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## **Volatile out gassing characteristics of highly filled ethylene vinyl acetate binder materials: Gas phase infra-red spectroscopy studies**

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### **Abstract**

Gas phase Infra-red (IR) spectroscopy has been used to investigate volatile out gassing properties of highly filled poly (ethylene-co-vinyl acetate) materials. In these studies, a Scout-EN<sup>TM</sup> heated gas cell was interfaced to a vacuum FTIR spectrometer, and the quantification of evolved species was achieved through calibration of the gas cell with certified gas standards. The volatile out gassing properties were monitored as a function of time during storage at 75°C under vacuum conditions (< 1mbar). Acetic acid, carbon dioxide and water were identified as the major out gassing products through IR absorption peaks at 1797, 2354 and 3853 cm<sup>-1</sup>, respectively. A comparison of three highly filled poly (ethylene-co-vinyl acetate) resins is reported. In each case, low molecular weight silicone impurities were identified in the headspace. Repeat sample testing with regular evacuation of the headspace generated an estimate of likely 'inventory' levels (i.e. material present within the binder phase from earlier degradation processes potentially occurring in manufacturing and storage operations). Successive out gassing runs showed a diminishing release rate and level. Temperature sensitivity studies together with first order kinetic assessments suggests that the evolution of acetic acid is largely diffusion controlled with an Arrhenius activation energy of typically 13 kJ/mol (correlating to an acceleration coefficient of 1.17 per 10°C rise). Relatively novel multi-material trials have been reported investigating out gassing in the presence of an acetic acid 'sink'. The sink significantly alters the headspace gas composition by gradually depleting the acetic acid. Our experiments provide understanding of out gassing

rates at both the individual and multi-material levels, and support our core programmes in materials qualification and life assessment.

*Keywords: Volatile Out gassing, Infra-red Spectroscopy, Ageing, Poly (ethylene-co-vinyl acetate)*

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## 1. Introduction

Poly (ethylene-co-vinyl acetate) based materials (denoted here as EVA) are used commercially as adhesives and also as a binder phases in a number of specialised applications. The thermal stability and degradation properties of these materials have been studied and reported in the open literature [1,2,3]. These include a number of experimental studies undertaken to identify the nature of volatile organic species, understand temperature dependency and mechanistic pathways. The major test methods employed in these studies include headspace sampling with solid phase microextraction (SPME), gas chromatography-mass spectrometry (GC-MS), thermal volatile analysis (TVA), thermo gravimetric mass spectrometry (TGMS), infrared spectroscopy (FTIR) and pyrolysis [4].

The key volatile products observed from these materials are acetic acid, carbon dioxide and water. In most cases a quantitative assessment of out gassing rates and levels of species present as inventory (i.e. material present within the material from previous degradation processes such as during manufacturing/storage) is not reported. This is mainly due to the fact that moisture and acetic acid present significant technical challenges in terms of quantification as these species can be relatively reactive to metals and can readily adhere or be absorbed on to surfaces.

The dominant degradation reaction for EVA at elevated temperatures (greater than 300°C) is deacetylation with removal of the pendant acetate group and elimination of acetic acid [5]. However, thermally induced deacetylation (i.e. ester pyrolysis) is not believed to be significant at temperatures below 150°C, so despite being feasible, it may not be the sole reaction mechanism for acetic acid production. Acetic acid can also be produced through acid or base catalysis of the ester groups [6]. Low levels of acid would be required to initiate this reaction which, once started, would be autocatalytic with acetic acid as a reaction product. In the case of the acid-catalysed reaction, water and a proton source are required for

the reaction to proceed. Water is present in commercial EVA emulsions and it is possible that the proton source for hydrolysis could exist through manufacturing operations. Another potential proton source is carbonic acid, the product of water and carbon dioxide. Build-up of carbon dioxide in EVA matrices is not fully understood but could potentially occur through absorption from air, produced through decarboxylation reactions within the EVA or the oxidative degradation of ethylene in the EVA backbone.

Irrespective of the production mechanisms, acetic acid, carbon dioxide and water are recognised as key species present in and evolved by EVA based materials. These species are present at zero time (point of manufacture) as ‘inventory material’ and potentially created through real-time degradation events [7,8]. The volatile evolution or release of these species in a closed system environment potentially has compatibility implications. EVA based materials are therefore considered to have an influence on complex sub-assembly chemistry where the constituent materials are likely to age under highly complex ageing regimes that may include ionising radiation. In order to develop a predictive ageing model of these sub-assemblies, the ageing behaviour of the individual materials, as well as materials in combination (multi-materials) must be investigated and understood.

In this paper, we describe the development and practical use of a gas phase Infra Red method which enables quantitative volatile out gassing measurements to be made on highly filled EVA based materials and which enables a quantitative prediction of out gassing in other situations of interest. The technique is flexible with modification of the test method providing an opportunity to investigate multi-material trials.

The filled materials tested and reported here are employed in highly specialised assemblies. For these materials, our objective is to develop an ageing model capable of describing the out gassing characteristics for all species and which should incorporate parameters that describe sensitivity to key variables such as specimen processing, shelf storage, test temperature, resin type and surface area.

## 2. Experimental

### 2.1 Materials

Three different filled poly (ethylene-co-vinyl acetate) specimens were prepared and tested. These are Vinamul 3161, Airflux EP17 and Mowilith DM132. These resins were used as received and typically have vinyl acetate fractions of 66 wt% with polyethylene as the remaining main constituent of the copolymer.

The materials used in our experiments are of 'known pedigree', i.e. the thermal and storage history of the materials is known between production and analysis. This is important because volatile out gassing is often dependent on prior shelf storage and/or thermal regimes encountered by the material. The samples were produced as pucks and were filled with research grade inert particulate (75 wt %). The filler used in all these materials is metallic, inert and particulate in nature.

Small amounts of viscoslab, lithium stearate and water were used as additives as part of the manufacturing process which typically requires pressing of samples into shape at temperatures of 150°C for up to 2 hours. The manufacturing process also requires that the samples be stored over desiccant at elevated temperatures (75°C) for 2 weeks, and then stored in a dry box at room temperature under an argon atmosphere.

In some experiments we have tested highly filled Vinamul 3261 specimens. These are legacy specimens which have been stored over desiccant for 10 years at room temperature under a dry argon atmosphere.

### 2.2 Scout Gas Cells and Vacuum Infra-red Spectrometer

A Scout-EN<sup>TM</sup> heated gas cell supplied by CIC-Photonics Inc was used in all of our volatile out gassing studies. The gas cell optical path length was 10 cm and inner cell walls were nickel plated to reduce adsorption or reaction with vapours. The internal diameter is 19mm

and the free volume typically 30 cm<sup>3</sup>. BaF<sub>2</sub> windows installed on both ends of the gas cell provide the required Infra-red frequency range (7500 - 700 cm<sup>-1</sup>) and were sealed to the main body of the gas cell using Kalrez o-rings. The exit pipe on the gas cell was connected to a normally closed pneumatic valve (Swagelok 6LVV -DPVR4-P-C, actuated by a Jin-Air 200 air compressor), which in turn was connected to a vacuum provided by a rotary pump (Edwards E2M8).

The spectrometer used in these studies was a Jasco 6300 vacuum FTIR. The front plate of the spectrometer was modified to include a number of vacuum, electrical, temperature and compressed air feed-thorough lines. The Scout-EN<sup>TM</sup> heated gas cell was interfaced and incorporated to the vacuum Infra-red spectrometer.

### *2.3 Calibration*

The spectrometer and gas cells were calibrated using certified gas mixtures purchased from BOC Ltd. The gas species of known concentration was contained within a dry nitrogen gas balance. The gas standards were supplied at certified molar parts per million (ppm) concentrations independent of temperature. The experimental gas cell system was calibrated by evacuating (<1 mbar) and equilibrating the gas cell at 75°C. The cell was allowed to stabilise overnight to minimise adsorbed species (such as moisture) on the inner gas cell walls and provide a stable background spectrum. The gas cell was subsequently flushed with the calibrated gas mixture for five minutes and then filled to a pressure of 1000 mbar, before a sample spectrum was acquired. All spectra were acquired, over a 50-scan average at a resolution of 4 cm<sup>-1</sup>, at regular intervals until consistent results were obtained.

### *2.4 Experimental Procedure*

Approximately 4g of the rectangular sample was loaded into the gas cell. This was carried out within a dry box, so as not to expose the sample to air (i.e. moisture and carbon dioxide). In order to load the sample into the gas cell, one of the cell windows was removed.

Rectangular segments (5mm square, 26 mm length) of the sample were carefully positioned end to end, along the length of the cell, so as not to obscure the beam path. The second BaF<sub>2</sub> window was re-fitted and sealed to the cell. The cell was removed from the dry box, the window seals checked, and then transferred to the spectrometer.

The gas cell was located onto a base plate in the sample compartment of the spectrometer and the power supply, thermocouple, vacuum and compressed air connections were made. The position of the cell was adjusted to give maximum beam transmission and its position secured. To remove interference associated with absorption from air species (i.e. H<sub>2</sub>O and CO<sub>2</sub> etc.) within the gas cell head space and sample chambers, the spectrometer was evacuated using a scroll pump.

Prior to any experiment and with the gas cell under vacuum, a single beam background spectrum was collected with a 50-scan average at a 4 cm<sup>-1</sup> resolution. Time interval measurements were performed to monitor evolved volatile species over an initial 2 hour period. At the end of the initial run, a further background spectrum was obtained before the gas cell was re-evacuated to remove initial evolved gases and vapours. A spectrum of the headspace was obtained at regular intervals, until consistent spectra were obtained, indicating all of the initial evolved species had been removed and a consistent baseline was achieved.

Time Interval measurement to assess out gassing characteristics of the sample at 75°C was then repeated over 120 hours, followed by five runs over 150 hours. At the end of each run the headspace was cleared by evacuating back to <1 mbar and the next run started. It should be noted that the evacuation periods varied between runs.

### 3. Results and Discussion

#### 3.1 Speciation

The decision on which peak to monitor for acetic acid profiling was made by assessing the spectrum generated by a 200ppm acetic acid gas standard in nitrogen at 75°C. **Figure 1** shows that there are two strong acetic acid monomer bands which are suitable for quantification; the first is a doublet centred at about 1790  $\text{cm}^{-1}$  (from C=O) and the second an absorbance band at about 1177  $\text{cm}^{-1}$  (from C-O). The C=O stretch was selected for use in this study, because it was a relatively strong absorption band that can be observed above the water band.

For  $\text{CO}_2$ , the absorbance band typically appears as a strong doublet, of which the higher frequency band at 2358  $\text{cm}^{-1}$  was used in this analysis. This band is relatively clear of any interference and so was very easy to measure. In contrast, the spectrum of water vapour is made up of numerous bands covering the regions 4000-3500  $\text{cm}^{-1}$  and 2000-1200  $\text{cm}^{-1}$ . The band at 3853  $\text{cm}^{-1}$  was chosen because it had good intensity and band shape, as well as relatively less interference from other absorbance bands.

#### 3.2 Quantification

**Figure 2** and **Figure 3** show the calibration plots (obtained at a pressure of 1000 mbar and a temperature of 75°C) for acetic acid (1177 and 1797  $\text{cm}^{-1}$ ), carbon dioxide (2358  $\text{cm}^{-1}$ ) and water vapour (3853  $\text{cm}^{-1}$ ). The relative absorption (measured by peak height at the selected wavelength) versus concentration of species in the gas phase was found to be linear and the gradient can be used to calculate the concentration of the volatile species following acquisition of an absorption spectrum. All quantities reported here for acetic acid, carbon dioxide and water are based on the calibration plots reported in this paper. The gas phase composition of species at equilibrium is expressed in units of concentration ( $\text{g cm}^{-3}$ ) per

weight (g) of sample; and the out gassing rate is expressed in units of gas concentration ( $\text{g cm}^{-3}$ ) per weight (g) of sample per second (s).

### 3.3 Volatile out gassing profiles

**Figure 4** shows the typical headspace gas composition obtained from Vinamul 3261 specimen. In each case, a rapid initial evolution of volatile species is observed followed by a consistent evolution rate. The second run (see **Figure 5**) shows that the levels and rates of acetic acid, water and carbon dioxide evolved from the sample are significantly reduced. **Figure 6** shows that the gas phase concentration for each species reduces with repeat tests on the same sample. These observations suggest a significant ‘inventory phase’ is evolved into the headspace over time and which depletes with each test run. The ‘inventory phase’ represents species that are accumulated within the material from earlier degradation reactions such as during storage and manufacturing operations, and which are likely to be linked to physical processes such as diffusion.

Summation of the equilibrium gas phase concentration achieved at each test run provides an indication of the levels of species out gassed and initially present within the material. **Figure 6** shows that acetic acid dominates the headspace composition with the total concentration of acetic acid out gassed of the order of  $1.3 \times 10^{-6} \text{ g cm}^{-3} \text{ g}^{-1}$ .

Our observations suggest evidence for an ‘inventory’ of carbon dioxide which probably originates from dissolved and/or trapped material, and which slowly diffuses out into the headspace. It’s also possible that there may be minor contributions from real-time degradation events such as decarboxylation of the ester groups and/or residual ongoing oxidative degradation of the polyethylene segments (through residual peroxides generated from processing). Overall, the levels of carbon dioxide initially evolved were of the order of  $2 \times 10^{-7} \text{ g cm}^{-3} \text{ g}^{-1}$ , and these levels gradually deplete with repeat testing.

Our results suggest a relatively small but significant inventory of water within the bulk which is quickly exhausted with repeated testing (i.e. material is becoming dry). It is likely that the source of the water originally arises from the fact that the EVA resin used in manufacturing is emulsion based (and therefore contains water) and also a small amount of water is used as a processing aid. Although the highly filled specimens were stored over desiccant, it's possible that some moisture may have been picked up during shelf storage.

### *3.4 Impact of Resin Type*

**Figure 7** to **Figure 9** show the out gassing characteristics as a function of resin type. Profiles for acetic acid and carbon dioxide are similar and do not level off suggesting continuous steady state evolution from the material. In each case, the moisture evolved achieves a relatively flat profile over time. **Table 1** shows a summary of the out gassing rates and levels as a function of resin type. For each material, acetic acid dominates the headspace gas composition with out gassing rates of approximately  $10^{-14} \text{ g cm}^{-3} \text{ g}^{-1} \text{ s}^{-1}$ . The Airflux material evolves relatively higher moisture levels than the other resins and the dependency to resin type most probably originates from subtle differences in formulation from different manufacturers, and further work is underway to investigate chemical and physical differences between commercially supplied resins. Overall, from a compatibility perspective, the results suggest that Vinamul 3161 is most probably the best option and the preferred replacement resin for potential use in system applications.

### *3.5 Kinetic Studies*

**Figure 10** shows how the acetic acid out gassing rate and profile varies with temperature. We have carried out some preliminary kinetic analysis of this data to assess whether the evolution of acetic acid is representative of diffusion controlled processes. First order rate plots of natural log acetic acid out gassing (P) as a function of time is shown in **Figure 11**.

The plots are typically linear at elevated temperatures with evidence of minor curvature at low temperatures (75°C and below). For each temperature set, the slope of the linear regression fit through the data was used to derive the first order rate constant ( $k/s^{-1}$ ), and the temperature sensitivity was assessed for Arrhenius kinetics. **Figure 12** shows a reasonable good fit to the Arrhenius equation and the activation energy calculated from the slope is approximately 13kJ/mol. This equates to an acceleration coefficient (factor) of 1.17 per 10°C rise. This is relatively low and suggests that the evolution of acetic acid is potentially diffusion controlled mechanism rather than real-time production through chemical processes. Similar kinetic studies to assess the release of water and carbon dioxide are ongoing kinetic investigations and will be reported in future communications.

**Figure 13** shows a linear plot of the first order rate constant as a function of temperature. The equation of the trend line can be used to predict rate constants at lower temperatures particularly those potentially representative of long term service regimes. The first order rate constant for the diffusion controlled release of acetic acid at 32°C is found to be typically  $0.012 s^{-1}$ . From an ageing and compatibility perspective, this is regarded as very low and not regarded as a significant problem.

### 3.6 Sink Rates

In a multi-material or multi-component system where different materials can be positioned relatively close to each other, an understanding of volatile out gassing events (source) in conjunction with any potential absorption events (sink) is required to assess system level ageing. **Figure 14** shows the acetic acid out gassing profile when the specimen is in close proximity to an acetic acid sink. The sink used in this trial is a metallic hydride. Under these test conditions, the maximum quantity of acetic acid evolved was found to be approximately  $5.3 \times 10^{-8} \text{ gcm}^{-3} \text{ g}^{-1}$ . This is significantly lower than the acetic acid levels evolved in the absence of the sink (see **Figure 6**). This suggests that the sink reduces the acetic acid

inventory levels within the specimen as well as dramatically altering the volatile evolution profile by gradually depleting the acetic acid evolved by the sample. The headspace is typically exhausted of evolved acetic acid within 40 hr. The observed 'sink rate' may be potentially sensitive to surface events such as carbonisation of the sink material and may have complex dependencies to parameters such as sink surface area, distance from the source, quality and age of the metallic hydride. Our goal is to develop a deeper understanding of this relatively novel area of work.

### *3.7 Impurities in the headspace*

Our FTIR gas phase studies consistently show evidence of an impurity in the gas phase. **Figure 15** shows that the concentration of the unknown species reduces with repeat testing on the same sample. Comparison of the spectrum with reference spectra suggests that the head space impurity is silicone based. The source of this impurity almost certainly arises from the use of polysiloxane based moulds during manufacturing operations.

## **4. Discussion**

An important observation from our studies is the importance of inventory contribution to volatile out gassing. Its possible that three different phases exist, these are free, 'weakly' and relatively 'strongly' bound phases of volatile species. The free and/or 'weakly' bound phase(s) is evolved at early times whilst the relatively 'strongly bound' species is evolved during the later stages or at elevated temperatures. The 'strongly bound phase' may possibly be that closely associated with the particulate filler particles. On this perspective, the materials model of significant current interest in the open literature is the Edeskuty and Amundson dual resistance model [9] depicted by the schematic shown in **Figure 16**. This assumes that local adsorption/desorption processes are dominant and the overall out gassing rate (C) is dependent on parameters such as the concentration of species within the binder

( $C_o$ ) and at the surface ( $C_s$ ); as well as the diffusion constant ( $D$ ); the filler-species absorption ( $K_a$ ) and desorption rate constants ( $K_d$ ). Initial exploratory studies tend to suggest that this model shows good potential to explain most if not all of the key features observed in the IR out gassing trials; however our work in this area remains ongoing and will be reported in future publications.

From a life assessment and system ageing model perspective, our interests lie not only in the quantification of the various inventory phases (free, weakly bound and strongly bound) but also on identifying any potential contributions from real-time reaction (e.g. acetic acid generated from hydrolysis of the acetate groups). Under the test conditions investigated here, the contribution from real-time degradation appears to be very minor (if any), and that out gassing is dominated by species already present from earlier degradation such as during manufacturing.

This is further supported from first order kinetic studies which show that the evolution of acetic acid is largely a diffusion controlled process with low activation energy. Our work has been successful in delivering quantified out gassing rates and inventory levels in highly filled EVA materials. For acetic acid, the release rate is typically of the order of  $10^{-14} \text{ g cm}^{-3} \text{ g}^{-1} \text{ s}^{-1}$ . The levels of acetic acid inventory material appear to be at least  $10^{-7} \text{ g cm}^{-3} \text{ g}^{-1}$ . The first order rate constant for the diffusion controlled release of acetic acid at temperatures closely representative of service regimes ( $32^\circ\text{C}$ ) is estimated at  $0.012 \text{ s}^{-1}$ .

Further work is still required to understand dependency on the following variables: specimen surface area; test temperature; specimen storage duration (over desiccant); sensitivity to particulate filler loadings; and impact of processing variables such as temperature and pressing loads. In particular, the presence of the filler particles may influence mass transfer and/or diffusion processes of key species in a complex manner, and is currently under investigation.

It should be noted that the filled materials tested and reported here are used in highly specialised assemblies and as such have not previously been reported in the open literature. The same holds for our novel multi-material trials where materials are tested in combination to understand highly specialised system level ageing events.

## 5. Conclusions

A gas phase Infra-red (IR) spectroscopy strategy has been used for investigating volatile out gassing profiles from highly filled poly (ethylene-co-vinyl acetate) materials. The quantification of evolved species has been achieved through calibration with certified gas standards.

A comparison of out gassing from three different highly filled poly (ethylene-co-vinyl acetate) resins has been carried out. For all materials tested, the release of inventory material appears to dominate the out gassing characteristics. Kinetic studies show that the underlying processes are complex with the evolution of acetic acid largely diffusion controlled with an Arrhenius activation energy of approximately 13 kJ/mol (correlating to an acceleration coefficient/factor of 1.17 per 10°C rise). For acetic acid, the out gassing rates are potentially of the order of  $10^{-14}$  g cm<sup>-3</sup> g<sup>-1</sup> s<sup>-1</sup> with 'inventory levels' of at least  $10^{-7}$  g cm<sup>-3</sup>g<sup>-1</sup>.

We have reported on our relatively novel multi-material trials investigating out gassing in the presence of an acetic acid sink. The sink significantly alters the headspace gas composition by gradually depleting the acetic acid. The 'sink rate' is an important input parameter in developing our understanding of ageing in complex sub-system assemblies. Our experiments provide understanding of out gassing rates at both the individual and multi-material levels, and support our core programmes in both materials qualification and life assessment.

## **6. Acknowledgements**

The work reported here was performed under joint working agreements between AWE and the US, and includes studies carried out by the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. In particular, the authors would like to thank Dr Phil Monks (AWE) for his research work on the Edeskuty and Amundson model, and Dr Robert Bernstein (SNL) for his participation in this collaborative project.

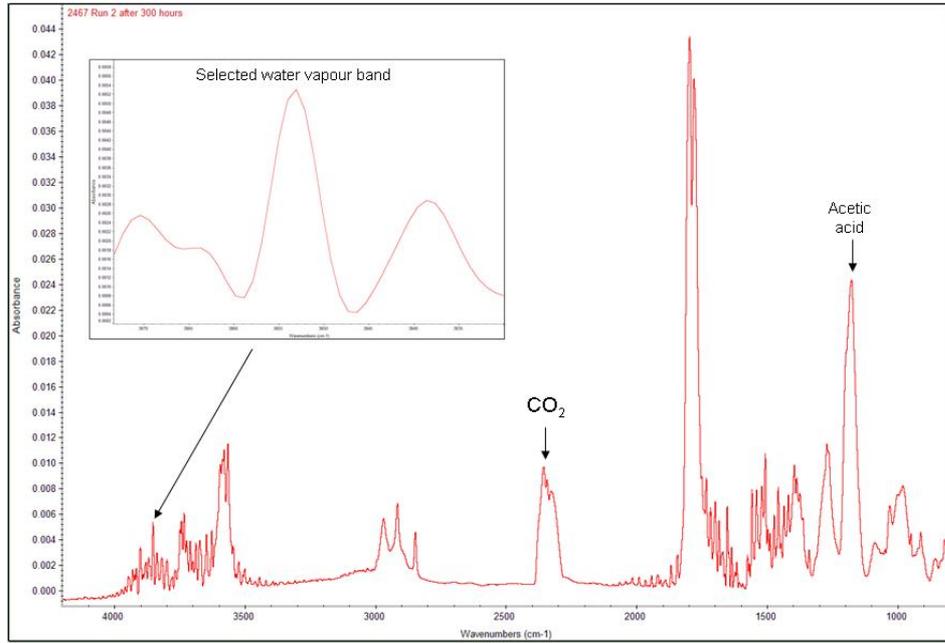


Figure 1: Typical Infra-red spectrum of the headspace at 75°C. The acetic acid, carbon dioxide and water absorbance suitable for quantification are indicated. The specimen tested is Vinamul 3261.

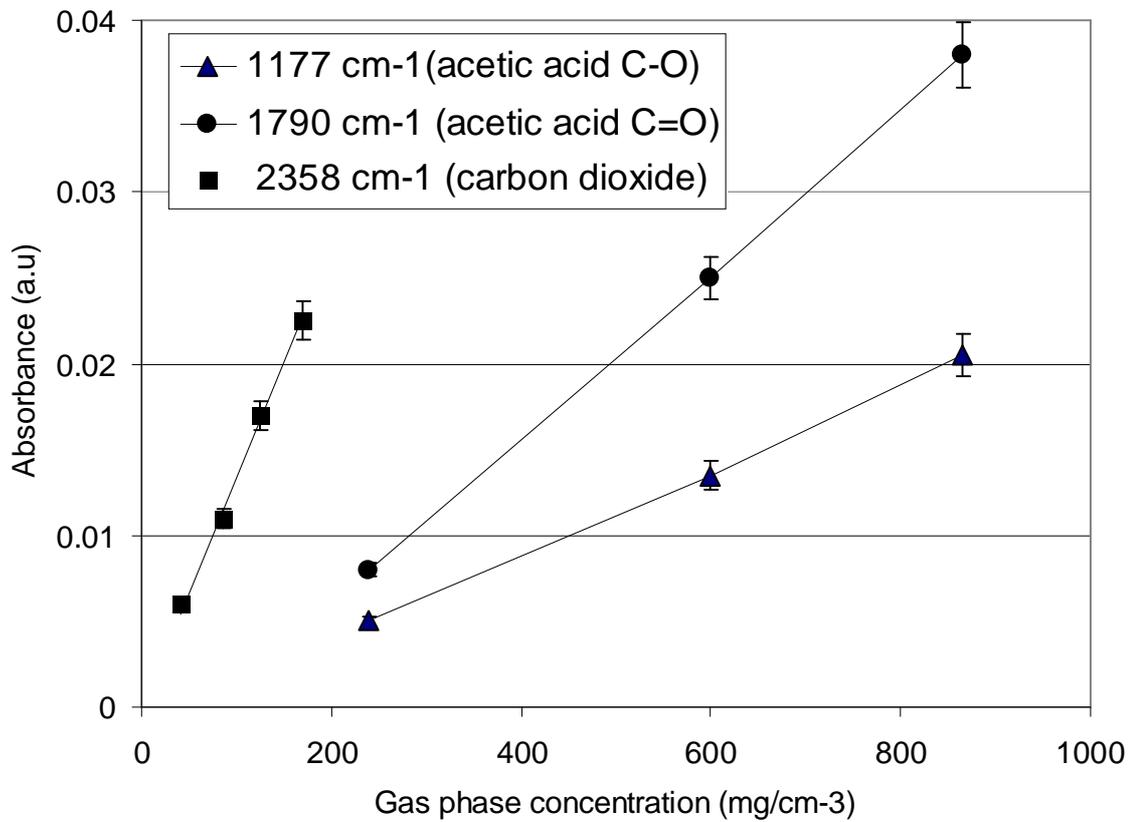


Figure 2: Calibration plots for acetic acid and carbon dioxide.

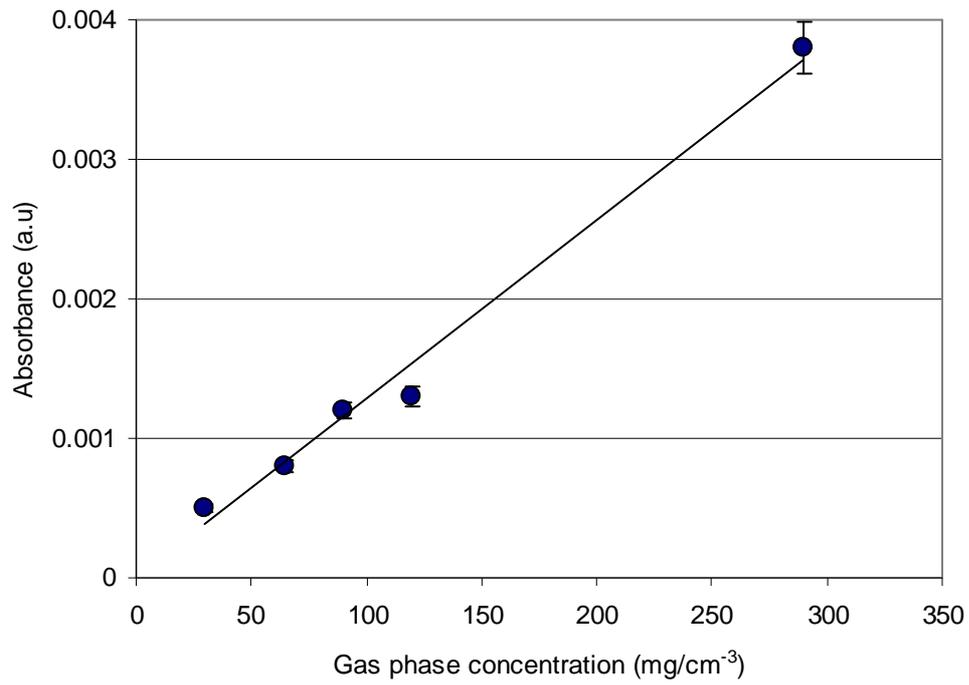


Figure 3: Calibration plot for water using the absorbance peak at 3853 cm<sup>-3</sup> generated using gas standards.

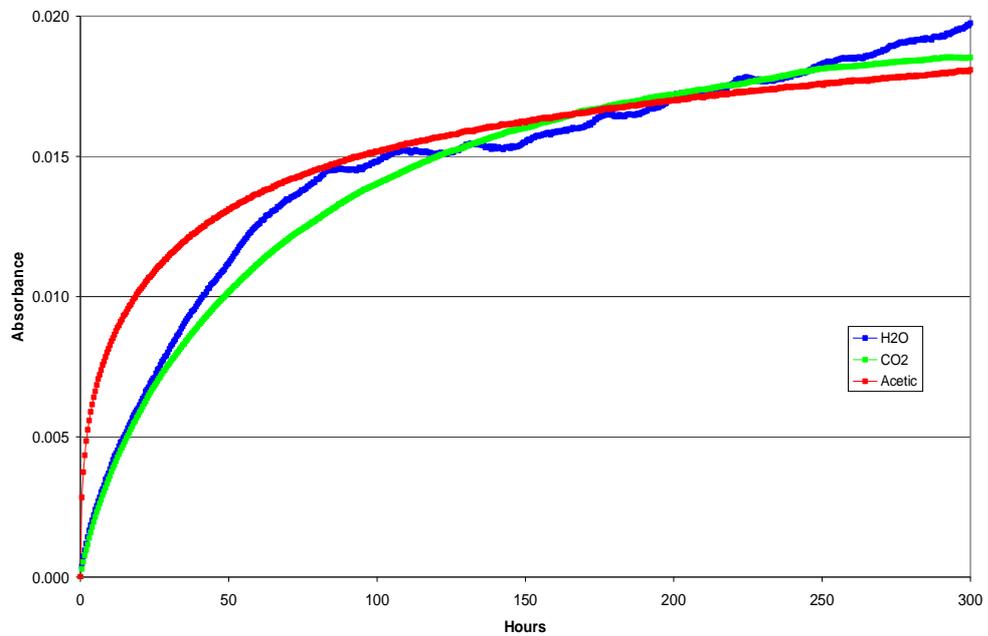


Figure 4: Volatile evolution (first run) from highly filled Vinamul 3261 specimen. Red, acetic acid; Green, carbon dioxide; Blue, water

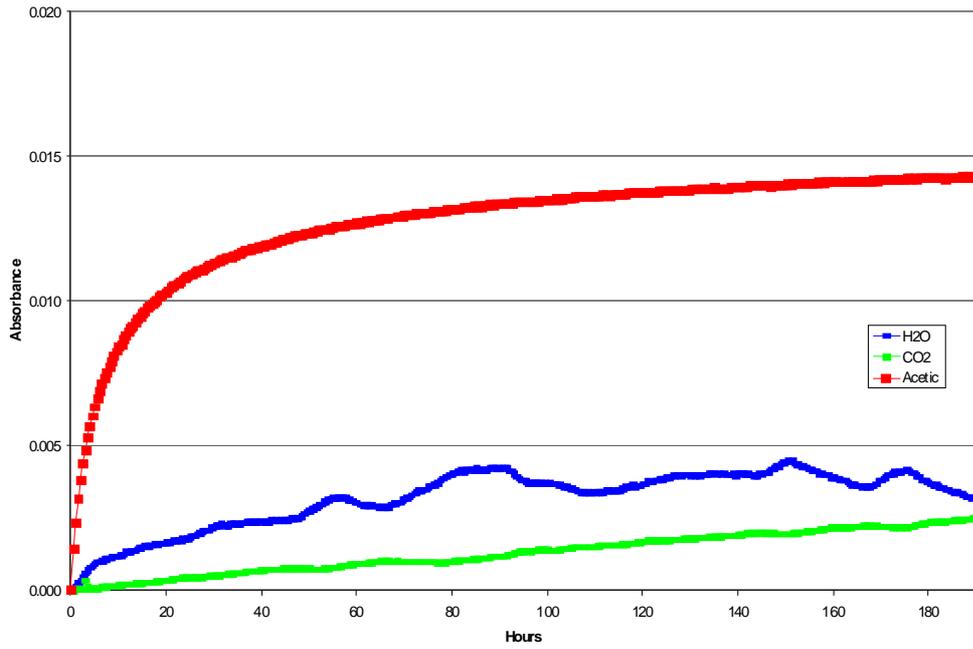


Figure 5: Volatile evolution (second run) profiles from highly filled Vinamul 3261. Red, acetic acid; Green, carbon dioxide; Blue, water

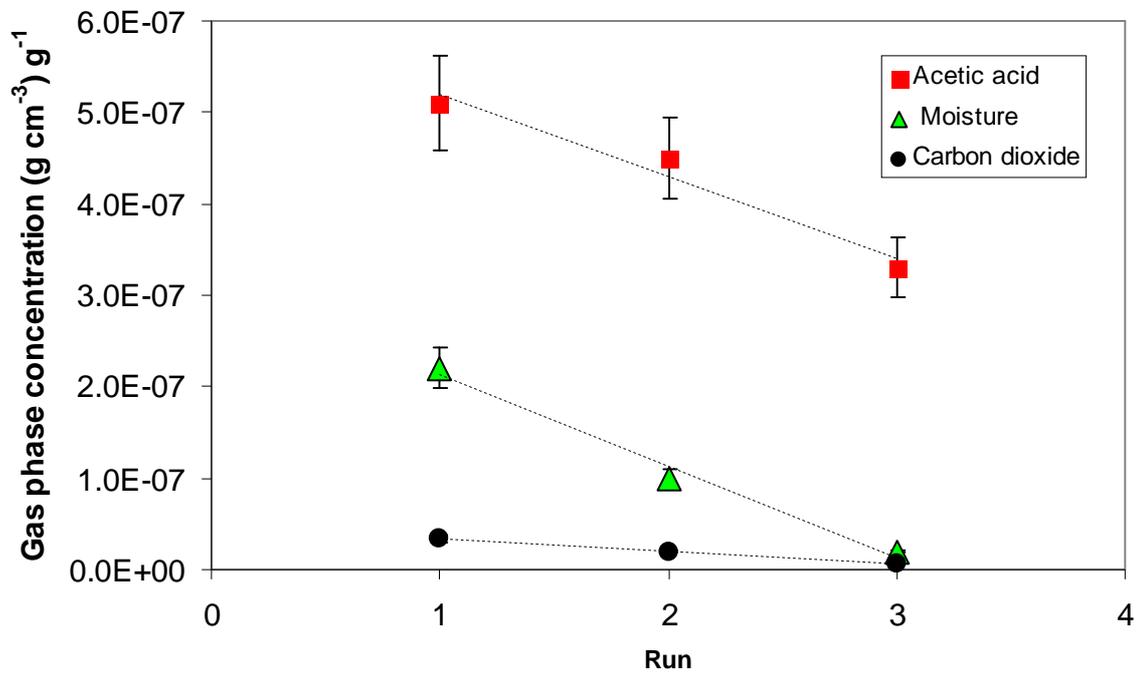


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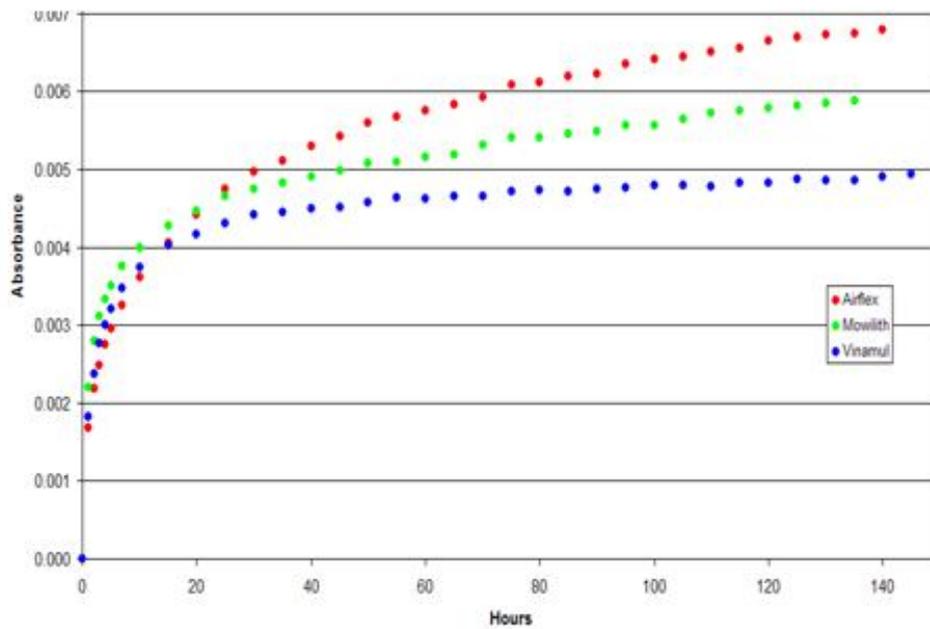


Figure 7: Acetic acid evolution as a function of time and resin type. Specimens tested are Vinamul 3161 (blue), Airflux EP17 (red) and Mowilith DM132 (green)

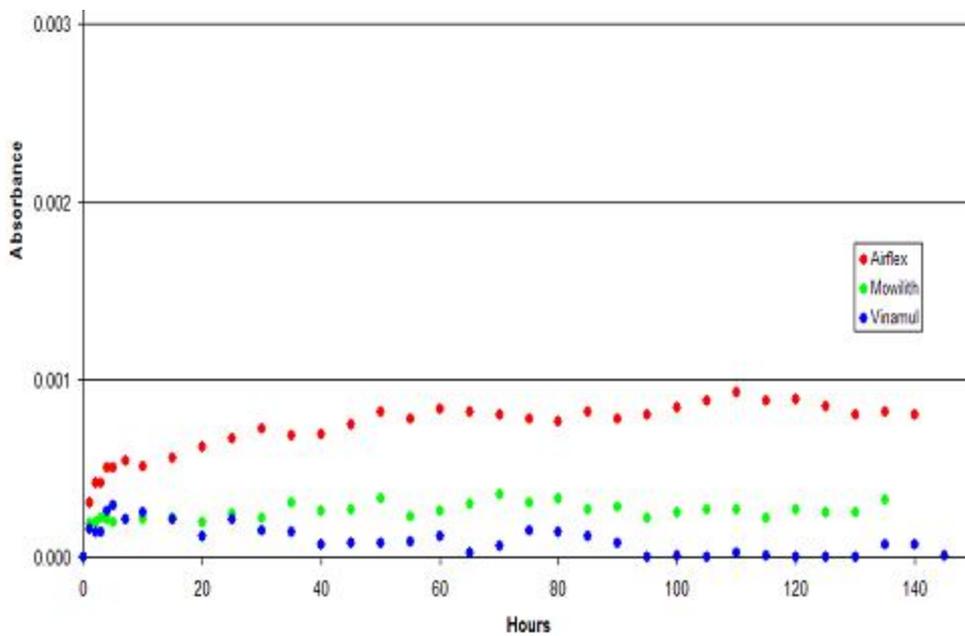


Figure 8: Moisture release as a function of time and resin type. Specimens tested are Vinamul 3161 (blue), Airflux EP17 (red) and Mowilith DM132 (green).

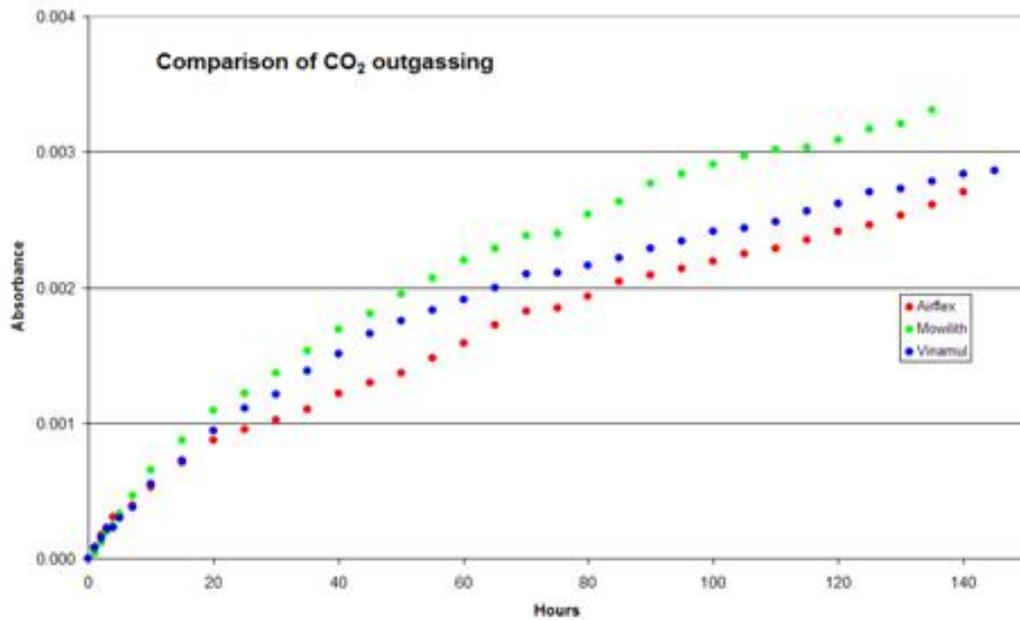


Figure 9: Carbon dioxide release as a function of time and resin type. Specimens tested are Vinamul 3161 (blue), Airflux EP17 (red) and Mowilith DM132 (green)

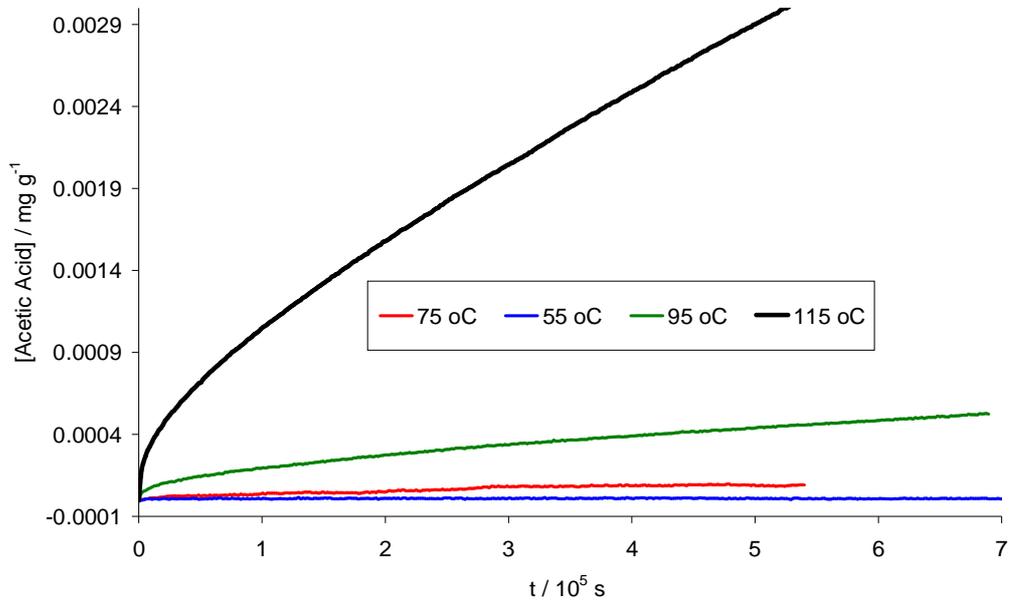


Figure 10: Acetic acid concentration as a function of time at a number of different temperatures. The specimens tested is Vinamul 3161.

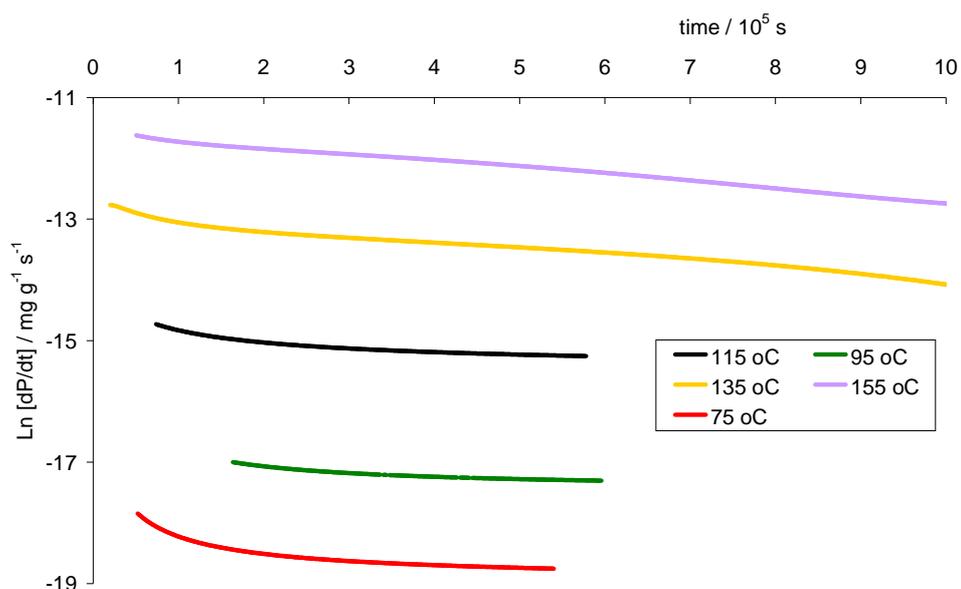


Figure 11: First order rate equation plot of natural log acetic acid out gassing (P) as a function of time. For each temperature, the slope of the linear regression fit provides the first order rate constant ( $k / \text{s}^{-1}$ ).

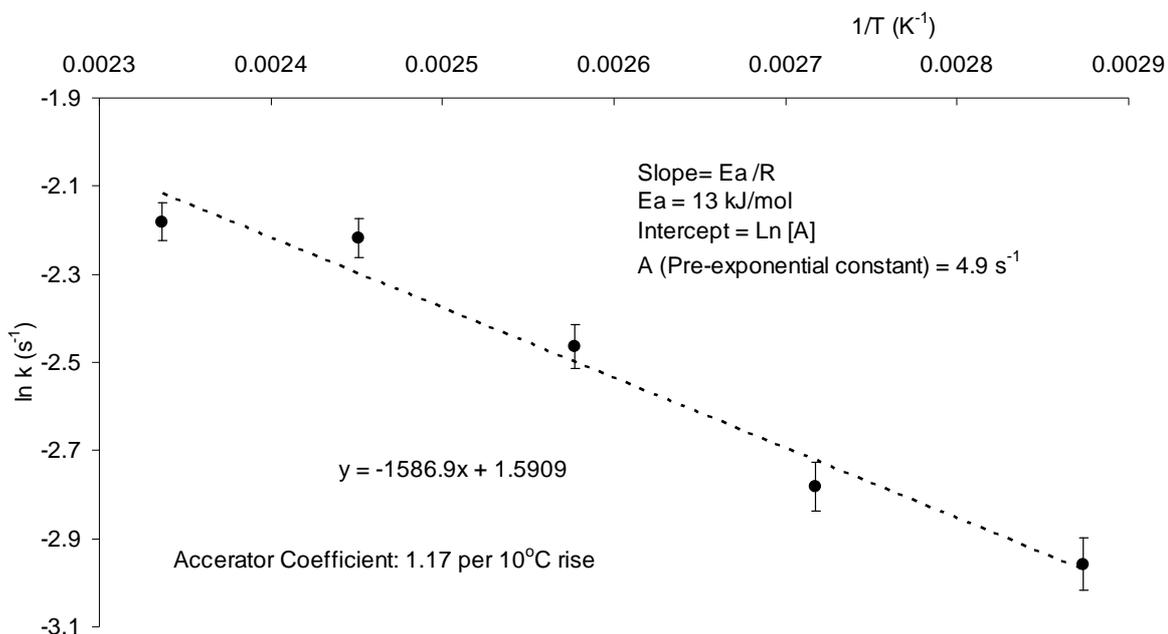


Figure 12: Arrhenius plot of first order rate constant versus reciprocal temperature for acetic acid out gassing. Low activation energy suggests a diffusion controlled physical process.

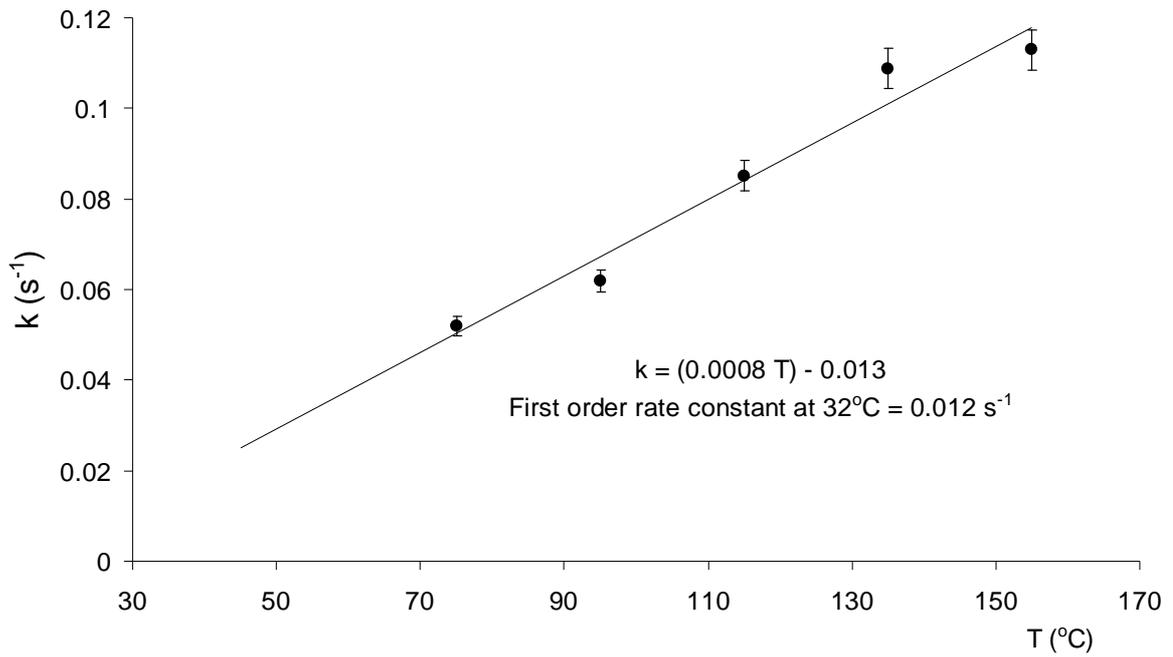


Figure 13: First order rate constant as a function of temperature. Line is extrapolated to lower temperatures to predict rate constant representative of long term service temperatures.

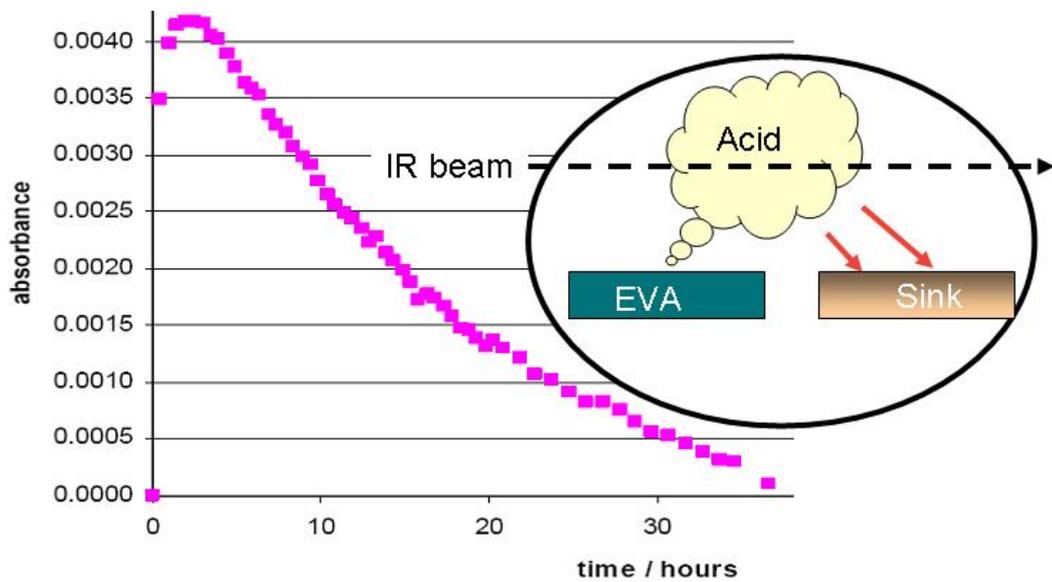


Figure 14: Multi-material trial showing acetic acid out gassing from filled EVA. The maximum quantity of acetic acid evolved equates to approximately  $5.3 \times 10^{-8} \text{ g cm}^{-3} \text{ g}^{-1}$ . The specimen tested is Vinamul 3261.

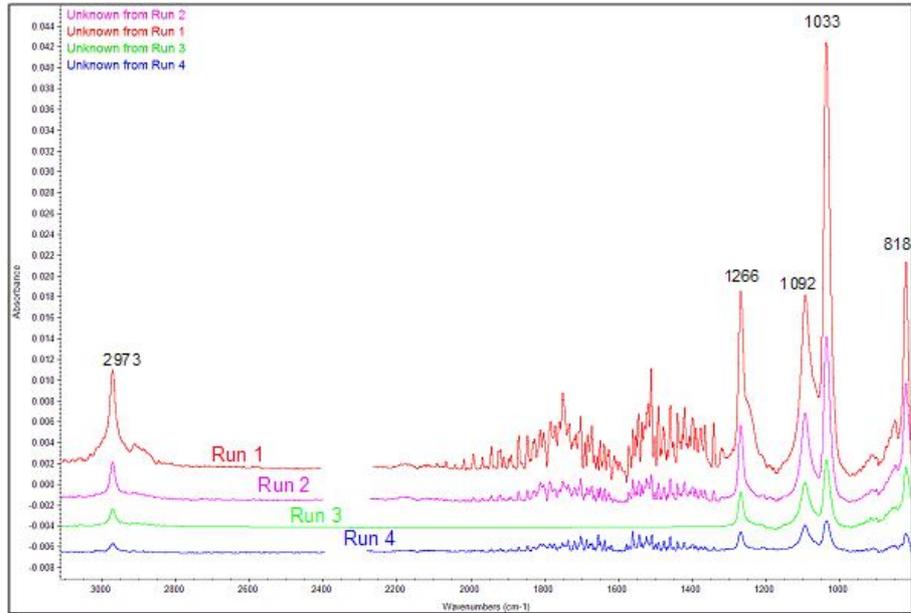


Figure 15: FTIR gas phase studies show evidence of a silicone based impurity in the headspace. Repeat testing of the sample reduces the concentration of the impurity within the gas phase.

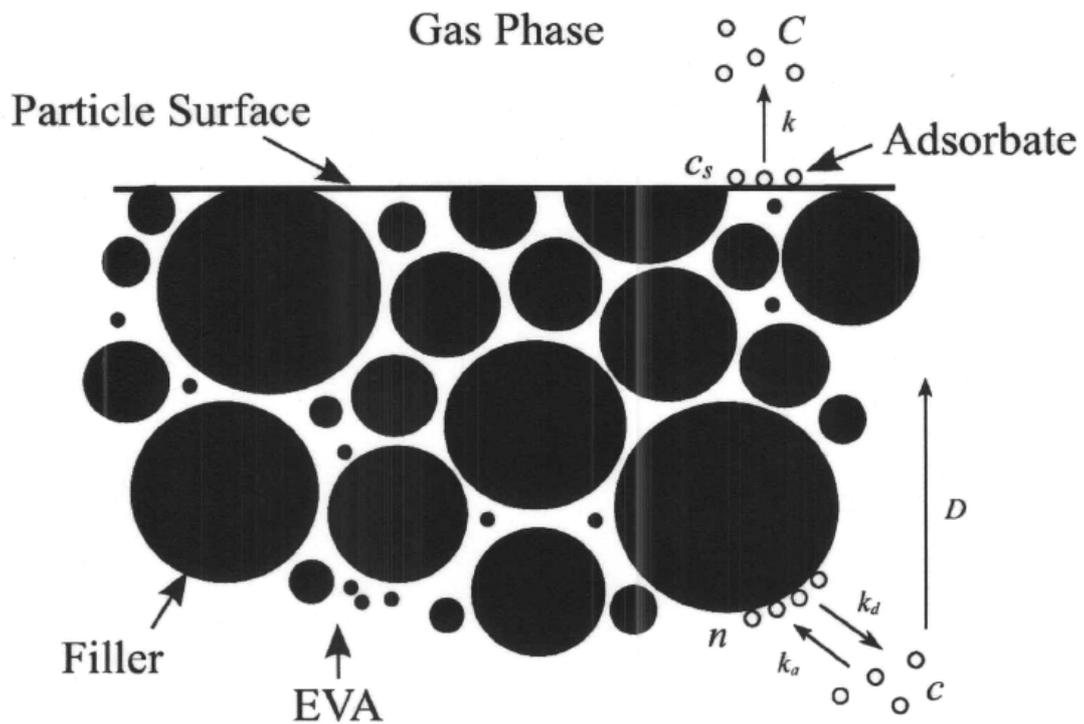


Figure 16: Schematic of the Edskuty and Amundson out gassing model [9] for highly filled poly (ethylene-co-vinylacetate).  $C$  represents the concentration of species out gassed which is dependent on the surface concentration ( $C_s$ );  $D$  the diffusion constant; and  $K_a$  the filler-species absorption and desorption ( $K_d$ ) rate constants.

	Acetic Acid			Carbon Dioxide		Moisture	
	Gas phase concentration/ (g cm <sup>-3</sup> ) g <sup>-1</sup>	% of total headspace	Release rate/ (g cm <sup>-3</sup> ) g <sup>-1</sup> s <sup>-1</sup>	Gas phase concentration (g cm <sup>-3</sup> ) g <sup>-1</sup>	% of total headspace	Gas phase concentration (g cm <sup>-3</sup> ) g <sup>-1</sup>	% of total headspace
Vinamul 3161	6.10E-08	91	1.70E-14	5.60E-09	8	2.00E-10	1
Mowilith (DM132)	1.20E-07	93	4.70E-14	6.50E-09	5	2.00E-09	2
Airflux (EP17)	1.40E-07	85	5.50E-14	5.50E-09	3	2.00E-08	12

Table 1: Volatile out gassing parameters as a function of resin type.

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