

Thermal Analysis of Primers and Coatings as a Prediction Model

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Abstract

Thermal characteristics of primers and coatings can be a useful prediction model on how the material will perform under heat exposure from manufacturing processes and product applications. Two chemistries, poly(vinyl alcohol) and polyethylenimine, have been analyzed using the techniques of Thermogravimetric Analysis (TGA), TGA coupled to a Mass Spectrometer (TG/MS), TGA coupled to a Fourier Transform Infrared Spectrometer (TG/IR), Modulated Differential Scanning Calorimetry (MDSC), Dynamic Mechanical Thermal Analysis (DMTA).

Introduction

When designing and developing new packaging structures predicting performance is theoretical. Most will make the structure and then test containment and product integrity. If a simple analytical technique could be used to screen these design ideas, it would save time and money that are usually limited resources. Using an appropriate analytical experiment can predict performance of the structure in the packaging application and the manufacturing process.

In this paper, two primers with different chemistries were analyzed using a variety of thermal analysis techniques. One set of experiments was designed to predict performance of the primer in the packaging application; the other set of experiments was designed to predict the feasibility of the primer performance in the manufacturing process.

The first set of experiments tested a modified polyethylenimine (PEI) primer for evolved gases during the heat sealing step in the packaging fabrication. It is vital to the packaging application that only species non-reactive to the contained product be evolved during the sealing of the product into the package.

The second set of experiments tested a poly(vinyl alcohol) (PVOH) based primer for thermal stability properties to determine if the primer could be sent through a tenter frame as a surface barrier coating on film. If the material decomposes or doesn't have the proper visco-elastic properties the coating will not stretch uniformly and not have the desired properties for the targeted application.

Experimental

Modified PEI primer

The sample was prepared by drying to a thin film on a glass slide in an oven until dry. The temperature was ~140°F. This is a typical exit web temperature for a coating station used on extrusion lines. This thin film was used for all of the experiments discussed.

The first two thermal analysis techniques used were Thermogravimetric Analysis (TGA) and Modified Differential Scanning Calorimetry (MDSC). The techniques examine the thermal stability and weight loss of the material as it is heated. TGA precisely measures the weight change of a material as it is heated at a controlled rate.

Explanation of modulated DSC

Differential Scanning Calorimetry (DSC) is used to determine a physical property of a material, such as the glass-transition temperature (T_g), or the melt temperature (T_m). A sample and a reference material, usually an empty sample pan, are heated at a controlled rate. When a transition occurs in the sample, such as melt point, an input of energy/heat is required keep the sample and reference at the same temperature. This difference is recorded on the DSC scan as a function of temperature.

Modulated DSC provides the same physical and chemical information as conventional DSC. It also provides data that is unavailable with conventional DSC. The effects of slope and curvature on the baseline are reduced, thereby, increasing the sensitivity of the analysis; and overlapping events are separated, such as molecular relaxation and glass transitions.

Both modulated DSC and conventional DSC measure the difference in heat flow between a sample and an inert reference. The sample and reference cells are identical. Modulated DSC uses a different heating profile. Conventional DSC measures heat flow as a function of a constant rate of change in temperature, and modulated DSC superimposes a sinusoidal temperature modulation on this rate change in temperature. The sinusoidal change in temperature permits the simultaneous measurement of heat-capacity and kinetic effects.

Typical experimental parameters for modulated DSC experiments are a heating rate from isothermal to $5^\circ\text{C}/\text{min}$, with a modulation amplitude from 0.01 to 10°C . This modulation period can vary from 10 to 100 seconds and be expressed as a frequency (10 - 100 MHz).

Two purge gases were used in the MDSC and TGA experiments: air (oxidative environment) and nitrogen (inert environment). This will identify any decomposition products by oxidation or by internal thermal degradation.

Figure 1 is a TGA curve of the modified PEI primer sample purged with an inert gas (nitrogen). Figure 2 is a TGA curve of the modified PEI primer sample purged in an oxidative environment (air). Both experiments were run from room temperature to 260°C (500°F), with a temperature ramp rate of $10^\circ\text{C}/\text{min}$ and a purge gas flow at $50\text{ ml}/\text{min}$.

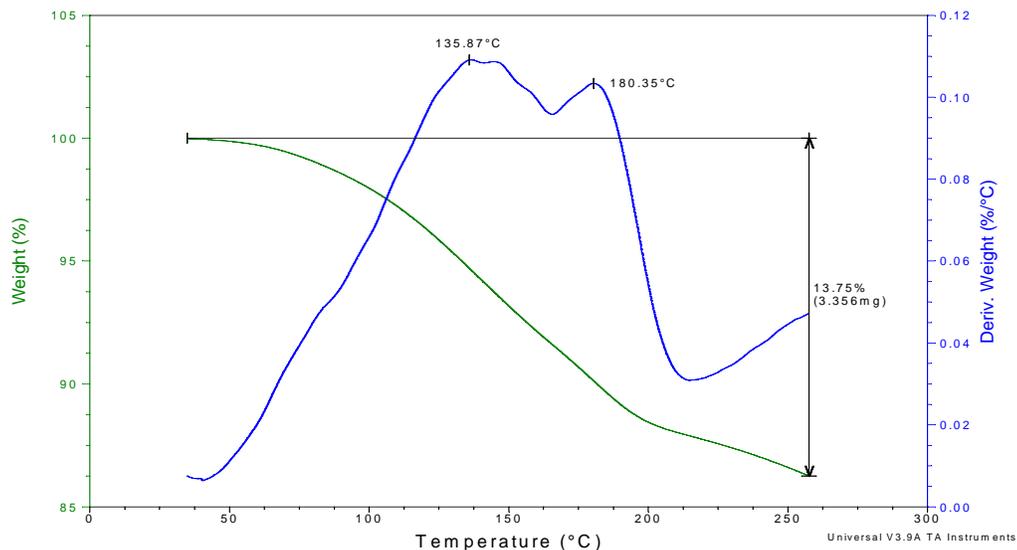


Figure 1: TGA Curve of a Modified PEI primer, purged with nitrogen.

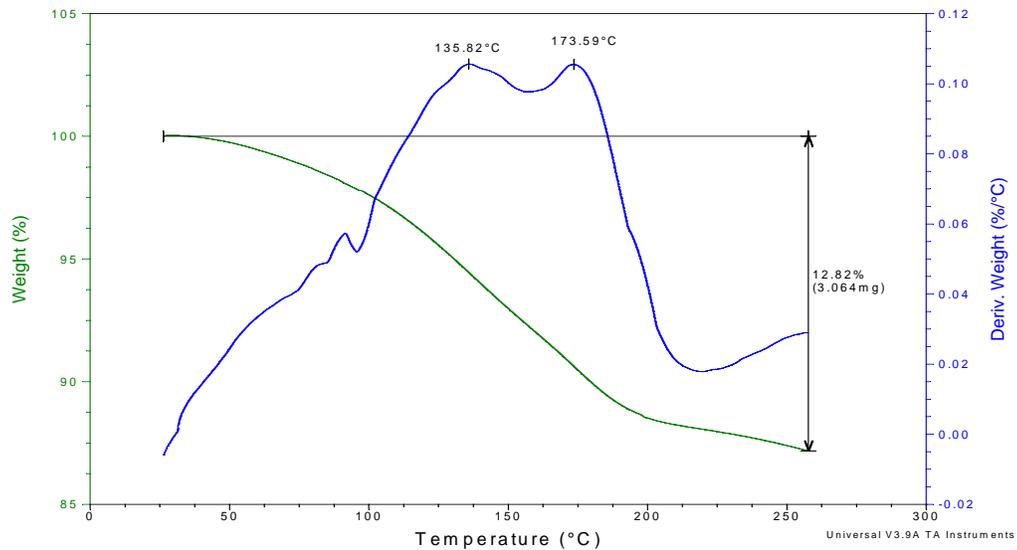


Figure 2: TGA Curve of a Modified PEI primer, purged with air.

Figure 1 shows a total weight loss of 13.75%. The derivative curve, found in figure 1, shows there are two overlapping weight losses. By calculating the first order derivative in the weight change as a function of temperature, the calculated derivative reveals two weight losses that may be from two separate evolved species. Figure 2 also shows the same weight loss profile, with a total of 12.82%. The oxidative environment has less weight loss than the inert atmosphere; this difference is the oxidation of the non-volatile portion of the primer.

The MDSC was designed to measure two physical properties of the sample, any glass transitions, and chemical reactions. The heating profile was run from -100°C to 100°C. The purge gas was inert (nitrogen). Figures 3, 4, 5 are the initial heating, cooling step, and second heating of the MDSC experiment.

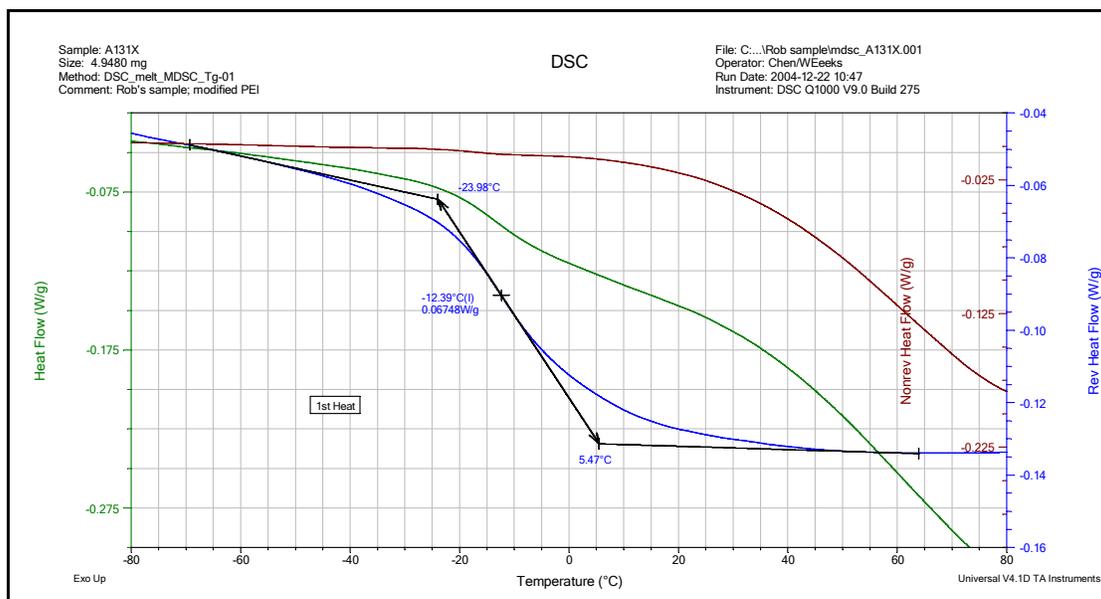


Figure 3: MDSC Scan of the first heating of modified PEI primer.

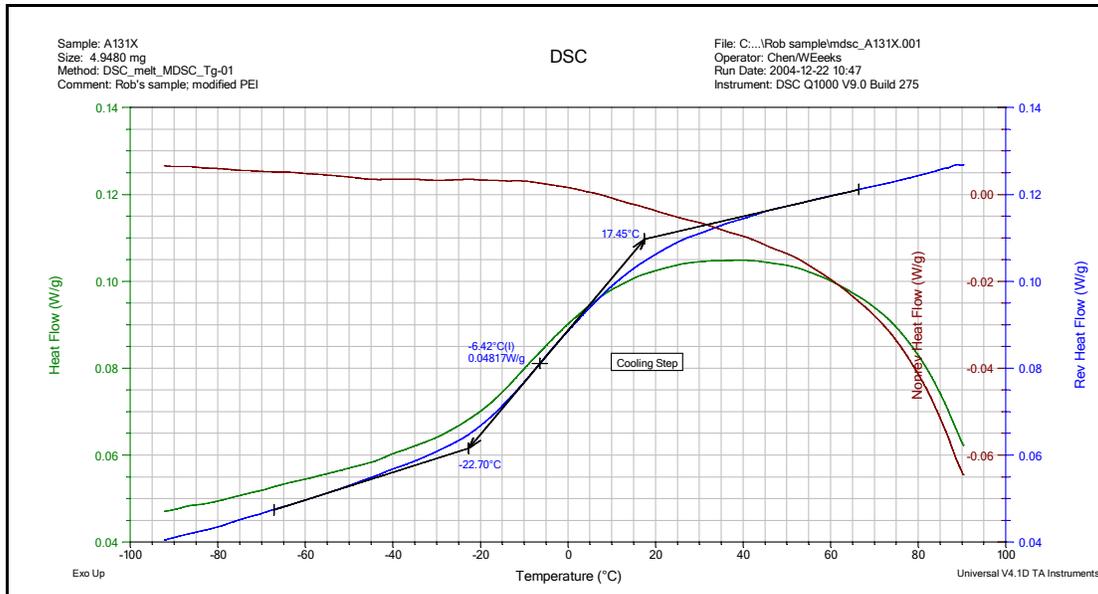


Figure 4: MDSC Scan of the cooling of modified PEI primer.

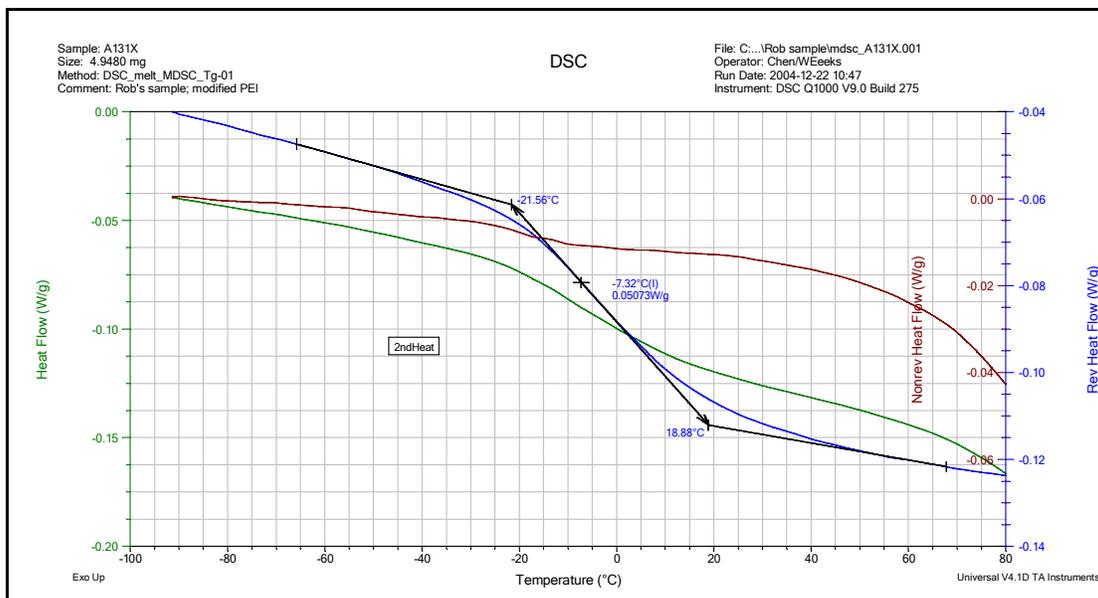


Figure 5: MDSC Scan of the second heating of modified PEI primer.

The series of experiments show a reversible T_g just below 0°C . The T_g is shifted and reduced after the initial heating and cooling step. The data indicates the sample does not decompose up to 100°C . The TGA curve shows a double weight loss (figures 1, 2), and the MSDC data (figures 3, 4, 5) shows this weight loss is not a decomposition of the sample, but rather an evolved gas from the primer formulation. To identify these two weight losses, two other thermal analysis techniques will be useful; Thermogravimetric Analysis coupled with Fourier Transform Infrared (TG-IR) and Thermogravimetric Analysis coupled with Mass Spectrometry (TG-MS).

Explanation of TG/IR

This technique couples a TGA with a Fourier Transform Infrared Spectrometer (FTIR). The evolved gas species from the TGA are purged into a gas cell in the FTIR. This gas is then analyzed in the FTIR spectrometer.

The infrared spectroscopy examines the vibrational and rotational frequencies of diatomic molecules. The molecule is exposed to electromagnetic energy and the bonds holding the atoms together. When the applied frequency matches the natural frequency of the atomic bond vibration, a resonance occurs. This resonance is a characteristic frequency for that atomic bond.

These characteristic frequencies for a particular molecule are determined by its vibrations, dependent upon the masses of the atoms of the molecule, their spatial geometry, and the strengths of the connecting bonds; therefore they are reproducible and considered a fingerprint for that molecule.

The FT portion of the technique is a mathematical analysis of the raw data (Fourier Transformation). This results in the spectrum showing characteristic frequencies in the mid-infrared range between 4000 cm^{-1} and 400 cm^{-1} .

Explanation of TG/MS

This technique couples a TGA with a Mass Spectrometer (MS). The evolved gas species from the TGA are purged into the MS. The sample is bombarded with an electron beam having sufficient energy to fragment the molecule. The positive fragments produced (cations and radical cations) are accelerated in a vacuum by a magnetic field and then are sorted based on their mass-to-charge ratio (m/z). The bulk of the ions produced in a mass spectrometer have a unit positive charge, therefore the value m/z is equivalent to the molecular weight of the fragment. The analysis of mass spectroscopy data involves the re-assembling of these fragments, by working backwards to generate the original molecule.

The instrument sends a very low concentration of sample molecules into the ionization chamber that is under a very high vacuum. The molecules are bombarded by a high-energy electron beam. The molecules fragment and the positive ions are accelerated and sent into an analyzing tube. The path of the charged molecules is bent by an applied magnetic field. Ions having the proper mass-to-charge ratio will exit through the slit and collide with the Collector. Continuously changing the magnetic field will scan a full spectrum of chemical masses (m/z).

The TG/MS samples were analyzed on a TA 2960 SDT interfaced to a Fisons VG Thermolab Mass Spectrometer by means of a heated capillary transfer line. The samples were heated from room temperature to 260°C , at a rate of $10^\circ\text{C}/\text{min}$, under a flowing atmosphere of air or nitrogen, at a flow rate of $50\text{ ml}/\text{min}$.

The capillary transfer line was heated to 120°C , and the inlet port on the mass spectrometer was heated to 150°C . The Fison unit is based on a quadrupole design with a mass range of 1-100 amu. The sample gas from the interface was ionized at 70 eV . The system was operated at a pressure of 1×10^{-6} torr.

The mass spectrum for the sample analyzed in an air atmosphere is shown in figure 6 and the sample analyzed in an inert (nitrogen) atmosphere is shown in figure 7.

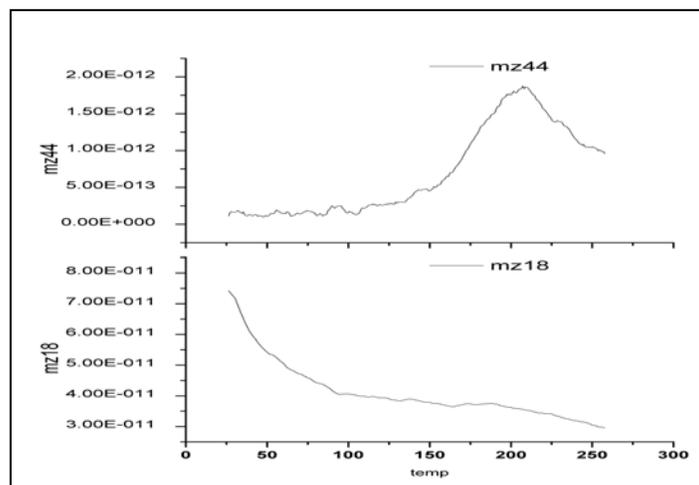


Figure 6: Mass Spectra of Modified PEI primer, in air.

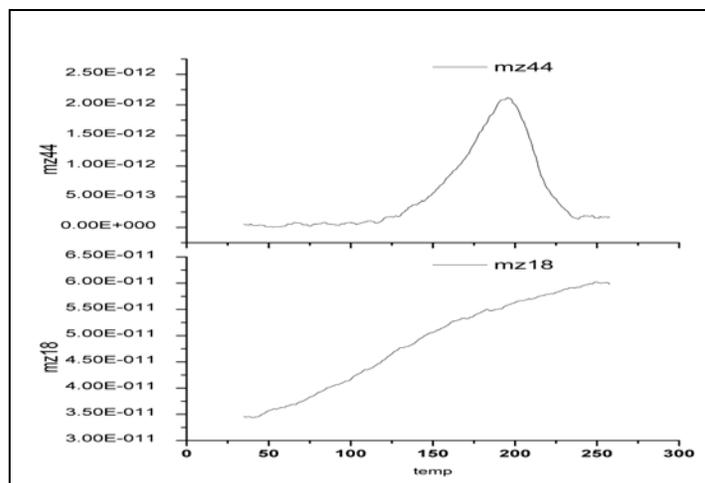


Figure 7: Mass Spectra of Modified PEI primer, in nitrogen.

Both Mass Spectra (figures 6, 7) have m/z values at 18 and 44. An educated guess for these two molecular weights would be water (18 amu) and carbon dioxide (44 amu), but with TG/IR the molecular species can be definitively identified.

The TG/IR samples were analyzed on a TA 951 Thermogravimetric Analyzer interfaced to a Perkin Elmer 2000 Fourier Transform Infrared Spectrometer. The transfer of evolved gases used a capillary transfer line that was heated to 120°C, and the inlet port on the spectrometer was heated to 150°C. The samples were heated from room temperature to 260°C, at a rate of 10°C/min, under a flowing atmosphere of air or nitrogen, at a flow rate of 50 ml/min.

The FTIR 2D spectrum for the sample in an air atmosphere is shown in figure 8. This is a snapshot of all the evolved gases from the TGA. Figure 9 is the 2-D spectrum for the sample in nitrogen, apart from the relative intensities, both spectra show the same absorbance bands, indicating the same species are being evolved in both atmospheres.

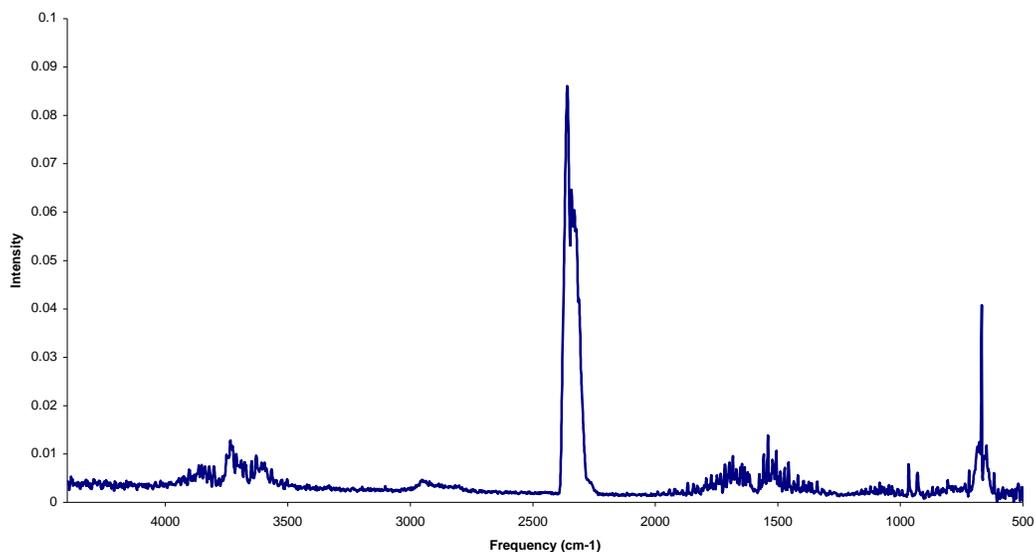


Figure 8: 2-D Spectrum of Modified PEI primer, purged in air.

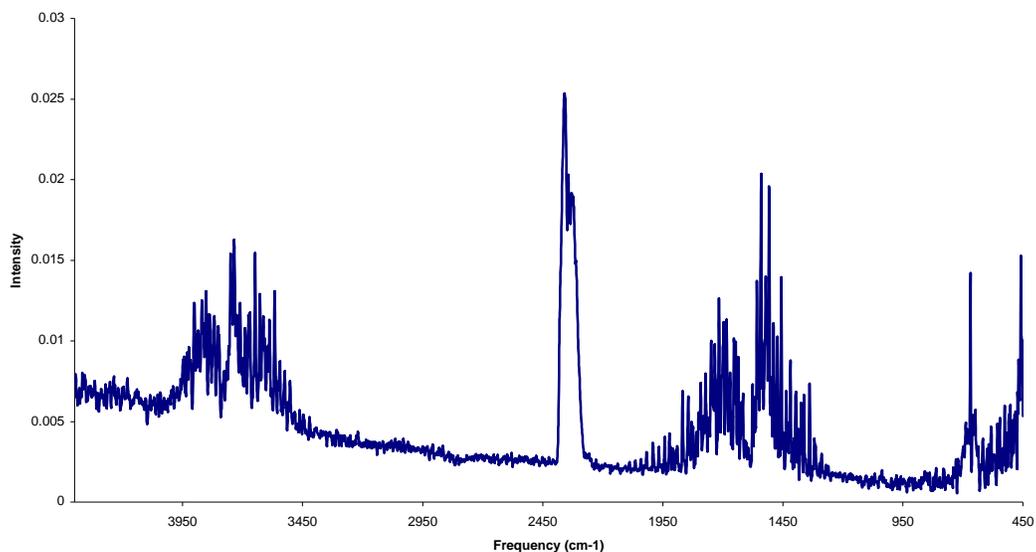


Figure 9: 2-D Spectrum of Modified PEI primer, purged in nitrogen.

To get a better perspective and better separation of the two species a 3-D spectrum will enhance analysis. The 3-D spectrum of the Modified PEI primer, purged in air (figure 10) clearly shows the two gases evolved. The 3-D spectrum shows the infrared absorbance spectrum in a dynamic format as the sample is heated in the TGA and the gases are evolved.

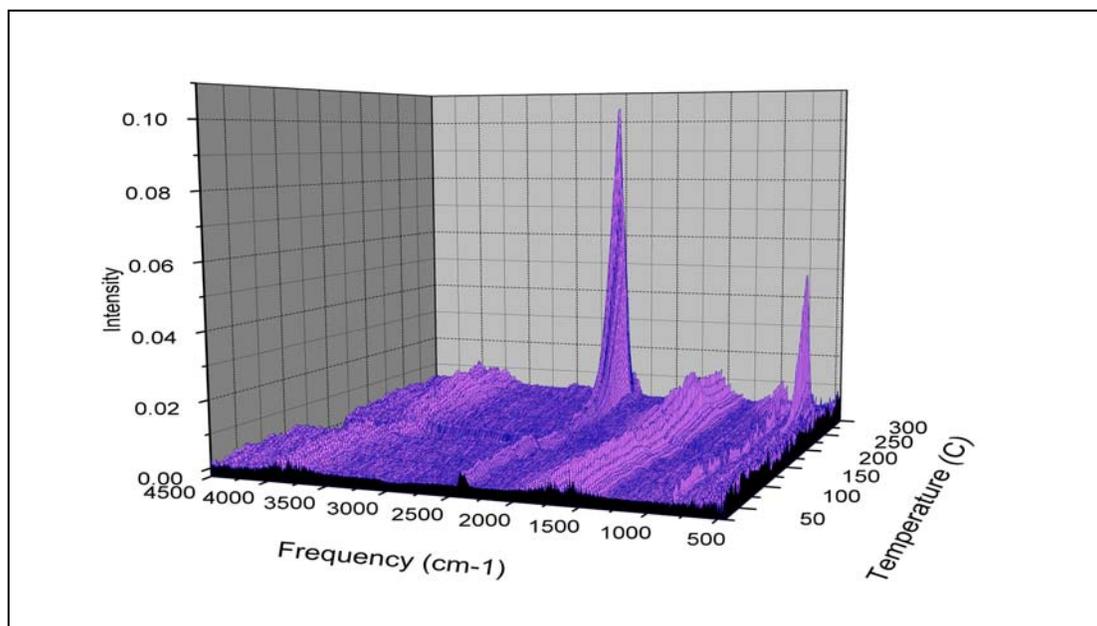


Figure 10: 3-D FTIR Spectrum of Modified PEI primer purged in air.

The 3-D spectrum of the sample purge in an inert atmosphere (figure 11) shows that both environments have no affect on the stability of the primer and the same gases are evolved during the TGA temperature profile. The nitrogen purged experiment has a more defined and cleaner transition than the air purged experiment.

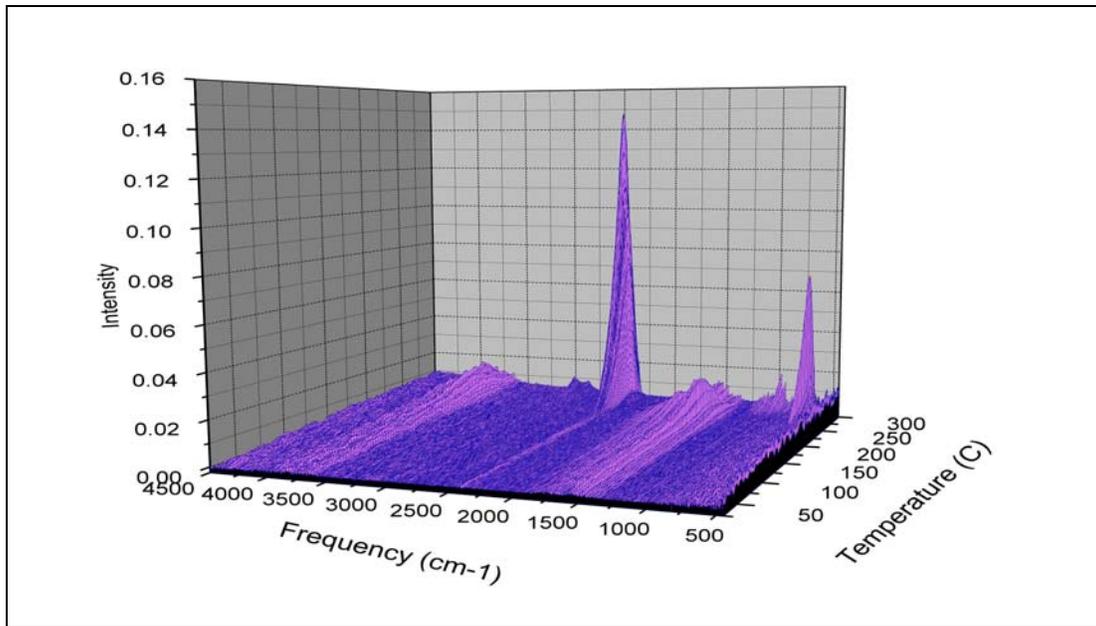


Figure 11: 3-D FTIR Spectrum of Modified PEI primer purged in nitrogen.

PVOH based coating

The sample was prepared by drying to a thin film on glass slide in an oven until dry. The temperature was ~140°F. This is a typical exit web temperature for a coating station used on extrusion lines. This thin film was used for all of the experiments discussed.

TGA and MDSC were used to screen the sample thermal stability. All experiments were done in an inert atmosphere (nitrogen). The data generated will determine if the thermo-mechanical experiments will yield any useful information. The TGA experiment was run from room temperature until the sample had fully decomposed (750°C). The TGA curve (figure 12) has at least three weight losses.

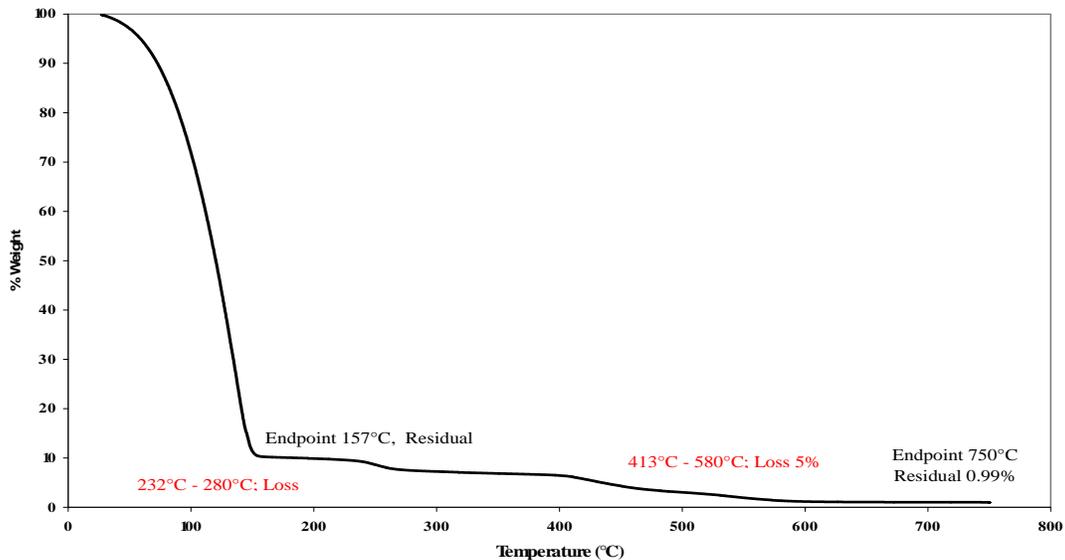


Figure 12: TGA curve of PVOH based coating.

The MDSC experiment was run from room temperature to the maximum temperature for the tenter frame oven (200°C), in an inert atmosphere (nitrogen). The MDSC scan (figure 13) shows a reversible transition at 120°C.

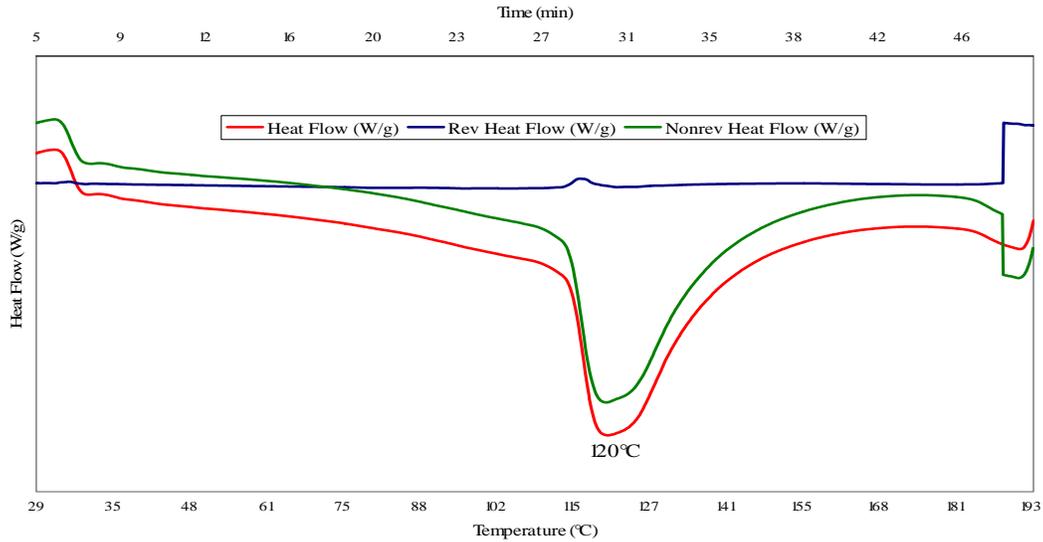


Figure 13: MDSC scan of PVOH based coating.

Based on these analyses it appears that rheological testing is feasible. Rheological testing of thermoplastics was done on both solid samples and melts. Rheological testing on the melts gives valuable information on the material's flow properties that translates into processing characteristics such as, melt or extensibility. Rheological properties can be measured continuously as the sample is heated through a programmed temperature ramp. In a dynamic heating and testing cycle the DMTA test simultaneously measures two key components of viscoelastic melt behavior: the storage (elastic) modulus (G'), and the loss (viscous) modulus (G'').

The proper visco-elastic melt behavior is critical for this coating to work properly as it is sent through a tenter frame. The tenter frame will stretch the coating with the substrate film in the machine and transverse directions as it passes through each oven zone. The oven zone temperature is increased until the film and coating are stretched to the desired size, which can be many times the original size.

Two types of rheological testing equipment were used to determine the melt behavior; a Rheometrics Solids Analyzer, Model RSA-II, and a TA Instruments AR1000 Strain Rheometer with parallel plates. In figure 14 is the Solids Analyzer plot and figure 15 is the strain rheometer plot.

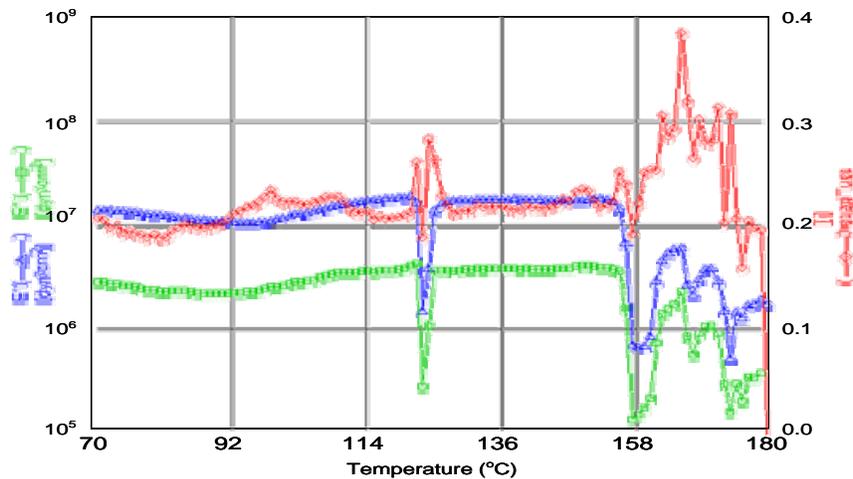


Figure 14: Solids Analyzer DMTA plot of PVOH coating.

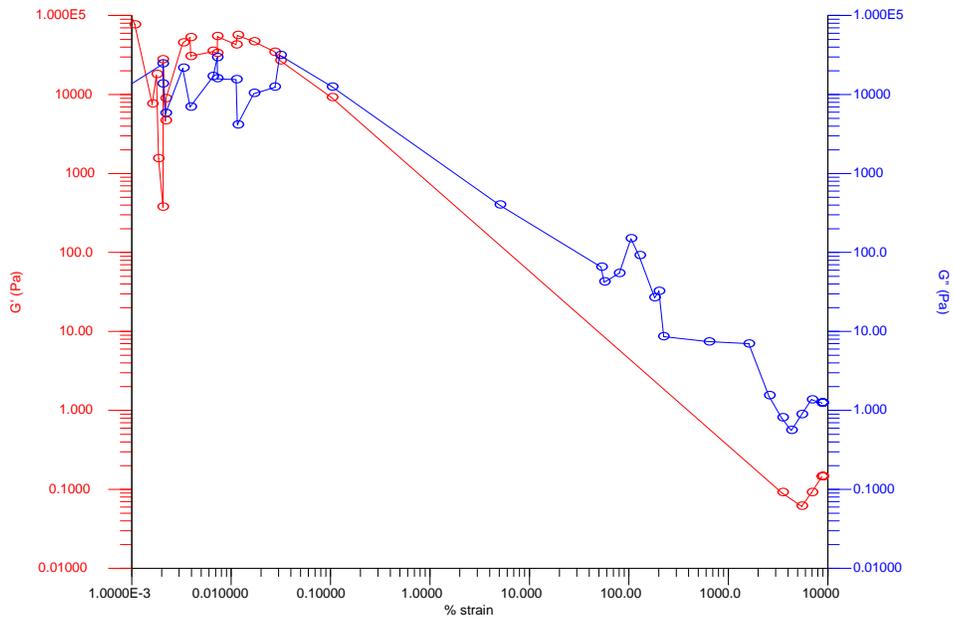


Figure 15: Isothermal Strain sweep of PVOH coating.

All rheological tests were done in air, because the target application will also be done in air. The DMA had a programmed heat ramp of 5°C /min, from 70°C to 180°C, run in compression mode. The parallel plate experiment was run on a TA AR1000 strain rheometer. Aluminum parallel plates 40 mm in diameter were used to make the measurements. The strain sweep conducted isothermally at 30°C, the strain was measured over a wide range at 10 data points per decade.

To determine the linear viscoelastic region (LVR) of the polymer a temperature ramp program used a strain of 0.05% and heated the film from 30°C to 220°C at a heating rate of 5°C/min. Figure 16 shows the temperature ramp data for the LVR.

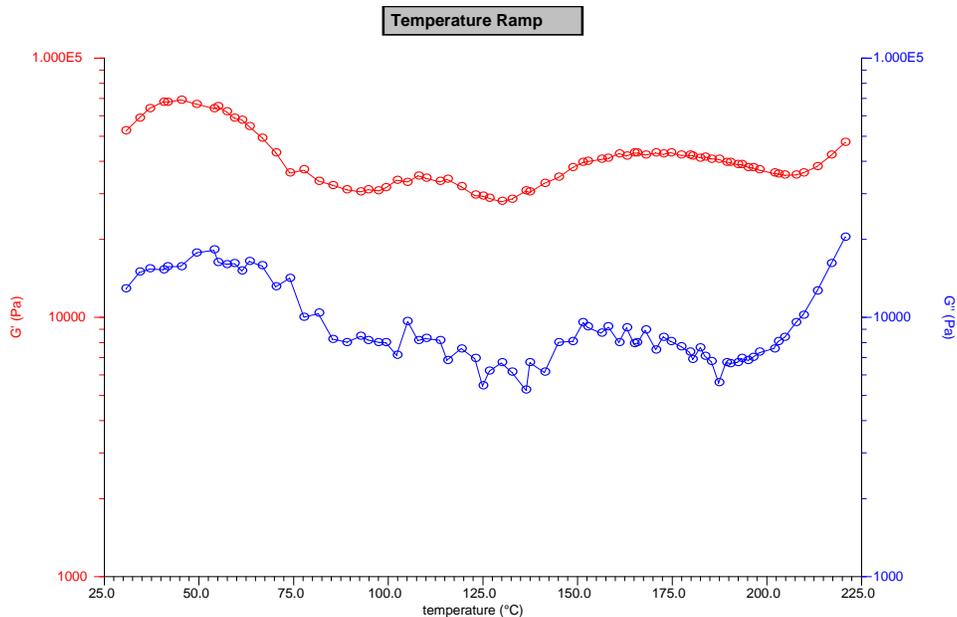


Figure 16: Dynamic temperature profile for the linear viscoelastic region of PVOH coating.

Results & Discussion

PEI Modified primer

The TGA results are found in Table 1; there are two species evolved during the programmed temperature ramp. The weight loss difference between the oxidative and the inert atmosphere is 1%; this difference is most likely due to the incorporation of oxygen into the polymer chain at the amine sites. The onset of the first loss is 136°C and the onset of the second loss is 180°C for the inert atmosphere and 174°C for the oxidative atmosphere, this difference may be the change in slope on the weight loss curve and not a change in the onset. The MDSC data (figures 3, 4, 5) show only a glass transition temperature just below 0°C, the primer appears stable throughout the rest of the programmed temperature range.

Table 1: TGA weight losses for air and nitrogen purged experiments.

<u>Purge gas</u>	<u>Weight Loss (%)</u>	<u>1st loss (°C)</u>	<u>2nd loss (°C)</u>
Air	12.82	136	174
Nitrogen	13.75	136	180

The TG/MS and TG/IR data identify these two materials being evolved. The TG/MS experiments purged in air and nitrogen yielded the same results. In figures 6 and 7, the mass-to-charge ratios (m/z) for the effluents are 18 and 44. These correspond to the atomic mass for the molecules. The TG/IR experiments identify these two materials. The TG/IR data for the two purges gases yielded the same results.

The 3-D spectrum of the air purged experiment (figure 11) shows infrared absorbance bands at; 3700cm⁻¹, 2300 cm⁻¹, 1500 cm⁻¹, 700 cm⁻¹. These absorbance bands and the m/z values identify the two effluents as water and carbon dioxide. In Table 2 is a summary of this data.

Table 2: Summary of the m/z values and absorbance bands for the TG/MS and TG/IR analyses.

Mass Spectroscopy spectra indicate two species evolved; m/z = 18 (water) m/z = 44 (carbon dioxide).
FTIR spectra have absorbance bands identifying the two species as; 3700cm ⁻¹ , 1500 cm ⁻¹ (water) 2300 cm ⁻¹ , 700 cm ⁻¹ (carbon dioxide)

PVOH based coating

The TGA data (figure 12) shows three weight losses, the first occurs from room temperature to 157°C. This appears to be water from the coating, the second weight loss occurs from 232°C to 280°C, this could be bound water on the PVOH, the third loss occurs from 413°C to 580°C, without running TG/MS and TG/IR identification of these materials is unknown.

Since the purpose of this set of experiments is to determine the visco-elastic properties of the coating for the tenter frame application, a MDSC scan can determine if these weight losses are from the material decomposing. The MDSC scan (figure 13) shows a transition at 120°C, the transition is absorbing energy (adding heat to the system). The transition occurs during the water evaporation of the coating; typically an endothermic reaction is a melt point. This transition may be a melt point.

The Heat Flow portion of the MDSC scan represents the heat capacity of the sample; the reversible heat flow portion is an indicator of crystallization or glass transitions. The non-reversible heat flow is an indicator of

chemical reactions such as, evaporation, decomposition, oxidation, or solvation, when coupled with a weight loss.

Based on the TGA data and this transition at 120°C, it appears that the predominant feature is the evaporation of water from the PVOH found in the coating; there is a small transition that occurs right at the 120°C region in the reversible heat flow scan, this might be crystallization of the coating. If this is crystallization of the coating the visco-elastic properties may not be good for the tenter frame application.

The DMTA data (figure 14) shows a transition at 120°C which is consistent with the MDSC scan (figure 13). The DMTA plot has a sharp drop in E' , E'' , and $\tan \delta$, this is characteristic of a melt but the plot becomes erratic after that which indicates decomposition. Based on the TGA, MDSC, DMTA, it appears that the coating slightly crystallizes at 120°C and melts, upon completion of the melt the coating immediately starts to decompose.

The parallel plates Strain Rheometer curves (figures 15, 16) are not what would be expected of typical thermoplastic materials, in which the storage modulus (G') would drop off in a single step upon reaching the glass transition temperature.

Conclusions

The PEI primer experiments successfully demonstrate that water and carbon dioxide are the only gases being evolved from the primer during a simulated heat sealing. The design of a package that contains items that are non-reactive with these gas species can be made with a high degree of confidence. This primer will be chemically inert during the packaging formation.

The PVOH coating experiments are not as clearly defined as the PEI primer experiments, but the data indicates a very low success rate for the coating to retain uniform and continuous coverage while undergoing the tenter frame application. The coating appears to decompose under shear conditions above 155 °C. The tenter frame oven exceeds this temperature while still stretching the film in the transverse direction.

These two experiments demonstrate the value of a few thermal analysis techniques that can determine feasibility of the product before actual fabrication. When comparing the cost of these experiments and the limited resources of personnel time and the cost of machine time; it makes sense to thermally test these product designs before needlessly using valuable resources.

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