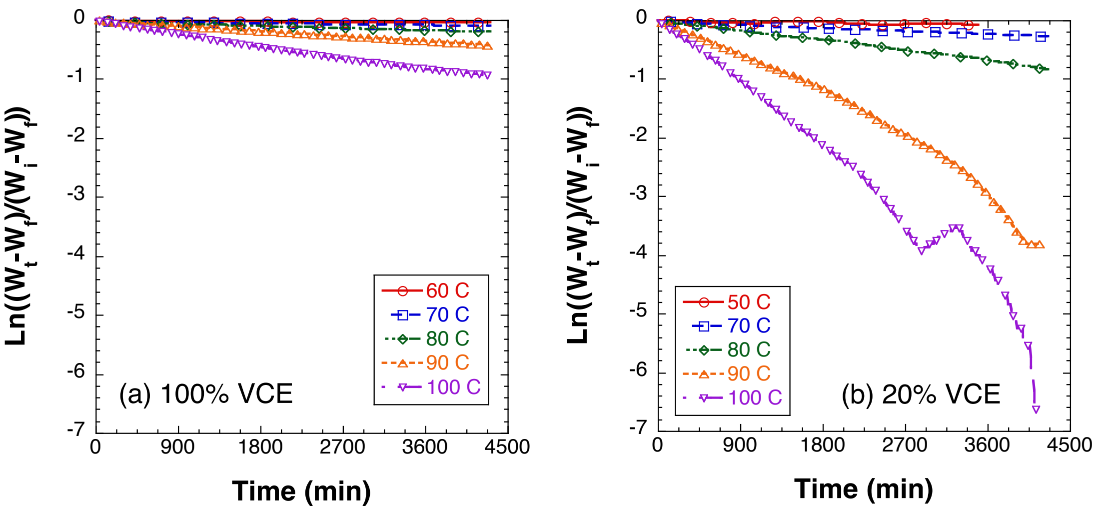

Figure 8. The normalized weight loss vs. time for (a) 100% VCE/NP and (b) 20% VCE/filler/NP composites at different temperatures. The results were deducted from the data in Figure 7 using Eq 1.

Table 2. Summary of desorption rate, diffusivity and activation energy of NP desorption in the VCE polymer and VCE/filler composites.

| **VCE Conc. (wt%)** | **Temperature (°C)** | ***k* x $10^7$ (1/sec)** | ***D* x $10^9$ ($cm^2$/sec)** | **$E_{act}$ (kJ/mol)** |
|---|---|---|---|---|
| 100 | 60 | 1.37 | 0.34 | |
| | 70 | 3.15 | 0.79 | |
| | 80 | 7.48 | 1.88 | |
| | 90 | 16.50 | 4.15 | |
| | 100 | 41.16 | 10.35 | 87.4 |
| 50 | 60 | 1.71 | 0.66 | |
| | 70 | 3.73 | 1.45 | |
| | 80 | 9.85 | 3.82 | |
| | 90 | 25.05 | 9.72 | |
| | 100 | 44.36 | 17.21 | 87.1 |
| 30 | 70 | 12.39 | 1.87 | |
| | 80 | 36.68 | 5.53 | |
| | 90 | 68.70 | 10.36 | |
| | 100 | 95.17 | 20.55 | 83.5 |
| 20 | 50 | 0.28 | 0.66 | |
| | 70 | 16.73 | 3.92 | |
| | 80 | 31.27 | 6.79 | |
| | 85 | 68.47 | 14.86 | |
| | 90 | 107.84 | 23.40 | |
| | 100 | 198.54 | 43.42 | 85.0 |

Using the Arrhenius equation, we estimate the activation energy ($E_{act}$) of the NP desorption process, as summarized in Table 2. These activation energies (83.5 – 87.4 kJ/mol) are slightly less than the heat of NP vaporization (~88.9 kJ/mol) reported by Behrens[21]. The decreased activation energy suggests that the interaction strength between NP and VCE molecules are less than that among the NP molecules, which results in a lower $DT_{NP}$ of NP in the VCE matrix than that in its liquid form. The impact of the filler addition on the morphology and thermal conductivity of the VCE composites is responsible for the extra decrease in the activation energy of the NP desorption from the VCE/filler composites.

To further examine the filler effect on the NP desorption, we conducted the 100 °C isothermal experiments for the mixtures only consisting of filler particles and liquid NP with the different NP concentrations. Figure 9 presents the logarithmic normalized weight loss using Eq. (1) verse time, which indicates that the NP evaporation rate significantly increases as the NP concentration decreases. When the mixture only contains 4.2% NP, NP completely vaporizes within 1200 min at 100 °C, which is much faster than other conditions. The increased evaporation rate is due to two factors: 1) the large surface area possessed in the mixture with the less NP content, and 2) the large enhancement on the thermal conductivity of the NP/filler mixture.

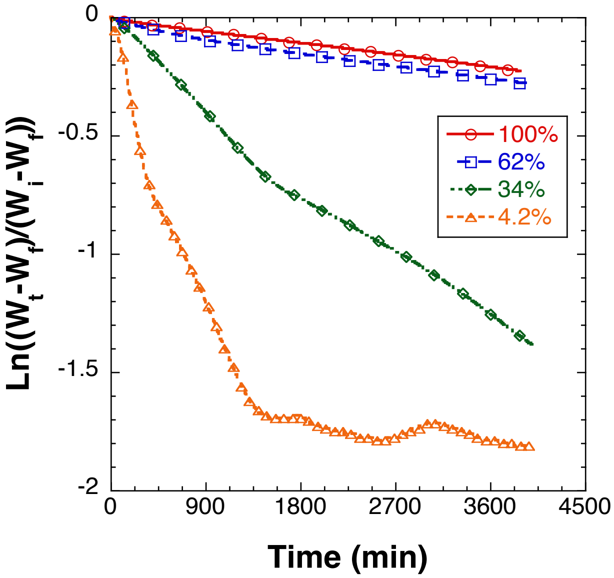

Figure 9. Effect of NP concentration (wt%) on the 100 °C isothermal results of the NP/filler mixtures (since the filler particles do not change weight at this condition, the weight loss are calculated based on the NP initial weight).

Furthermore, the changed slopes in the isotherms of the 34% and 4% NP/filler mixtures suggest the changed mechanisms of the weight loss during the isothermal runs. In addition to simple NP evaporation, NP molecules might start to degrade at the later portion of the runs. This study demonstrates that the NP stability can be significantly deteriorated when NP liquid coats at the surface of the filler particles.

Now, we will give more discussion about the abnormal behaviors in the 90 and 100 °C isotherms of the VCE/filler/NP composites in Figure 8(b). Prior to the test, all samples were saturated with NP. Since the isothermal runs were conducted under the nitrogen purge, the NP molecules at the sample surface evaporate first while the NP molecules inside the sample diffuse out. The elevated temperature increases this diffusion process due to the increased diffusivity of NP and mobility of the polymer segments, increases the NP evaporation, and results in the decreased NP concentration. When the sample contains a large amount of NP, to evaporate from the VCE composites, the NP molecules need to overcome not only the attraction force from the VCE molecules, but also the attraction force among themselves. As the NP concentration decreases, the sorption layers of NP inside the VCE/filler matrix change from multi-layers to a single layer. Consequently, the interaction among NP molecules diminishes. Therefore, when the concentration of NP reaches this critical point, to evaporate, the NP molecules only need to overcome the attraction force from the VCE molecules, which allows NP to evaporate at a faster rate than that from the samples containing a lot of NP. The changed evaporation rate are responsible to the changed slope in the 90 °C isotherm curve. However, the bump in the 100 °C isotherm indicates more complicated changes. Instead of losing weight, the sample seems to gain weight between 2850 and 3275 minutes. One possible explanation is that the some fragments from the degraded NP react with the VCE to cause the weight gain. To confirm the possible degradation of NP and VCE in these samples, we analyzed the residual sample using TGA and FTIR spectroscopy. Figure 10 presents the TGA results. Table 3 summarizes the weight loss of the samples at different temperature ranges. The results suggest that the NP concentration in the 50 °C sample is slightly less (<0.5%) than that before the isothermal experiment. For the 90°C sample, only <1% of NP is left in the sample. For the 100 °C sample, the weight loss at the temperature < 277 °C is identical as that of the pristine

VCE, which confirms that there is no NP present in the sample. The vinyl acetate concentration decreases for the 90 °C samples, but slightly increases for the 100 °C sample, which indicate some chemical changes in the samples.

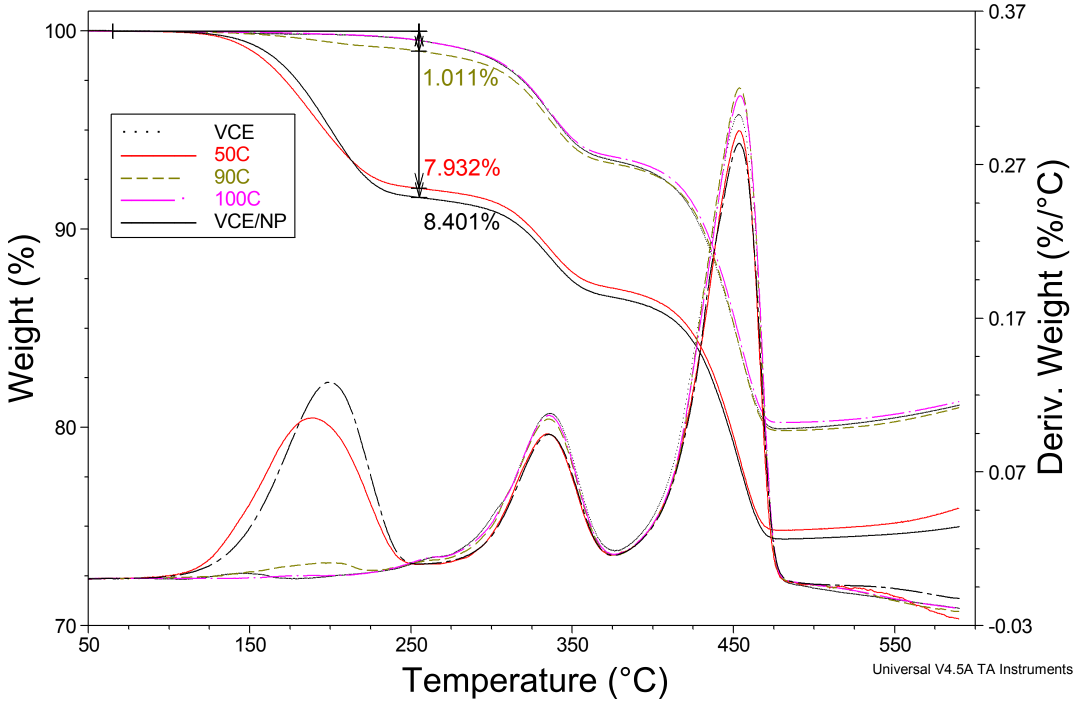

Figure 10. The TGA results of the 20% VCE/filler/NP composites after the isothermal runs at different temperatures.

Table 3. Summary of weight loss at different temperature ranges for the VCE samples before and after isothermal experiments.

| **Sample label** | **Wt loss (%) at different temp. ranges** | | | **Polymer* (wt %)** | **VAc (%)$^a$** |
|---|---|---|---|---|---|
| | **1st <277 °C** | **2nd 277-390 °C** | **3rd 390-500 °C** | | |
| Pristine VCE/NP | 8.40 | 5.06 | 12.16 | 17.8 | 44.5 |
| 50 °C | 7.93 | 5.06 | 12.17 | 18.3 | 43.1 |
| 90 °C | 1.01 | 5.70 | 13.43 | 20.0 | 41.3 |
| 100 °C | 0.50 | 5.90 | 13.38 | 20.0 | 42.5 |

[a]: We assume that the weight loss between 277 and 500 °C is due to the polymer decomposition. With this assumption, we calculate the polymer weight (wt %) in the sample. The content of VAc in the VCE polymer is calculated based on the weight loss between 277 and 390 °C.

Figure 11 presents the FTIR results. To better illustrate the results, the spectra were divided into three regions. In the same figures, two references were included - the pristine VCE (black dot line) and NP treated VCE composites but without aging (black

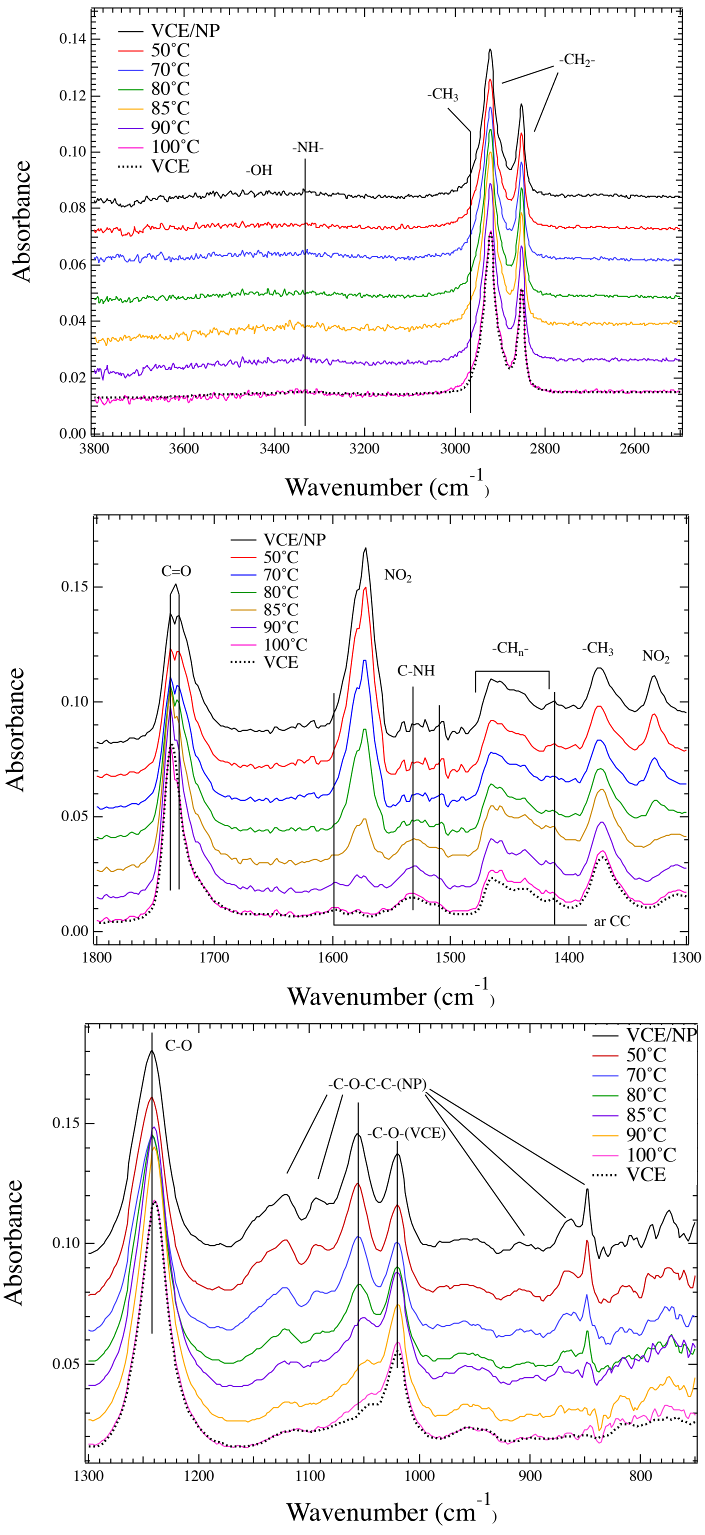

Figure 11. FTIR spectra of the pristine VCE and the 20% VCE composites containing different amounts of NP aged at 70 °C for 18 months (NP concentrations were calculated based on the sample weight).

solid line). First, let us examine the FTIR spectra of two reference samples. From 3800 to 2000 $cm^{-1}$, the -$CH_2$- stretch between 2800 – 3100 $cm^{-1}$ from VCE dominates the spectral feature. The –$CH_3$ stretch (from the acetate group) is embedded at the shoulder of –$CH_2$- peak. In contrast, NP absorption in this region is very weak. Even in the fully saturated sample, NP makes very little contribution to these peak areas. From 1800 to 1300 $cm^{-1}$, the main absorption peaks of NP are the $NO_2$ group - found at the wave numbers of 1570 and 1325 $cm^{-1}$ while the main absorption peaks of VCE are >C=O, -C-NH-, -$CH_n$, and -$CH_3$ (from the acetate group). Since the main peaks of NP and VCE do not overlap, the $NO_2$ peak can be used to detect the presence of NP in the VCE samples. From 1300 to 750 $cm^{-1}$, the most notable peaks are related to the –C-O- features, which come from both VCE and NP molecules as indicated in Figure 11(c). The important evidence is that the –C-O- peaks from both molecules do not overlap either. Therefore, all of these spectral signatures can be used to probe the NP presence and the structural changes in the VCE polymer. Using the peak area of $NO_2$, we can quantify the NP concentration in the VCE sample[31]. Furthermore, NP uptake does cause a noticeable change - a new tiny peak at ~1760 $cm^{-1}$ near the >C=O peak (~1780 $cm^{-1}$)[19]. We attribute this peak to the physical interactions between VCE and NP molecules (e.g. H-bonding).

Now, let us examine the FTIR spectra of the residual samples after the isothermal experiments. Comparing the 50 °C sample to the control sample, we do not observe noticeable changes in their spectra, which is consistent with the TGA result. Their almost identical spectra suggest that the 50 °C isothermal treatment for 3600 minutes does not chemically change the structures of VCE and NP. As the temperature increases from 50 to 85 °C, the absorbances of two $NO_2$ peaks largely decrease, which suggests the NP evaporation. Accordingly, the tiny peak at ~1760 $cm^{-1}$ gradually disappears. The rest of spectra remains more or less the same, which suggests that the chemical structures of both NP and VCE do not significantly change at these conditions. For the 90 °C sample, the main $NO_2$ peak at 1570 $cm^{-1}$ is almost gone, which suggests only a trace amount of NP left in the sample. For 100 °C sample, the $NO_2$ peaks are not detectable, which confirms the absence of NP in the sample. All of these results are consistent with the TGA results.

In addition to the disappearance of the $NO_2$ peaks, comparing to the spectrum of the pristine VCE, we also observe the following spectral changes in the 100 °C sample: 1) the intensities of $–CH_3$ stretch increase at different regions (e.g. ~2970 and 1350 $cm^{-1}$); 2) the intensity of –NH–C-O- (from the cross-linker in VCE at 1040 $cm^{-1}$) increases. Accordingly, the intensity of the shoulder near to the –NH-C-O- peak increases, which might be due to the formation of -C-OH; and 3) the intensities of the peaks associated with the aromatic –C=C- increases in the region of 1500-1400 $cm^{-1}$ and ~ 780 $cm^{-1}$. All of these changes suggest that the chemical structures in this 100 °C sample are different from those in the pristine VCE. Although the FTIR spectroscopy is not sufficient to pinpoint the exact degradation mechanisms occurring during the 100 °C isothermal experiment, the results do suggest that the VCE polymer in its highly filled composites starts to degrade at the elevated temperature with the presence of NP.

### *3.4 Long-term Aging Studies of VCE Composites with and without NP*

In the isothermal experiment, the oven was purged with nitrogen. Therefore, vapor phase was essentially replaced by the inert gas. However, in a closed system, the outgassed vapor will accumulate in the headspace where the polymers age under a much more complicated environment than those in the isothermal experiments. Motivated by this consideration, we conducted a long-term aging experiment in which the VCE composites were thermally aged in a closed system at 38, 55, and 70 °C with different NP concentrations (0, ~4, and ~8 wt%) in the samples.

Figure 12 presents the FTIR spectra of the 18 month aged VCE samples aged at 70 °C and pristine VCE (black solid line). The variable here is the NP concentration. Without the presence of NP, the aging slightly changes in the FTIR spectra (red solid line) of the VCE composites. The absorbance of the broad peak – associated with –OH at the region of 3700 – 3100 $cm^{-1}$ slightly increases. Accordingly, the peak absorbance at ~ 1120 $cm^{-1}$ – associated with –C-OH alcohol, increases, which suggest that some –OH group form after 18 month aging. Furthermore, the peak ~800 $cm^{-1}$ – associated with –C=C- bonds, emerges as well, which suggests that some double bonds are detected. Overall, the FTIR spectral changes are not significant. The VCE polymer, without the presence of NP, is thermally stable after being aged at 70 °C for 18 months.

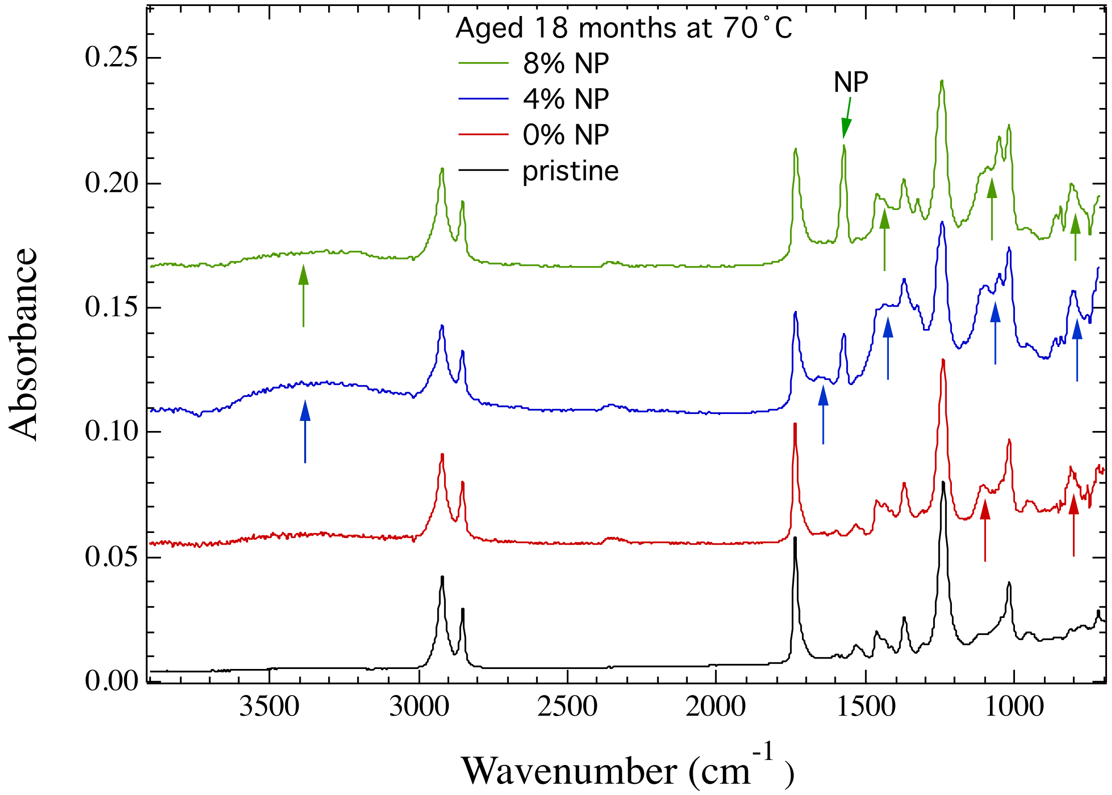

Figure 12. FTIR spectra of the pristine VCE and the 20% VCE composites containing different amounts of NP aged at 70 °C for 18 months (NP concentrations were calculated based on the sample weight).

On the other hand, with the presence of NP, the spectral changes are obvious. In addition to the $NO_2$ peaks (at ~1570 and 1325 $cm^{-1}$) from NP, the major changes are following: 1) the broad peak associated with –OH group at ~3350 $cm^{-1}$ and the –C-OH peak at ~1120 $cm^{-1}$ grow even more; 2) the peaks between 1500 – 1300 $cm^{-1}$ greatly change, which suggest that new functional groups are formed. These new functional groups could be $–CH_2$-CO-, -C-OH, -C=C-H, -N=O; 3) one new peak at ~1650 $cm^{-1}$ starts to emerge, which may be also related to the –C=C-, -C=N-, and/or – N=O. All these spectral changes suggest that the chemical structures in VCE and NP change after being aged at 70 °C under the NP environment for 18 months.

Interestingly, the sample with 4.57 wt% NP shows the greater change than the sample with 7.67 wt% NP. This observation confirms that the NP molecules in the samples with a small concentration of NP can evaporate faster than the samples with a high concentration of NP. It is reported that NP goes to different decomposition pathways when it is thermally treated at the low temperature (e.g. 60 - 75 °C)[22] and high temperature (>150 °C)[21]. Instead of forming radicals and $NO_2$ at the high temperature, the non-radical reaction generates HONO with a low activation energy (<42 kcal/mol) at the low temperature. In the liquid NP, due to the cage effect, the formed HONO can add back to the NP fragment before diffusing out of the liquid. However, HONO molecules in the vapor phase can be reactive, and form water and oxidizing $NO_x$ gases. The acidic chemical species in the vapor phase will attack the –CO- group in the acetate group and/or the cross-linkers, and are responsible for the newly formed functional groups.

With respect to the effect of temperature, Figure 13 presents the FTIR spectra of the VCE/filler/NP composites aged at different temperatures for 18 months. All aged samples contained 4.04 – 4.57 wt% NP prior to the aging experiment. After the 18 month aging, the NP concentration decreases as the temperature increases based on the TGA measurement. For the 38 °C sample, the NP concentration decreases from original 4.04 to 3.92 wt%. For the 55 °C sample, the NP concentration decreases from original 4.32 to 3.64 wt%. For the 70 °C sample, the NP concentration decreases from original 4.57 to 3.35 wt%. The decreased NP concentration may be not only due to the NP evaporation, but also due to the NP degradation. As the temperature increases, the spectra change in the following ways: 1) the absorbance of the board peak at ~3350 $cm^{-1}$ increases, which suggests more –OH group formed; 2) the absorbance of the new peak ~1650 $cm^{-1}$ increases, which suggests newly formed -C=C- bonds; 3) the spectra between 1500 and 1300 $cm^{-1}$ dramatically change; and 4) the spectra between 1200 – 1000 $cm^{-1}$ dramatically change. All of these spectral changes are attributed to the degradation of NP and VCE. For the 38 °C samples, although the NP weight lose is not significant, the spectral changes clearly indicate the VCE degradation after being aged for 18 months, which was not anticipated prior to this study.

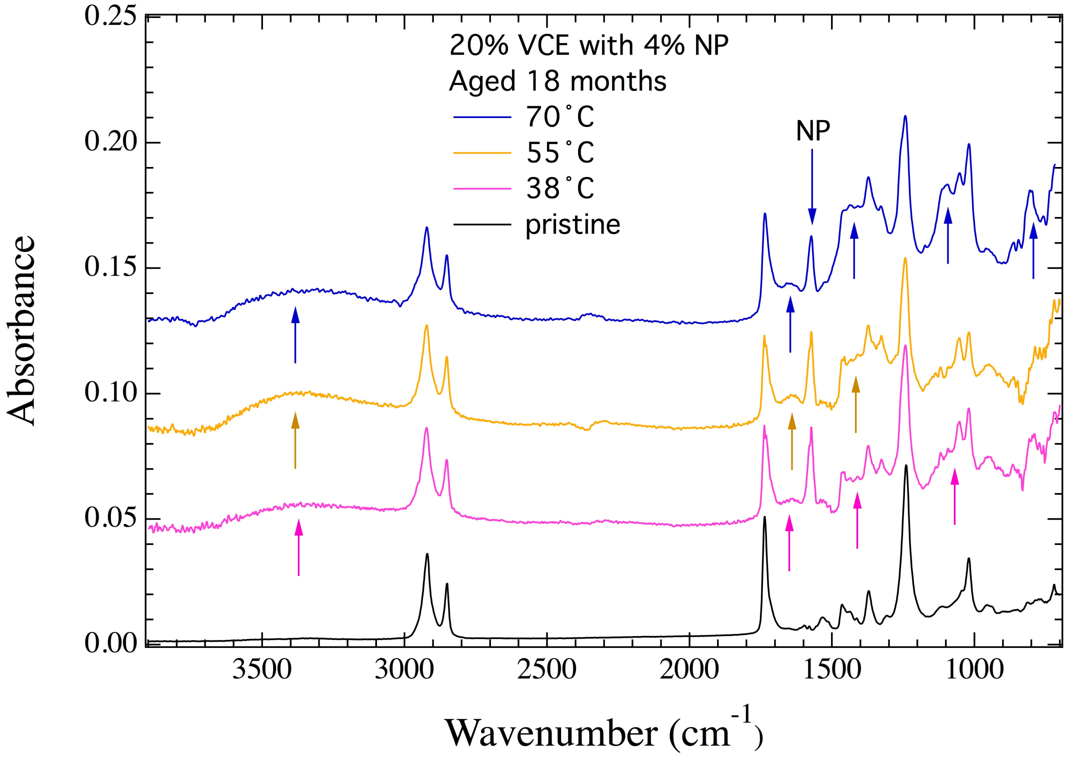

Figure 13. FTIR spectra of the pristine VCE and the 20% VCE composites containing ~4% NP aged at different temperatures for 18 months (NP concentration was calculated based on the sample weight).

## 4. Summaries and Future Work

From this study, we confirm that the interaction between NP and VCE molecules is weaker than that among the NP molecules. Therefore, the NP molecules can evaporate more easily from the VCE sample than from the NP liquid. The addition of the filler particles into the VCE composite further accelerates the NP evaporation because of two factors: 1) the greatly increased interfacial area between the solid phase – including filler particles and VCE and NP, and 2) the enhanced thermal conductivity of the VCE/filler/NP composites. Therefore, in the highly filled VCE composite, the thermal stability of NP significantly decreases, which allows the NP molecules vaporize at even faster rate from the VCE composite than that from the VCE polymer. Since some chemical species in the vapor phase, such as HONO, are detrimental to the polymer, VCE starts to degrade at 38 °C after being exposed to the NP vapor for 18 months. Now, the three-year aging experiments are underway for the VCE/filler composites at different environments and different temperatures. With more characterization techniques, we should better understand the degradation mechanisms of VCE in its composite form at the relative mild aging conditions. These results will be discussed in our future reports.

## Acknowledgements

We thank John Barton (KCP) for helping on the VCE material production. This work is funded by the US Department of Energy's National Nuclear Security Administration under contract DE-AC52-06NA25396.

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