NON-DESTRUCTIVE EVALUATION OF URETHANE-ESTER COATING
SYSTEMS USING THE SCANNING KELVIN PROBE TECHNIQUE

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ABSTRACT

NON-DESTRUCTIVE EVALUATION OF URETHANE-ESTER COATING SYSTEMS USING THE SCANNING KELVIN PROBE TECHNIQUE

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The research described herein examines the effect of hydrolytic decomposition on the work function of polyurethane rain erosion coatings (REC). Two groups of panels, one group coated with REC containing carbon black and one group coated in REC without carbon black, were exposed to high temperature and humidity conditions in a steam autoclave for various periods of time. The work function of each unique exposure time was measured with a scanning Kelvin probe (SKP) and compared to unexposed coated panels to determine the magnitude of change in the REC coating. For both sample groups, results from the SKP analysis showed that as the coated panels were exposed for longer periods of time, the work function increased compared to an identical panel that was not exposed. The extent of the polymer coating degradation was determined by Raman spectroscopy and thermomechanical analysis (TMA).

Raman analysis indicated a decrease in ester bonds, while with TMA a decrease in polymer strength was observed with increasing exposure time. These results demonstrate that there is decomposition of the REC occurring from the exposure and it is due to hydrolysis of the ester bonds. The change in REC structure/composition was able to be detected by the Kelvin probe in a non-destructive manner, making it a valuable tool in assessing the decomposition of polyurethane rain erosion coatings.

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CHAPTER 1

INTRODUCTION

Aircraft Coating Service Life

High performance aircraft are subjected to harsh environmental factors during operation including impacts with water and other particles, as well as high temperature and humidity [1]. Rain erosion coatings (REC), made from polyurethane (PU), are used to protect the metal surfaces and other underlying coatings from these damaging elements by absorbing the force of impacts and providing a barrier against corrosive substances. Over time these coatings break down and may fail in flight by delamination. Failure of a coating leads to unplanned downtime and expensive refinishing procedures [1]. Coatings that are exposed to high temperature and humidity are particularly susceptible to degradation [1], leading to the assumption that the cause is hydrolysis or pyrolysis. These types of decomposition lead to a breakdown of the polymer network structure and reduce both the tensile strength and glass transition temperature of the coating, increasing the likelihood of failure [1].

The dynamic nature of weather makes predicting when the PU REC will fail using traditional lifecycle estimates extremely difficult since aircraft are exposed to different environmental conditions at different geographical locations or areas of operations. Currently no non-destructive method exists for accurately detecting when a

particular aircraft coating will fail prior to degradation being visible. Therefore, there is a need for a reliable non-destructive method to detect the changes in the surface coating that indicate when it is close to failure or has begun to fail. Previous studies have shown that it is possible to detect change in alkyl chain length in polymers using a Scanning Kelvin Probe (SKP) system [2]. Additionally, Hansen et al. demonstrated the ability to detect the changes in length and conformation of DNA molecules using an SKP system [3], I.R Peterson detected work function differences on gold plated slides covered with a monolayer of phospholipid [4], Bastide et al. observed changes in the work function of photoactive organic layers on semiconductor surfaces upon exposure to light [5], and Grundmeier et al. demonstrated that the SKP could detect the diffusion of water and ions through adhesive coatings and how they interact with the polymer metal interface [6]. In addition, the ability of the SKP to detect the corrosion/degradation of metal substrates and/or corrosion product underneath polymer coatings is well known, [7] [8]. All of these show the sensitivity of the SKP to changes in surface material and indicate that the SKP should be able to detect chemical changes in a degraded PU coating as well.

Objective

This research aims to determine if the SKP can be used to detect the work function changes in polymer coating associated with degradation as well as characterize the degradation of PU RECs as a function of exposure to elevated temperature and relative humidity.

CHAPTER 2

LITERATURE REVIEW

Scanning Kelvin Probe

The principle of operation of the Kelvin Probe is illustrated in Figure 1 (left – right). Three energy level diagrams depict two metals, kept equidistant, each having a constant work function and Fermi level of (ϕ_1, E_1) and (ϕ_2, E_2) , respectively. In the first diagram, (Figure 1a) the metals have no electrical contact and differing Fermi levels. When electrical contact is made (Figure 1b) the flow of charge allows the Fermi levels to equalize and gives rise to a surface charge [9]. The potential difference, V_{CPD} , is related to the difference in work function:

$$-eV_{CPD} = \phi_1 - \phi_2 \quad (1)$$

Figure 1: Relationship between work function (Φ) and Volta potential ($\Delta\Psi$) [5]

where e is the electron charge. The inclusion of an external backing potential, V_B (Figure 1c) allows for a nulling of the surface charge at a unique point where $V_B = -V_{CPD}$. This

point represents the work function difference between the two materials. V_B is varied automatically to ensure that the null point is always maintained and thus the potential at which nulling occurs equates to the work function difference between the probe and sample. This approach to measuring work function has been used for quite some time to measure the Volta potential difference or contact potential difference (CPD) between a probe tip and a surface of interest. The Volta potential difference is defined by IUPAC as the electrical potential difference between one point in vacuum close to the surface of a metal and another point in vacuum close to the surface of another metal where both metals are uncharged when brought into electrical contact [10]. The contact potential difference is analogous to the Volta potential, defined as being the potential difference between a conductive scanning tip and a conductive sample in air, when the surface potential is considered to be equivalent on both the probe and sample surfaces [11]. The ability of the SKP technique to resolve potential differences between a conductive scanning probe tip and a conductive sample in air at ambient conditions and temperature is defined by the relationship:

$$\phi = \psi + \chi \quad (2)$$

where the inner Galvani potential (ϕ) is defined to be equal to the sum of the Volta potential (ψ) and the surface potential (χ). In this relationship, the Volta potential is the electric potential difference between the surfaces of the conductive sample and probe tip. The surface potential accounts for any interactions occurring on either of the two conductive plates. The work function can also be expressed as:

$$\Phi = \mu_e + e\chi \quad (3)$$

where the work function (Φ) is the sum of the inner chemical potential of an electron (μ_e) and the energy required to move an electron across the interface of the metal (charge, e , times the surface potential, χ) [12]. Therefore, when considering two separate areas on a sample surface, Equations 2 and 3 can be combined (4): showing that variations in the measured CPD represent the spatial differences in the work function of the material as a result of surface potential changes.

$$-\Phi_1 + e\chi_1 = -\Phi_2 + e\chi_2 \text{ or } \Phi_1 - \Phi_2 = e(\chi_1 - \chi_2) = \Delta\Phi \quad (4)$$

It is clear then that Volta potential differences are the result of galvanic activity involving an electrolyte, whereas contact potential differences arise from differences in work function between the probe and the sample substrate.

Figure 2: SKP operation diagram [5]

Figure 2 shows a simplified schematic of the SKP system with the vibrational amplitude d_1 and the sample-probe electric connection. The Kelvin probe system works by vibrating a probe which induces an AC current due to the change in capacitance caused by the varying distance between the surface and the probe tip. From equation (5) the capacitance is dependent on the dielectric permittivity (ϵ), probe area (A), working distance (d), and vibration frequency (ω). The constant (ϵ_0) is also present, representing

the permittivity of free space [8]. The current generated (i) is governed by equation (6) which is equal to the change in capacitance multiplied by the difference in work function between the sample and reference ($\Delta\Psi$). The system uses a controller to null the induced current with a bias voltage V_B (7). When the current is brought to zero, the voltage applied as a bias is the opposite of V_{CPD} , or difference in work function [8]. The work function of the probe material is known so the work function of the sample is the work function of probe plus V_{CPD} assuming that d_o is kept constant [9].

$$C = \epsilon\epsilon_0 \frac{A}{\bar{d} + \Delta d \sin(\omega t)} \quad (5)$$

$$i = \Delta\Psi_{sample}^{ref} \frac{dC}{dt} \quad (6)$$

$$i = (\Delta\Psi - V_B) \frac{dC}{dt} \quad (7)$$

Figure 3: Overall view of the scanning Kelvin probe system (left), a closer view of the probe above a sample (middle), and up-close probe tip (right)

The system used in these experiments was a Model 470 Scanning Probe Electrochemistry System (Figure 3) from Bio-Logic Science Instruments SAS (Claix, France), which can perform a variety of tests in addition to SKP. The SKP probe tip (Figure 3 right) is made of tungsten with a brass insulating case to shield it from electromagnetic environmental noise. In addition to a Kelvin probe there is non-contact surface profiler which uses a laser to map out topographical changes on the surface of the sample. The laser is attached to the same scanning head as the Kelvin probe. When it is finished mapping the surface topography the data is integrated into the Kelvin scan parameters causing the probe tip to move up and down during the scan, allowing it to maintain a constant distance from the surface. In earlier systems the height could not be accurately accounted for so it was important to have the sample surface parallel to the scanning plane of the Kelvin probe tip. The distance from the surface is important because if there is a change in distance there will be a change in the reference capacitance which will cause a change in voltage not related to the surface potential of the material. This phenomenon is evident from the capacitance equation (5) and was observed on the M470 system by measuring the work function of a specific location at a variety of different working distances. There is no good way to discern what change is caused by capacitance and what is caused by change in work function. The most straight forward way to get around this is to take the change in height, and thus change in capacitance, out of the equation by keeping the probe at a constant distance from the surface.

Polyurethane Rain Erosion Coat

The composition of Caapcoat B-274, Figures 4 and 5, is 39.6wt% xylene, 13.8wt% methyl isobutyl ketone, 0.2wt% carbon black, and 45.9wt% isocyanate terminated polyester prepolymer (CAS: 54954-83-5) [13]. Xylene and methyl isobutyl ketone, Figure 4, are used as solvents. The prepolymer is composed of polycaprolactone (PCL), 1,1-methylenebis(4-isocyanatocyclohexane) (HMDI), and 2,2-oxybis(ethanol) (DEG) [14] seen in Figure 5 [14].

Figure 4: Caap Coat B-274 Solvents: Methyl isobutyl ketone (left) and Xylene (right)

Figure 5: Polyester Prepolymer Components: Caprolactone (left), 1,1-methylenebis(4-isocyanatocyclohexane) (middle), and 2,2-oxybis(ethanol) (right) [ChemSpider]

Figure 6: Polyester Prepolymer Reaction: Caprolactone (top right), and methylenebis(4-isocyanatocyclohexane) (top left) reacting, and 2,2-oxybis(ethanol) (bottom) used for chain extension [16]

The mixture polymerizes according to the reactions in Figure 6 with chain extender DEG instead of 1,4-Butane Diol (BD) as indicated in the figure. The Urethane formation is catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO) (CAS#280-57-9) [13] which is a highly nucleophilic amine commonly used in polyurethane synthesis [15]. Urethane bonds are formed in the prepolymer when the isocyanate reacts with the alcohol group on both the PCL and DEG. These are considered the hard component of the polyurethane due to their lack of flexibility. The flexible (soft component) structure between the hard urethane bonds is made from the polyester PCL. The polymer properties can be varied depending on the formulation of soft component and chain extender. For example the soft component PCL can be lengthened or more chain extender DEG can be added [16]. Adding more DEG will increase the ether content and adding more PCL gives the polymer more ester bonds. Polyether based PUs have better thermal and hydrolysis resistance whereas polyester based PUs have better chemical resistance [17]. The latter is chosen in most REC applications to prevent deicers and hydraulic fluids from degrading the polymer [1]. The choice of an aliphatic over an aromatic diisocyanate is to avoid toxic monomer components and degradation byproducts [18].

Polyurethane Degradation

The three major bonds that connect the cured polymer, besides carbon-carbon bonds, are esters, ethers and urethanes. Out of these, esters are the most active and will be the site of hydrolysis reactions. The products of this chain breakage are carboxylic acid and alcohol (8). Hydrolytic decomposition occurs when water bonds with the carbonyl carbon adjacent to both oxygens in the ester [19]. This process is very slow under standard conditions but in the presence of acid the carbonyl oxygen is protonated

making the carbonyl carbon much more likely to be attacked by a water molecule. Hydrolysis produces acid as a byproduct and therefore, once it starts, the buildup of protons makes subsequent reactions proceed faster. Heat will also increase the reaction speed.

Thermal decomposition can also occur in two different ways depending on the temperature the polyurethane is exposed to [20]. These are: dissociation to isocyanate and alcohol as described in equation (9) and dissociation to primary amine, carbon dioxide and olefin as described in equation (10).

A chemiluminescence study by Malíková et al. showed that at temperatures below 109°C hydrolysis occurs as per equation (8) and at temperatures between 109 and 202°C there is hydro-peroxide catalyzed decomposition as per equation (10). The activation energies of these two temperature regions, 36kJ/mol and 80kJ/mol respectively, were calculated by looking at the light emissions that occur when chemical bonds are broken [19]. The test conditions reach a temperature of 120°C so it is expected that in addition to hydrolysis there will be thermal decomposition as well. The reversion reaction (9) only happens at or above the glass transition temperature [21] (>200°C for Caapcoat B-274) so it is not expected to occur under the exposure conditions.

Raman Spectroscopy

Raman spectroscopy is a method of determining the bonds and functional groups that are present in a sample. This is done by exciting the atoms with a monochromatic laser in the UV, visible, or near IR spectra. The excitation induces a dipole in the atoms with a moment dependent on the polarizability of the electron cloud [22]. Most of the energy will be re-emitted elastically, meaning that it has lost no energy compared to the incident radiation. This is referred to as Rayleigh scattering and restricted from entering the detector by a strong holographic filter [23]. Suppression of the most intense scattering allows the detector to pick up on the inelastic Raman scattering which is much weaker. Raman scattering occurs due to a change in polarizability when the molecule is excited and can take one of two forms. Stokes Raman scattering is given off by molecules initially at the ground vibrational state and produce radiation that is lower energy than the incident beam. Anti-Stokes Raman scattering is radiation of higher energy than the incident beam and is produced by molecules initially at the excited vibrational state [22, 23]. Stokes radiation will be more intense than anti-Stokes, therefore, the Stokes region is normally analyzed. [23].

Raman spectra are presented as intensity versus the Raman wavenumber ω (cm^{-1}), which corresponds to the difference in frequency between the inelastically scattered electromagnetic radiation and the incident radiation [23]. The change in polarizability, and thus the shift in wavelength in the Stokes region, is dependent on the types of atoms (mass) and the types of bonds (force constant) [23]. This gives a unique shift depending on the type of bond, but only for an ideal case where the bond is considered in isolation. For most materials there are a variety of other factors which cause shifts to occur over a

broader range including adjacent bonds, the bond orientation and the degree of crystallinity. These are referred to as vibration bands. Even with the variation of vibrational shifts there are still consistent patterns for where certain bonds and functional groups appear. The combination of unique vibration bands allows for the composition of the material to be inferred by its “Raman fingerprint” which is unique for every material.

Attenuated Total Reflectance Fourier-transform Infrared Spectroscopy

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR FT-IR), as the name suggests, uses a beam of infrared light to measure chemical signatures in a material. The beam is directed through an optically dense crystal with a high refractive index. Instead of passing through the material the beam interacts with the first few microns ($0.5\mu\text{m}$ - $5\mu\text{m}$) of the material in contact with the crystal through evanescent waves created by the internal reflections. The interaction with material slightly changes the incident radiation which passes on to the detector, generating a spectrum [24]. Unlike Raman, which polarizes the electron cloud to excite molecular vibration, FT-IR induces a change in dipole which excites molecular vibration [22]. This allows it to detect things like water and CO which have a strong dipole but are not very polarizable. However, diatomic molecules such as oxygen, which have no dipole moment, are IR inactive [22].

Spectroscopy Peaks

Table 1 gives the general locations of the vibration bands of the bonds expected in Caapco B-274 for Raman and FT-IR spectra. In general the vibration bands for Raman and FT-IR are similar with a slight shift in wavenumber [23]. Figures 7 and 8 show the

two different representative spectra from this study with the relevant peaks labeled, and the intermediate 2600-2000 cm^{-1} wavenumber range removed.

Table 1: FT-IR and Raman Band Assignments [22, 23, 24, 25, 26]

	Band Origin	Wavenumber (cm^{-1})	Assignment
1	N-H O-H	3400-3300	Hydrogen Bonded N-H and O-H Vibration Band
2	R-CH ₂ -R	2900-2800	Asymmetric and Symmetric Methylene Stretch
3	C=O	1730	Ester C=O Stretching
		1630	Urethane C=O Stretching
4	C=C	1600	Carbon Black?
5	(C=O)-NH-	1520	Amide II N-H Bend
6	R-CH ₂ -R	1440	Methylene Asymmetric Bend
7	(C=O)-O-C	1350-1200	Ester Symmetric Stretching
		1200-1100	Ester Asymmetric Stretching
8	C-O-C	1090	Ether Stretching (crystalline)
		1040	Ether Stretching (amorphous)

Figure 7: Representative FT-IR Spectra of Clear REC with peak wavenumber labels. Diagonal line in the x-axis represents removal of the 2600-2000 cm^{-1} wavenumber range.

Figure 8: Representative Raman Spectra of Black REC with peak wavenumber labels. Diagonal line in the x-axis represents removal of the 2600-2000cm⁻¹ wavenumber range.

Thermomechanical Analysis (TMA)

TMA is a type of material analysis that monitors dimensional changes of a material as temperature is increased. The heating rate is generally between 5 and 20 °C/min [28]. The heating rate is kept constant and slow to assure that the sample has come to equilibrium and has the same temperature that a thermocouple is reading. This can be used to estimate the glass transition temperature (T_g) of a polymer or determine the coefficient of thermal expansion (CTE). The two most common modes of operation are puncture and standard expansion. In the standard expansion the T_g is determined by the point where the CTE (slope of the displacement by temperature graph) changes. The intersection of the asymptotes of the two CTE indicates the T_g , as seen in Figure 9 (dotted

lines). In penetration mode the T_g is determined by the point when the probe tip penetrates the surface. The 1 mm diameter penetration probe is made from quartz.

Figure 9: TMA Expansion mode (left) and Penetration mode (right) [28]

Statistics

The Paired Student's t -Test [27] compares the variation within two groups to the difference between the groups. The first part determines if the data from a small sample size is likely to represent the true result (looking at many more samples or the entire population). It then compares two different treatments, for example between an exposure of 6 hours and an exposure of 8 hours, to see if their values are different given the variation in both data sets. To do this, first, a t -value is calculated from two data sets using equation (11). Then a p -value is calculated using the t -value calculated and the mean of the differences, using Excel™ function $Tdist(t, N-1, 2)$.

$$\frac{(\sum D)/N}{\sqrt{\frac{\sum(D^2) - \frac{(\sum D)^2}{N}}{(N-1)(N)}}} = t \quad (11)$$

In this equation, D represents the difference between the two samples and N is the number of samples. Rejection of the null hypothesis (results are not different) occurs if there is a 95% chance that difference in the two data sets did not happen by chance (ie. $p < 0.05$). This test assumes that the data is normally distributed and that the sample sizes are equal. It is also assumed that the samples are the same before exposure because they were all coated at the same time with the same batch of material.

Standard error is used to calculate error bars for the data sets. It is another way of looking at the variation in a sample. It is calculated by dividing the standard deviation by the square root of the number of samples.

CHAPTER 3

HYPOTHESES AND OBJECTIVES

Hypotheses to be tested in this study are as follows:

1. Polyurethane degradation is caused by a combination of hydrolysis and thermal decomposition at elevated temperature and humidity. The breaking of the bonds will cause a change in work function of the PU coating.
2. The change in work function can be detected by the SKP allowing it to distinguish between degraded and pristine PU rain erosion coats.
3. Raman and ATR FT-IR spectroscopy will detect changes in the spectral vibration bands of degraded PU.
4. Thermomechanical analysis will detect a decrease in T_g in degraded areas of the exposed PU coating and these changes will correlate with the change in work function as measured and identified from SKP area scan measurements.

The objective of this research is to use a SKP as a non-destructive technique to characterize the level of degradation as determined by the work function of the surface material. This includes being able to distinguish between the rain erosion coat and the primer layer.

The following tasks (1-4) will be used to test the hypotheses (1-4):

1. Simulate the conditions that lead to PU coating degradation on a 2024-T3 aluminum panel, coated with Caapcoat B-470, using elevated temperature and humidity of 121 °C and 100% relative humidity (RH).
2. Characterize exposed panels with a Bio-Logic M470 SKP and compare them to pristine samples in order to determine changes in work function (or change in CPD values). Localized changes of work function will also be identified.
3. Verify chemical changes in coating structure using Raman and ATR FT-IR spectroscopy
4. Measure thermomechanical properties (T_g) of the reverted coatings will be measured using TMA.

CHAPTER 4

MATERIALS AND METHODS

Research Areas

The methods below were applied to two different REC polymer coating systems from the same manufacturer. The first REC contained carbon black and the other REC was identical except carbon black was not added by the manufacturer. This recipe modification was done to protect the polymer from the Raman laser which was observed to heat up the carbon black, burning the sample.

Sample Preparation

The base of each sample is a 3 inch by 6 inch aluminum alloy (2024-T3) panel with a thickness of 0.0315 inches. The panels were first cleaned with methyl ethyl ketone (MEK) to remove contaminants. The samples were then spray painted in a booth controlled to 77°F and 50% RH as per coating manufacturer's directions. The spray gun used was a Devilbiss GTI HVLP with 40psi of wall air pressure. One side of the panel was sprayed with a primer layer of Deft 02Y40 primer approximately 0.65 mils thick. After a 5 hour dry time, Caapcoat B-274 rain erosion coating was spray applied on top of the primer to approximately 12 mils thick. This layer took roughly 13 passes to build with a 15 minute flash time between each layer to allow the solvent to evaporate. Fresh material was mixed every 30 minutes to prevent thickening in the spray gun. The three layer setup can be seen in Figure 10. After the final coat was applied, the panels were

cured for a minimum of 24 hours at the coating conditions (77°F and 50% RH). This was followed by a 2 week cure at ambient conditions in a well ventilated room. After a completed cure the sample was cut into two 3 inch by 3 inch sections using a blade press. Contamination was noticed after the third black REC sample was cut so for the remaining black and all of the clear REC samples, a layer of polyethylene was placed over the REC to protect it from contaminants on the cutting blade. Coating and cutting were performed at the Coatings Corrosion Erosion Laboratory (CCEL) at Wright Patterson Air Force Base. A second batch of samples was made in the same way as the first except carbon black was not present in the REC. These will be referred to as clear REC samples because without carbon black the top layer is transparent.

Figure 10: Cross section of coated panel

Degradation Process

One cut half from each 3x6" panel was taped around the perimeter with 0.75 inch high temperature poly tape (ULTRUST-00750, Echo Supply Indianapolis, IN) to prevent edge delamination, then exposed to 121°C and 100% RH. Exposure conditions were achieved using a Systec DE 45 autoclave. These conditions were selected by a previous Air Force study because they best simulated the degradation process of the REC at an accelerated rate. Each sample received one of the following exposure times of 4, 6, 8, or 12 hours, to produce a variety of degradation stages. Clear REC samples were exposed in the same way.

SKP Analysis

Scanning Kelvin Probe examination was performed 2-3 days after exposure for all black samples and 1 week after exposure for clear samples. More time was added between exposure and SKP analysis to be sure the sample was completely dry before the work function was measured. The degraded and pristine halves were reconnected using conductive carbon tape and then secured to the Tri-Cell™ scan platform (Figure 11) to prevent movement. A BioLogic Model 470 system (Figure 3) which includes a 650nm laser for optical surface profilometer (OSP) surface height measurement as well as the Kelvin probe was used to scan the specimen. An OSP scan was performed first to record the surface height profile; this allowed the probe to track a specific height above the surface in the SKP scan. The probe tip was 500μm in diameter and the working distance was set at 100μm from the surface. The Kelvin scan parameters were as follows: gain 100, 5.00mV full scale sensitivity, output time constant of 1 second, and a step size of 250μm. Clear REC samples were scanned separately from their unexposed halves. The settings were the same except that a 0.1 second time constant was used with a 500μm step. Using a larger step size on the clear samples allowed for larger areas to be scanned making the average of the points more representative of the whole surface. The whole surface could not be scanned due to machine constraints and large areas at high resolution crashed the computer.

Figure 11: Sample before (top) and after (bottom) connection to scan platform

Chemical Analysis

Raman was used on the black REC coating in an effort to detect the chemical byproducts of decomposition including carboxylic acid, alcohol, and isocyanate groups. The unit used was a Thermo Scientific DXR Raman Microscope with a 780 nm laser at a power of 0.5mW. Six measurements were taken of each sample from randomly chosen flat areas that represented the average surface (features like craters and high work function spots were avoided). To further ensure accuracy, 21 scans are averaged for each sample point. This reduces the effect of machine variability. The spectra were baseline corrected using the OMNIC software algorithm. This helps remove changes in intensity caused by fluorescence. The average of the six point averages was used to compare changes in vibration band intensity between exposures. Calibration of the instrument used an inserted photodetector. This detector analyzes the light source to ensure that it is the correct intensity and that it is aimed correctly. A background scan was also taken before the Raman scan to suppress strong signals not caused by Raman scattering.

Due to recommendations from Dr. Andrew Phelps (UDRI personal communication) FTIR was performed on the clear REC samples using a Thermo Scientific Nicolet IS50. This followed the observation that analysis by Raman spectroscopy of the clear REC was displaying high fluorescence in the form of a severely

sloped baseline. Dr. Phelps suggested that because carbon black has many acceptor states, it is able to facilitate energy transfer through nonradiative dipole-dipole coupling with the excited hydroxyls. Therefore its removal makes the polymer less able to quench fluorescence. Without quenching these fluorescent reemissions are picked up by the detector causing an increasing in intensity not related to the Raman shift, which manifests as a sloped baseline. Example results can be seen in Appendix A: Clear REC Raman. FT-IR yields almost identical peaks to Raman and is used for the same purpose of tracking degradation. No baseline correction is needed because FT-IR is not susceptible to fluorescence which is why it was selected. Auto calibration was performed at startup and background was collected after cleaning the diamond ATR crystal with acetone. The instrument was run with a gain of 8, an optical velocity of 0.4747cm/s, aperture 80% open, resolution of 4cm^{-1} , and 12 samples per point. Three points were evaluated for each sample (again avoiding features) giving six distinct measurements per exposure time. The averages of the six different areas of each exposure were compared.

Figure 12: TMA setup; Sample pan (left), Sample and probe (middle and right)

Thermomechanical Analysis was used on both coating types to test the change in glass transition temperature (T_g) of the degraded and pristine sections. The TMA system

used was a TA Instruments Q-400 (New Castle, DE). The panels were first dipped in liquid nitrogen and then flexed to separate the coating from the aluminum panel. A 0.12 inch diameter circle was cut from the coating and put in the TMA apparatus with the probe resting on the top surface (Figure 12). The temperature ramp was 5°C/minute with a maximum temperature of 300°C in nitrogen atmosphere using 50mL/min purge gas. The measurements were made in penetration mode with a 1mm tip and an applied load of 0.05N. Penetration mode was used in this experiment because the desired data is from a specific local point (1mm circle) on the sample and not the sample as a whole. Also, in the longer exposures there was not a large enough flat area to use a larger probe. The device was calibrated using an aluminum foil standard to make sure the linear variable differential transformer (LVDT) was measuring expansion correctly. The thermocouple was calibrated with indium (a low melting point metal) with known melting temperature to ensure that the thermocouple and the sample are the same temperature. Clear REC TMA measurements were carried out on the same model instrument in a different lab. The procedures were identical except the clear REC was removed by peeling and not liquid nitrogen and bending.

Data Analysis

Qualitatively the data can be analyzed in the form of a 2-dimensional image generated by the SKP system where each point measured is given a color based on its work function value. However, the data can also be exported as text and put into Microsoft Excel™ to yield a more quantitative approach. The latter method assigns each data point to a unique cell (Figure 13), which allows for more calculation flexibility than the M470 software which only allows a single line scan to be viewed at a time and

will not calculate averages. It also gives the ability to average together multiple scans taken of the same area, further improving accuracy.

To perform statistical analysis on each sample the scan area was broken into 9 sections. Figure 14 (top) is the data from multiple scans of the same area averaged together. Below is the same data (Figure 14 bottom) with the tape area removed and grids with 9 equal sections placed on top. The data points inside each box were averaged together and the box treated as an independent sample. This allowed for the assumption of independence because the data points that interact (touch) are minimized. By treating each section as independent, variance can be calculated using a standard error calculation with a sample size of 9. Some areas near the edge of the tape (exposed side) or cut edge (unexposed side) were excluded if substantial contamination was observed (see Figure 14).

To determine if an exposure was statistically different from the untreated side as well as a different exposure time, the paired Student's *t*-Test was used, equation (11). The *t*-value was used to calculate a *p*-value using the function $Tdist(t, N-1, 2)$ in the Excel™ software package. It was applied to work function and spectroscopic data only, because TMA had only one data point for each exposure. The same tests were used evaluate the decomposition of the clear REC samples. In this case there were two independent replicates each divided into 9 sections giving $N=18$ for statistical calculations.

Figure 13: Data points exported to Excel TM with each cell representing a unique section of the surface

Figure 14: Excel TM data: Average SKP area scan from multiple scans of the same area (top), same area with tape removed and sectioned with black grids for statistical analysis (bottom)

CHAPTER 5

RESULTS

Scanning Kelvin Probe Analysis (Black REC)

The first sample was exposed for 4 hours under the standard conditions of 121°C and 100% RH, which was used for all samples. As seen in Figure 15a, the 2-dimensional work function area scan map included part of the unexposed sample (blue) and a larger section of the exposed sample (blue/green) with a tape line (green) down the middle. The color maps of the work function data are all in peak auto-scale meaning the lowest value is blue and the highest value is red. This makes the area maps for the different exposures look more similar than they actually are. For the 4hr sample, the average change in work function between the unexposed and exposed sections is 156mV (± 3.6). This comes from taking the average of all the points in the exposed section and subtracting the average of all the points in the unexposed section. Figure 15b shows a plot of the line scan data as indicated by the horizontal black line in the area scan (top). The 6hr sample yielded an average change in work function between the unexposed and exposed sections of 72.7mV (± 6.9) Figure 16. The 8hr sample had an average change in work function between the unexposed and exposed sections of 105mV (± 5.4). The data in this case was taken from the top half of Figure 17a. This was done to avoid the contamination on the lower half evident by the high work function area in the unexposed panel. Photographs of the sample show dirt present on the surface in the same area as the high work function

signal (see discussion in Appendix A, Sample Contamination). The 12hr sample had an average change in work function between the unexposed and exposed samples of 246mV (± 3.78).

Figure 19 summarizes the Black REC SKP data which shows a general trend of increasing work function with increasing exposure time with the exception of the 4hr exposure. From the *t*-Test analysis, the average change in work function between the exposed and unexposed samples for all exposure times were statistically different from each other, since the *p*-values were below 0.05 (6hr vs unexposed is 0.0004, 4hr vs 6hr is 0.0017, 6hr vs 8hr is 1.1×10^{-7} , and 8hr vs 12hr is 3.5×10^{-12}). Statistical calculations can be found in Appendix C.

Figure 15: SKP area map of 4hr exposure (a)
Representative single SKP line scan of black line (b)

Figure 16: SKP area map of 6hr exposure (a)
Representative single SKP line scan of black line (b)

Figure 17: SKP area map of 8hr exposure (a)
Representative single SKP line scan of black line (b)

Figure 18: SKP area map of 12hr exposure (a)
Representative single SKP line scan of black line (b)

Figure 19: Black REC: Average Change in Surface Work Function by Exposure (exposed-unexposed)

Sample Topography (Black REC)

Each exposure had a unique surface topography with varying shapes and sizes of cratering. Figure 20 (left) shows a representative unexposed surface, which is relatively uniform except for dust particles on the surface. The right image is the 4hr exposed surface which is covered by rings that look like water marks, although the sample is dry, along with darkening spots. These appear to be the beginning of crater formation, which can be seen to a greater extent in longer exposures.

Figure 20: Raman Microscope images of unexposed (left) and 4hr exposed (right)

Figure 21: 4hr exposure scan area (top) OSP area map (bottom)

Overall, the 4hr exposure was flat as seen in the laser OSP topography scan Figure 21 (bottom). The color change seen in the OSP scan is due to the exposed sample not being level. The slope is taken out in the Kelvin scan using the OSP file. Figure 22 shows part of the 6hr exposed section from the SKP map. There are three distinct sections; a smooth area (bottom) that is very similar to the 4hr exposure (Figure 22), an area with many small shallow craters (middle), and an area with shallow craters which appear to be precursors to the ones seen on the 8hr exposure (Figure 24). In Figure 23 (bottom), the rough area can be seen in the form of red dots around the smooth area. However, there is no discernable difference between the height profile of the large circle area and the smooth area.

Figure 22: Raman Microscope images of the 6hr exposure at three different surface morphologies at 2x, 5x, and 50x magnification

Figure 23: 6hr exposure scan area (top) OSP area map (bottom)

The close-up images of the 8 hour exposed surface (Figure 24) show deep craters with most that appear to be more severe manifestations of the ones seen on the 6hr. They range from being 300 to 700 μm in diameter, with depths approximately 70 μm .

Figure 24: Raman optical microscope images of 8hr exposure crater rim (left) and crater bottom (right)

Figure 25: 8hr exposure scan area (top) OSP area map (bottom)

A majority of the 12hr exposure surface was smooth with 100 μ m deep craters that seem to have shriveled up due to their wrinkled sides Figure 26 (left). There are a few large craters with diameters of over 1000 μ m and depths of 200-300 μ m as seen in Figure 26 (right). The transition from 4 to 8hr seems relatively straight forward, however, between the 8 and 12hr the surface covered in craters has changed. These were likely formed when the polymer flowed back into the craters after removal from the autoclave.

Figure 26: Raman optical microscope images of 8hr exposure crater rim (left) and crater bottom (right)

Figure 27: 12hr exposure scan area (top) OSP area map (bottom)

Raman (Black REC)

Raman intensity data of the black REC, Figure 28, show five major vibration band intensity changes from the spectra in Figure 29. It is evident that the vibration bands at 1600cm^{-1} , 1350cm^{-1} , and 1260cm^{-1} are all decreasing in intensity. The p -values for all of the intensity comparisons on each of the three decreasing bands are below 0.05 so are considered statistically unique. There is an initial increase in 1730cm^{-1} , but it remains unchanged for all subsequent exposure times 4-12 hours. The 1440cm^{-1} increases in intensity until 6 hours and then decreases. Statistically for the 1730cm^{-1} band, the only unique value is between the 0hr and 4hr exposures (at a p -value of 0.005); the rest are not statistically different. The 1440cm^{-1} band has statistically different values in all cases except for the 6hr and 8hr which have a 65% likelihood of not being statistically different.

Figure 28: Black REC Raman Intensity: Each group of bars represents a distinct vibration band, and each individual bar represents the intensity at a specific exposure time

Figure 29: Raman Spectra Comparison: Exposures; 0hr (purple), 4hr (orange), 6hr (green), 8hr (blue), 12hr (red)

Thermomechanical Analysis (Black REC)

Thermomechanical analysis results, displayed in Figure 30, show a decrease in T_g with increasing exposure. All 4 unexposed samples had a T_g within 2 °C of 197 °C showing the repeatability of the measurement. The 4hr sample had a slight drop of 23 °C to 174 °C. Between the 4 and 6 hour samples there was a large drop of 103 °C to 61 °C. The 8 hour was almost identical to the 6 hour and there was a slight drop in the 12 hour of 21°C to 38 °C. One TMA measurement was taken from each panel from a flat area that had a representative (of the average) work function value, as determined by the SKP area maps.

Figure 30: Representative glass transition temperatures of black REC at different exposure times

Scanning Kelvin Probe Analysis (Clear REC)

In Figure 31, the change in average work function values of the clear REC experiment are shown. Noticeably, there is a more consistent trend of increasing work function with increased exposure time. Figures 32–40 show the two samples from each exposure optically (left) and Kelvin scan (right). The 4 hour exposure differed from the unexposed condition by 221 mV (± 4.9). The 6, 8, and 12 hour exposures have a 269 (± 10.9), 324 (± 7.0), and 366 mV (± 8.3) change from the unexposed average respectively. This leads to an increase of approximately 50 mV with each exposure time step with exception to the 12 hour which only increases by 40 mV over a twice as large time step. From the t-Test analysis, the average change in work function for all of the exposures are statistically different, including the 4 hour exposure (lowest change) which is statistically different from the unexposed (0 hour) panel. The p -values for all exposure comparisons were below 0.01 meaning that there is a <1% chance that the results happened by chance,

so they are statistically different. The images of the replicates of each exposure time can be found in Appendix A: Clear REC SKP.

Figure 31: Clear REC: Average Change in Surface Work Function by Exposure (exposed-unexposed)

Figure 32: Clear REC 0hr exposure sample 3B (left). Scan area (yellow box), SKP scan (right)

Figure 33: Clear REC 4hr exposure sample 6B (left). Scan area (yellow), SKP scan (right)

Figure 34: Clear REC 4hr exposure sample 5A (left). Scan area (yellow), SKP Scan (right)

Figure 35: Clear REC 6hr exposure sample 1A (left). Scan area (yellow), SKP scan (right)

Figure 36: Clear REC 6hr exposure sample 2B (left). Scan area (yellow), SKP scan (right)

Figure 37: Clear REC 8hr exposure sample 3A (left). Scan area (yellow), SKP scan (right)

Figure 38: Clear REC 8hr exposure sample 4A (left). Scan area (yellow), SKP scan (right)

Figure 39: Clear REC 12hr exposure sample 7A (left). Scan area (yellow), SKP scan (right)

Figure 40: Clear REC 12hr exposure sample 8B (left). Scan area (yellow), SKP scan (right)

Sample Topography (Clear REC)

The surfaces topographies of the clear REC samples are similar to that of the black, where the unexposed is flat, whereas there are small circles starting to form on the 4hr exposure. The 6hr exposure has one panel (Figure 36) that looks almost identical to the black REC 6hr exposure (Figure 16) and another (Figure 35) that more resembles the 8hr exposure (Figure 37), only with slightly shallower craters. The 8hr clear REC samples look more like the 12hr exposures from both black and clear REC, with a few large craters and mostly small pinhole craters. Figure 38 looks similar to Figures 27, 39

and 40 displaying a topographical progression from smooth area to large crater which may take place during exposure. It was observed that when the panels were removed from the autoclave, water had pooled up in the smooth areas as well as the craters. This suggests that the weight of the water might over time push the polymer horizontally along the panel, forming a crater.

FT-IR Analysis (Clear REC)

For the FT-IR of the clear REC, there was a change in peak intensity below 1000cm^{-1} but it does not follow a trend with exposure with exposure. The three peaks that change consistently were 1720cm^{-1} , 1227cm^{-1} , and 1160cm^{-1} . These correspond to ester C=O stretching and ester symmetric/asymmetric C=O-O stretching, respectively, similar to the black REC. For all these there was a decrease in peak intensities with increasing exposure. Figure 41 graphically shows the average intensity for each of the three changing vibration bands from the spectra in Figure 42, with respect to exposure time. All three bands have statistically significant intensities for 0, 4, 6, and 8 hour exposures. Also, in all cases, the 12 hour exposure is not statistically different from the 8 hour. The associated *p*-values for the first 4 exposures on each of the three bands are below 0.05. All the other peaks above 1000cm^{-1} had no change including the vibration band at 3400cm^{-1} assigned to OH and NH hydrogen bonding (Figure 43).

Figure 41: Clear REC: FT-IR absorbance; Each group of bars represents a distinct vibration band. and the individual bars represent each exposure time for that band

Figure 42: FT-IR Spectra Comparison: Exposures; 0hr (purple), 4hr (orange), 6hr (green), 8hr (blue), 12hr (red)

Figure 43: FT-IR Spectra: Comparison of 0-12hr exposures for water vibration band 3360cm⁻¹

Thermomechanical Analysis (Clear REC)

Glass transition temperature measurements of the clear REC (Figure 44) follow the same pattern as the Black REC: the unexposed T_g is 188°C and there is the same large drop between the 4hr and 6hr exposures where the T_g goes from 163°C to 65°C. The 8hr and 12hr exposure T_g values are 58°C and 48°C respectively.

Figure 44: Average glass transition temperature of clear REC at different exposure times

CHAPTER 6

DISCUSSION

SKP Comparison

Looking back at Figure 19, there is a clear trend of increasing work function in the 6, 8, and 12 hour black REC exposures. However, the 4 hour exposure does not fit this trend being higher than both the 6 and 8 hour exposures. Presently there is no explanation for the large change in work function between the 0hr and 4hr exposures. It was initially thought that the panel that was exposed for 4 hours had not fully cured because it was the first panel tested. To test this, another 4 hour exposure was repeated as the forth panel (after the 8hr and 6hr respectively) to make sure the result was representative. Both had an equally large increase in work function from their unexposed halves. This trend was not seen with the clear REC so it may have something to do with carbon black. Even though the 4hr exposures do not fit the trend, what is clear is that there is an increase in work function associated with an increase in exposure time to heat and humidity from 6-12 hours. The 6, 8, and 12 hour samples were not repeated for the black REC because only 6 panels were made in the first batch. To improve the correlation with more data points, a second set of panels was made with clear REC.

The clear REC test procedure was modified to correct issues with the methodology of the black REC test. The first change was to add more standardization, by taking equal sized scan areas in the middle of the sample and scanning the unexposed and

exposed panels separately. This change meant a larger area of each panel could be scanned and that edge effects from contamination or edge delamination could be avoided. This led to a less variable work function value between the different unexposed panels and presumably reduced the variability in the exposed values as well. The average value of all the unexposed was subtracted from each exposed average to come up with the difference in work function between the two. In addition to larger standard scan areas, there were two panels exposed for each time.

Changes made to the clear REC experiment yielded data that is more compelling than the black REC experiment and brings the trend of increasing work function into focus. There was also a difference between the work function change with exposure with the clear REC changing more with each exposure than the black. There are many possible explanations of this the most likely being the differing procedure which eliminated uncontrolled variables. However, there could be a difference in the electrical resistance of the polymer which leads the black REC to have a lower work function.

Raman Comparison

Substantial decrease in intensity in the vibration band $1300\text{-}1100\text{cm}^{-1}$ is indicative of loss of ester bonds, which are part of the main polymer chain [16]. Hydrolysis occurs most rapidly on esters so an intensity decrease in these bands is expected with increasing exposure to heat and humidity [1]. Along the entire spectrum (Figure 45), this region has the most significant intensity change so it is likely the primary result of decomposition. The 1440cm^{-1} peak is assigned to the CH_2 bending vibration band which shows an initial increase followed by a decrease. This could be caused by a change in density of free functional groups associated with polymer crystallinity. The 1730cm^{-1}

peak is assigned to the carbonyl C=O stretching vibration band which is present in urethanes, carboxylic acids, and esters. The fact that the intensity of the 1730cm^{-1} peak increases between the 0hr and 4hr samples could signal initial chain reorientation. The intensity remains constant for all exposures after 4 hours which is expected because the carbonyl bond is preserved in the decomposition reactions.

Figure 45: Raman Spectra Comparison: Exposures; 0hr (purple), 4hr (orange), 6hr (green), 8hr (blue), 12hr (red)

It was observed that a peak in the 1600cm^{-1} vibration band did not appear in the spectrum of the clear REC which was identical to the black REC with the exception of carbon black. This band could either be caused by carbon black-mediated crosslinking between the polymer strands or the result of the shifting of the 1630cm^{-1} peak.

An FT-IR study of the effect of carbon black on polyurethane properties showed no peaks appearing due to an addition or increase in carbon black content [29]. The

study did show that as more carbon was added, there was a slight decrease of vibration band wavenumber and the bands became less defined. Their hypothesis was that the wavenumber shift was caused by interactions with the hard urethane segments and the loss of definition from the carbon disturbing the interactions between the soft polyester segments thereby reducing polymer chain mobility. In addition, rheological measurements confirmed the existence of a bond network between the polyurethane chains and carbon black by the improvement of thermal properties as more carbon was added [29]. While there appears to be no reports of similar studies in the literature using Raman spectroscopy to detect the presence of carbon black in a polymer coating, the data presented in Figure 46 clearly demonstrate spectroscopic differences between a PU REC with carbon (blue) and one without carbon (red). The most noticeable difference is the absence of the peak at the 1600cm^{-1} vibration band in the sample without carbon. Also, as was seen with the FT-IR [29], there appears to be a loss in band definition in the Raman spectra with the addition of carbon black.

Figure 46: Effect of Carbon Black on Raman Spectra; Black REC (dark blue) and Clear REC (red)

The coatings formulations are identical with the exception of carbon black (0.1wt%) in the black REC. The spectra in Figure 46 were taken from unexposed coatings using the same measurement parameters. The combination of the conclusions from Álvarez-García et al. [29] and the Raman comparison in the present study suggests a strong indication that the 1600cm^{-1} band is caused by carbon crosslinking and not a shift of a main chain vibration band.

TMA Comparison

Figures 30 and 43 show that there is a sharp decline in T_g after 4 hours of exposure to elevated heat and humidity and a relatively constant T_g for the 6, 8, and 12 hour exposures. However, in Figures 46 and 47 it can be seen that even though the 6 and 8 hour exposures have almost the same T_g (the point at which the probe begins to penetrate the coating film) the 6 hour exposure sample has a much slower penetration rate as seen in the slope of the blue line in Figure 47 and two blue lines (star symbols) in Figure 48. This “fuller picture” of the TMA test indicates that the 6hr likely has a greater average molecular weight per chain so there is still decomposition occurring between 6, 8, and 12 hours. The data from the black and clear REC groups were very close with the clear having a T_g 8°C lower for the 0hr and 4hr exposures with the 6 and 8hr being approximately the same (63°C and 59°C respectively). The 12hr black REC was lower than the clear by 10°C . With the assumption of a dry polymer (no plasticization), the decreasing polymer strength shows that there are bonds broken in the exposure process and that more chains are broken with longer exposure times.

Figure 47: TMA curves of black REC for different exposure times. The two 6hr lines represent smooth and rough areas. The two 8hr lines represent crater vs rim

Figure 48: TMA curves of clear REC for different exposure times

FT-IR Comparison

Fourier Transform Infrared spectroscopy was used on the clear REC because when the carbon black was removed the polymer no longer quenches fluorescence which leads to baseline slope. The baseline slope in the clear coat Raman was so severe it covered up vibration band intensity changes due to Raman shifts. Since there is no baseline shift, FT-IR is a better tool to analyze the clear REC because band changes can be confidently attributed to chemical changes and not artifacts of baseline correction. Also, water is FT-IR active and measurements show no change in water content between the exposed and unexposed panel in the 3400cm^{-1} vibration band, removing the possibility of absorbed water as the culprit for work function change.

Vibration band assignments of FT-IR are similar to Raman with slight shifts in wavenumber. In general the 1720cm^{-1} peak shows ester C=O stretch and the 1227cm^{-1} and 1160cm^{-1} peaks represent ester C=O-O symmetric and asymmetric stretching, respectively. The spectra in Figure 49 show a decrease in all three of these peaks corresponding to esters, along with stable surrounding peaks clearly indicates that hydrolysis of esters is occurring with increasing exposure.

Figure 49: FT-IR Spectra Comparison: Exposures; 0hr (magenta), 4hr (orange), 6hr (green), 8hr (blue), 12hr (red)

The TMA, Raman, and FT-IR generally agree, showing values that increase by a lesser amount with each increase in exposure time (the largest change occurs between 4 and 6 hours and there is little difference between the 8 and 12 hour exposure values). This is not what is seen in the SKP results, where the work function continues to increase with exposure time. This could mean that the SKP is more sensitive to the changes that are occurring than other analysis techniques.

Observed Surface Features

For both clear and black REC coating systems there were localized areas with higher work function than the surrounding area (surface average). These are especially prevalent in the exposures longer than 4 hours and were not present on the unexposed

samples. Detailed analysis of these features was not in the scope of the project but represent an interesting development in the study of coating decomposition. Namely, does a coating break down uniformly or locally? Raman and TMA do not show differences between two distinct topographical areas for each exposure time in Figure 50. The two areas come from depressions in the coating referred to as craters. The left graph shows the spectra of the crater rim and bottom for the 8hr exposure and the right shows the crater and rim areas for the 12hr exposure. It is apparent from the almost identical spectra that Raman cannot detect a difference between the two locations. FT-IR could not be taken of crater bottoms, so no comparison was made

Figure 50: Raman Comparison: 8hr sample crater bottom (red) crater rim (blue) (left), 12hr sample crater bottom (red) crater rim (black) (right)

Initially it appeared that the high work function areas were specific to certain surface textures. This can be seen in Figure 51, but there is also part of the large smooth section as well as several other small smooth sections that do not have an increased work function. Also looking to Figure 52, which covers the whole 6hr exposed side, shows that areas on the same sample that have a similar texture do not have the same work function. This is especially clear in the upper right corner of the scan area (Figure 52),

which is visually identical to the smooth area in the bottom left, but does not have a high work function.

Figure 51: Clear REC 6hr exposure sample. SKP scan (left) Scan area (right)

Figure 52: Black REC 6hr exposure sample. SKP scan (left) Scan area (right)

There is also the question of whether the thickness of the coating makes a difference in the work function of a specific area. It was initially hypothesized that the features were caused by the probe being closer to the aluminum substrate when traversing down into a crater. This was determined not to be the case by looking at a unique area on the 12hr black REC sample Figure 53. From the topography scan (Figure 53 left) the

crater (a) is 200 μm deeper than the average surface (c) and the raised area around the crater (b) goes up 250 μm from the average. This means there is a greater height change in the raised area (c to b) than in the crater compared to the average surface (c to a). It would be expected that if coating thickness was a factor that there would be a change in work function in both cases. The corresponding SKP scan (Figure 53 right) shows no change in work function coming from the large raised area (b) making coating thickness an unlikely contributor to the change in work function.

Figure 53: Black REC 12hr exposure OSP height scan (left) and SKP work function scan (right) Large crater (a), raised area around crater (b), and average area (c)

Cause of Work Function Change

The work function measurement from the SKP is composed of two different components, the Volta potential and the surface potential. The Volta potential arises from electronic interactions at interfaces including galvanic activity and other surface dipole interactions. Nazarov and Thierry [30] studied the effects of the polymer metal interface on the work function measurement using an SKP. The results showed that for an interface between aluminum oxide and epoxy there was amino dipole formation (12) where the metal became negatively charged (donating proton) and the epoxy became positively charged (accepting proton).

These ionic interactions form an electric double layer which manifests as a decrease in work function of 600mV [30]. This is demonstrated by the Helmholtz equation (13) [30]:

$$\Delta\Phi^M = 4\pi\mu\alpha N_S \quad (13)$$

This can be re-written for a parallel plate capacitor [30]

$$\Delta V = \frac{\sigma}{C} = \frac{4\pi\sigma d}{\epsilon} = \frac{4\pi N_S \mu \cos \Theta}{\epsilon} \quad (14)$$

This shows that the change in work function induced by an adsorbed coating is proportional to the dipole moment (μ), surface coverage (N_S), and its polarizability (α).

In the Nazarov and Thierry study the same measurements were taken of a polymer that gave the metal a positive charge, which led to an increase in work function of 300mV [30]. This demonstrated the effect of the dipole moment (μ) on the interaction if the metal receives a negative charge, electron transfer is facilitated between the polymer and metal oxide (decrease in work function) and if the metal receives a positive charge, electron flow is restricted (increasing the work function). It was also shown in that study that the dipole interactions can be disrupted with the addition of water, in the form of 95%RH air, causing the potential change to return nearly to that of an uncoated aluminum panel due to the dipole surface coverage (N_S) being reduced to zero. When exposed to dry air for 50 hours, the dipole reformed causing, in the case of epoxy, the work function to drop again to the level seen before exposure to water.

Additionally, Delamarche et al. [31] have shown that the CPD of self-assembled monolayers (SAMs) of alkanethiols on gold correlates with the difference in the dipole-charge distribution between the SAMs and the surface potential of the gold. These

studies highlight how interfacial interactions can be manifested in the work function that is measured.

In this particular study there are four interfaces where a Volta potential could arise (Figure 54). The dipole formation discussed above occurs at the β_2 interface causing a drop in the work function compared to a bare aluminum surface. The β_1 interface contributes to a change in work function as well but is considered as constant over the entire surface with no change from exposure, since it is a stable uniform oxide. The β_3 interface is composed primarily of urethane bonds which form between free hydroxyls in the epoxy and isocyanates in the polyurethane during the polyurethane cure [32]. There is no charge separation at this interface so a Volta potential will not arise. The β_4 interface is very weak and is also present on the probe tip so it will be canceled out in the calculation of the difference between the probe and surface [30]. The β_4 interface could be changed by an adsorbed organic layer similar to that described by Delamarche et al. [31], in the form of oil or other contaminants. This is why sample protection was an integral part of the clear REC test. With no contamination, the β_4 interface can be ruled out as a cause of work function change.

Figure 54: Coating stack-up: Interface potentials (β)

The surface potential arises from the non-ionic interactions in the sample. The contribution of the dielectric can be seen as ϵ in equation (14). Hansen [33] demonstrated that the SKP technique is capable of discriminating between layers of a nitrocellulose paint based upon changing dielectric strength. The dielectric constant of a polymer is linearly related to the molecular polarizability of the dielectric material [3]. Water, being a polar molecule, could cause changes in dielectric strength of wetted polyurethane. Water content could also be a possible explanation for changes in the polymer metal interface β_2 , where water reverses the drop in work function caused by the metal oxide-epoxy dipole [30]. The black REC was only given 2-3 days to dry in 15%RH air. This is the same time that it took for the water to leave the interface in the study by Nazarov and Thierry [30]. However, in that study epoxy was not covered in a REC so the samples in this study would likely take longer to dry. For the clear REC tests, the samples were allowed to dry for a week and were scanned over 2 days so there is assumed to be no water in the polymer per the results of the wet dry cycling in [30]. There was also no increase in water content detected by FT-IR with increasing exposure times, further strengthening the assumption that increasing water content is not the cause of the work function change of the clear REC. This allows the β_2 interface to be ruled out as the cause of work function change because the dipole has been shown to reestablish after water is removed [30].

Change in probe height has also been ruled out by investigating high work function features on the surface, therefore eliminating all other variables that could affect the work function except for changes in the dielectric properties of the polyurethane rain erosion coat. From the spectroscopic measurements it has been shown that there is an

increasing loss of ester bonds as exposure time increases. This leads to a decrease in the thermal stability (strength) of the polymer according to TMA. These analyses point to a breakdown of the polymer network. The most likely explanation for the change seen in the work function is that the breaking of bonds creates many small interfaces where there was once continuous polymer. With higher chain mobility from bond scissions there will be greater dielectric loss from β -relaxation (rotating polar groups) [34]. Additionally, there would be an increase in the capacitance of the polymer (via an increase in dielectric permittivity (ϵ)) caused by an increase in polar hydroxyl groups at the interfaces [35]. The increase in hydroxyl groups could cause dielectric hysteresis to increase because they act as electron trapping sites [35]. Dielectric hysteresis is when the charge does not immediately dissipate because the electrons are not all released upon discharge. Since there are more charge trapping sites present in the more degraded polymers it is harder to remove the electrons, leading to a change in surface potential (χ) in the form of a higher work function. The dielectric loss from chain rotation changes the surface potential by dissipating some of the energy in the induced electric field which is indicative of a higher work function material.

Future Work

There is still room for improvement for future studies. One of the most important areas to investigate further is the role of water as a plasticizer of the REC. To verify that the REC is not absorbing water, another test such as TGA or quartz micro balance should be incorporated to measure the amount of water retained by each exposure time. This would verify the dry polymer assumption made in this study. Taking spectroscopic measurements of different depths in the coating would also show if the coating has

decomposed more on the top of if it is uniform throughout. Additionally, more replication would further increase the accuracy of the study. If six samples were exposed for each time then the variability of the exposures could be better studied. Also separating the same exposure condition into two groups of three and exposing them on different days would test the variation of the autoclave itself. To better develop a trend, a 2hr exposure could be added and the 12hr replaced by a 10hr exposure. This would show what is happening in the first stage of decomposition and keep a standard time interval between exposures. A standard cleaning procedure done before SKP scans would further improve the results by eliminating changes caused by surface contamination including dust and oil. Looking more into the feature areas could also help determine the mechanism of decomposition and answer the question of how degradation progresses. Finally, scanning the panels before and after exposure in the same area would determine if defects can be detected in the unexposed samples that lead to increased degradation upon exposure. This information would be very interesting for manufactures of aircraft to be able to assess the quality of the coating before the plane leaves the factory.

CHAPTER 7

CONCLUSION

Hypotheses 1 and 2 predicted that there would be a measurable change in work function as chemical decomposition of the REC occurred as a function of increased exposure time. This was detected by the SKP in both coating systems as an increase in work function with increasing exposure. In addition, hypotheses 3 and 4 were confirmed through a decrease in both glass transition temperature and spectral vibration band intensity with increasing exposure.

A combination of Raman, FT-IR and TMA analysis detected changes in both the chemical and physical properties of the coatings that occur due to hydrolysis. There are several ways in which the work function of this stack-up could change including: water inclusion in the bulk polymer or at the interface, probe height above the metal substrate, and contamination on the surface. All of these variables have been shown not to be present. Therefore, the likely cause of the work function increase detected is the change in dielectric properties of the rain erosion coat caused by hydrolysis with an increase in work function being the indicator of a greater degree of hydrolytic decomposition. It is known that the Kelvin probe is sensitive to a change in the dielectric properties of materials between two conductive plates of a vibrating capacitor. This presumably also means the localized areas of high work function represent areas of increases decomposition although more tests will have to be done to verify this.

This study shows that the scanning Kelvin probe is not only sensitive to the changes that occur when a polyurethane rain erosion coat undergoes hydrolysis, but more sensitive than other techniques used. This combined with its non-destructive nature makes the scanning Kelvin probe a great candidate for a tool to assess the integrity of coatings currently in service.

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APPENDIX A

Additional Information

Contamination

In Figure A1, scuff marks with significant dirt inclusions from the shearing process used to section the sample can be seen especially on the unexposed sides most notably on the side along the cut as well as in the middle. This contamination shows up in the SKP scan as two different signals; an overall increase in work function on the lower half of the scan especially on the unexposed side, as well as some lower work function points which are caused by metallic flakes in the coating. The contaminants were strongly attached to the surface and could not be removed by brushing or air blasting. This did not prevent the scanning of the sample, but it may have an effect on the results. A cleaning procedure was not implemented because of concerns that it would affect the work function measurement or the degradation process. The effect of the contamination was noticed part way through the black REC testing so the tests were finished using the same procedure to maintain consistency. The primary corrective action was taken on the next set of experiments where a polyethylene sheet was put over the sample when being cut. This prevented dirt and oil from contaminating the surface, removing an uncontrolled variable from the experiment.

Figure A1: Contamination of 8hr sample from the cutting process

Edge Delamination

An advantage of using a clear coating is that changes below the surface become visible. One such case is the delamination of the coating at the cut edge. Figure A2 (top) shows a closeup of the cut edge from an unexposed panel (top). When the coating was peeled back it was discovered that it was the epoxy primer layer that had delaminated and was stuck to the REC. Delamination occurred on all clear samples ranging from 1mm to 3mm. Later investigation showed that this occurred in the black REC samples as well but went unnoticed during the data gathering because of the topcoats high opacity. Delamination would change the interface between the coating and metal and would have

an effect on the work function. It was noticed that the area near the cut edge had a different work function than the bulk but at the time it was thought to be due to surface contamination. The combination of these two factors was the main justification for switching to a different scan method on the clear REC, where the edges were avoided altogether and the exposed and unexposed halves were scanned separately.

Figure A2: Edge delamination after cut (top) coating peeled back (bottom)

Clear REC Raman Slope

The reaction of the clear REC to the Raman laser was unexpected. Initial testing showed that for an unexposed panel, laser (780nm) powers of up to 15mW could be used without burning the sample and without causing fluorescence. However, when the exposed samples were tested there was substantial fluorescence as seen by the slopes in Figure A3. These slopes increased with increasing exposure and required baseline correction to achieve a reasonable spectra. When baseline corrected, the spectra exhibited increasing intensity with increasing exposure for all vibration bands, suggesting that the difference was caused by the differing degrees of fluorescence and not changes in specific vibration bands (chemical bonds). This made Raman ineffective at differentiating between exposure times which prompted the switch to FT-IR. Dr. Phelps suggested that hydroxyl bonds could cause this but there is no way to prove from fluorescence alone what functional group is the cause.

Figure A3: Clear REC Raman baseline slope (fluorescence)

Trend Speculation

There are not enough data points to confidently predict a trend. However, if the point (0,0) is added (unexposed should have no change from itself) along with proper time intervals a rough guess can be made. Figure A4 adds the necessary components and concludes that a logarithmic function is the best fit for the data. Unfortunately, this does not relate to the FT-IR data which is represented better by a linear decrease in intensity.

Figure A4: Clear REC: SKP data with best fit curve

APPENDIX B

Data

Table B1: Black REC SKP Data

Work function data from a variety of exposure times is presented below. Each average work function (AVG WF) value is the average of all the data points in that section as described in *Sample Sectioning* in Appendix A. These sections are then averaged together to calculate the average (Avg.) at the bottom. The standard error calculation using the standard deviation of the data is also calculated at the bottom.

4hr exp		6hr exp		8hr exp (top)		12hr exp	
Section	Avg WF	Section	Avg WF	Section	Avg WF	Section	Avg WF
1	-0.9093	1	-0.9623	1	-0.8428	1	-0.5764
2	-0.8910	2	-0.9918	2	-0.8514	2	-0.5860
3	-0.9097	3	-0.9879	3	-0.8665	3	-0.5875
4	-0.9012	4	-0.9012	4	-0.8281	4	-0.5580
5	-0.8693	5	-0.9665	5	-0.8487	5	-0.5786
6	-0.9022	6	-0.9794	6	-0.8573	6	-0.5525
7	-0.9148	7	-0.9123	7	-0.8148	7	-0.5279
8	-0.8850	8	-0.9370	8	-0.8382	8	-0.5579
9	-0.9091	9	-0.9733	9	-0.8480	9	-0.5595
Avg	-0.8991	Avg	-0.9568	Avg	-0.8440	Avg	-0.5649
S dev	0.0139	S dev	0.0309	S dev	0.0146	S dev	0.0180
S Err	0.0046	S Err	0.0103	S Err	0.0049	S Err	0.0060
4hr unex		6hr unex (center)		8hr unex (top)		12hr unex	
Section	Avg WF	Section	Avg WF	Section	Avg WF	Section	Avg WF
1	-1.0461	1	-1.0187	1	-0.9778	1	-0.8188
2	-1.0449	2	-1.0137	2	-0.9683	2	-0.8129
3	-1.0492	3	-1.0348	3	-0.9315	3	-0.8039
4	-1.0518	4	-1.0230	4	-0.9653	4	-0.813
5	-1.0588	5	-1.0275	5	-0.9609	5	-0.8102
6	-1.0593	6	-1.0244	6	-0.9327	6	-0.8047
7	-1.0718	7	-1.0348	7	-0.9367	7	-0.8136
8	-1.0551	8	-1.0520	8	-0.9409	8	-0.8129
9	-1.0584	9	-1.0367	9	-0.9290	9	-0.8106
Avg	-1.0551	Avg	-1.0295	Avg	-0.9492	Avg	-0.8112
S dev	0.0078	S dev	0.0108	S dev	0.0176	S dev	0.0044
S Err	0.0026	S Err	0.0036	S Err	0.0059	S Err	0.0015

Table B2: Clear REC SKP Data

Below is the sectioned data from the clear REC samples. There are 2 samples for each exposure shown by the section numbers 1-9 which repeat in each exposure for the second sample. Each average work function (AVG WF) value is the average of all the data points in that section as described in *Sample Sectioning* in Appendix A. These sections are then averaged together to calculate the average (Avg.) at the bottom. The standard error calculation using the standard deviation of the data is also calculated at the bottom.

4hr Exposed		6hr Exposed		8hr Exposed		12hr Exposed	
Section	AVG WF	Section	AVG WF	Section	AVG WF	Section	AVG WF
1	-0.584	1	-0.628	1	-0.482	1	-0.480
2	-0.598	2	-0.614	2	-0.499	2	-0.505
3	-0.588	3	-0.601	3	-0.530	3	-0.529
4	-0.600	4	-0.625	4	-0.503	4	-0.437
5	-0.611	5	-0.609	5	-0.530	5	-0.482
6	-0.597	6	-0.591	6	-0.529	6	-0.512
7	-0.591	7	-0.628	7	-0.524	7	-0.417
8	-0.618	8	-0.615	8	-0.537	8	-0.453
9	-0.595	9	-0.589	9	-0.528	9	-0.472
1	-0.601	1	-0.535	1	-0.467	1	-0.395
2	-0.616	2	-0.528	2	-0.466	2	-0.425
3	-0.623	3	-0.477	3	-0.464	3	-0.443
4	-0.590	4	-0.510	4	-0.487	4	-0.385
5	-0.603	5	-0.504	5	-0.467	5	-0.424
6	-0.612	6	-0.452	6	-0.441	6	-0.458
7	-0.591	7	-0.501	7	-0.514	7	-0.445
8	-0.598	8	-0.485	8	-0.512	8	-0.459
9	-0.610	9	-0.466	9	-0.492	9	-0.500
Avg.	-0.601	Avg.	-0.553	Avg.	-0.498	Avg.	-0.457
S Dev	0.011	S Dev	0.062	S Dev	0.028	S Dev	0.039
S Err	0.003	S Err	0.015	S Err	0.007	S Err	0.009

Table B2 Continued: Unexposed Clear REC Data

Unexposed					
	Section	AVG WF		Section	AVG WF
1b	1	-0.871	3b	1	-0.864
	2	-0.857		2	-0.854
	3	-0.844		3	-0.882
	4	-0.877		4	-0.869
	5	-0.864		5	-0.858
	6	-0.852		6	-0.891
	7	-0.886		7	-0.901
	8	-0.878		8	-0.887
	9	-0.865		9	-0.924
2a	1	-0.790	4b	1	-0.805
	2	-0.808		2	-0.810
	3	-0.833		3	-0.814
	4	-0.777		4	-0.797
	5	-0.805		5	-0.804
	6	-0.818		6	-0.811
	7	-0.781		7	-0.796
	8	-0.799		8	-0.804
	9	-0.810		9	-0.818
8a	1	-0.731		Avg.	-0.82233
	2	-0.734		S Dev	0.049131
	3	-0.788		S Err	0.007324
	4	-0.729			
	5	-0.735			
	6	-0.785			
	7	-0.746			
	8	-0.755			
	9	-0.798			

Table B3: Black REC Raman Data

Below is Raman band intensity data for the Black REC samples. The five peaks investigated were 1730cm⁻¹ (a), 1600cm⁻¹ (b), 1440cm⁻¹ (c), 1350cm⁻¹ (d), and 1260cm⁻¹ (e). Six measurements (column 1: 1-6) were taken from different locations on each panel which were averaged together (Avg.) for final comparison. Standard error bars come from the Error Bar row.

a)	1730cm-1					
	0hr	4hr	6hr	8hr	12hr	
1	645	865	844	803	746	
2	643	845	824	781	747	
3	600	802	780	774	731	
4	576	670	750	749	739	
5	589	652	705	734	752	
6	577	646	694	723	713	
Avg.	605	747	766	761	738	
Stdev	29	93	56	28	13	
Error Bars	8	46	23	11	5	

b)	1600cm-1					
	0hr	4hr	6hr	8hr	12hr	
1	1223	1013	861	838	707	
2	1194	1016	857	824	694	
3	1127	964	858	782	694	
4	1141	853	804	746	649	
5	1129	813	791	709	634	
6	1103	750	762	715	640	
Avg.	1153	902	822	769	670	
Stdev	42	102	39	50	29	
Error Bars	12	51	16	20	12	

Table B3 Continued: Black REC Raman Data

c)	1440cm-1				
	0hr	4hr	6hr	8hr	12hr
1	2066	2351	2442	2322	2226
2	2074	2328	2421	2291	2211
3	2014	2207	2324	2281	2155
4	2010	1975	2259	2271	2154
5	1985	1974	2128	2226	2145
6	1981	1969	2100	2171	2031
Avg.	2022	2134	2279	2260	2154
Stdev	36	167	132	49	63
Error Bars	10	84	54	20	26
d)	1350cm-1				
	0hr	4hr	6hr	8hr	12hr
1	1826	1587	1413	1413	1249
2	1794	1582	1412	1393	1252
3	1733	1530	1404	1356	1196
4	1724	1466	1392	1340	1203
5	1729	1482	1378	1292	1210
6	1700	1414	1344	1279	1198
Avg.	1751	1510	1391	1346	1218
Stdev	44	63	24	49	23
Error Bars	13	31	10	20	10
e)	1260cm-1				
	0hr	4hr	6hr	8hr	12hr
1	2031	1843	1761	1694	1594
2	1990	1844	1759	1662	1552
3	1947	1820	1700	1630	1534
4	1934	1792	1667	1614	1527
5	1930	1780	1651	1564	1518
6	1905	1762	1625	1549	1475
Avg.	1956	1807	1694	1619	1533
Stdev	42	31	52	51	36
Error Bars	12	16	21	21	15

Table B4: Clear REC FT-IR Data

Below is the Clear REC vibration band intensity data for 3 distinct wavenumbers 1720cm⁻¹ (a), 1227cm⁻¹ (b), and 1160cm⁻¹ (c). There are 3 measurements from 4 different panels for the 0hr and 3 measurements from 2 different panels from each exposure time. The values are averaged together to get an idea of the chemical composition of the entire surface.

a)	1720cm-1				
	0hr	4hr	6hr	8hr	12hr
1	0.36	0.347	0.347	0.34	0.337
2	0.358	0.347	0.344	0.338	0.335
3	0.357	0.347	0.34	0.335	0.335
4	0.355	0.342	0.338	0.331	0.334
5	0.355	0.3493	0.338	0.329	0.332
6	0.355	0.3428	0.335	0.326	0.332
7	0.354				
8	0.354				
9	0.354				
10	0.35				
11	0.347				
12	0.339				
Avg.	0.35317	0.34585	0.340333	0.333167	0.334167
Stdev	0.00537	0.002582	0.004028	0.004947	0.001772
Error Bars	0.00155	0.001291	0.001644	0.00202	0.000723

Table B4 (Continued): Clear REC FT-IR Data

b)	1227cm-1				
	0hr	4hr	6hr	8hr	12hr
	0.292	0.284	0.284	0.28	0.279
	0.29	0.284	0.282	0.278	0.278
	0.2897	0.284	0.282	0.276	0.277
	0.287	0.283	0.28	0.275	0.277
	0.287	0.288	0.279	0.273	0.277
	0.286	0.286	0.278	0.267	0.276
	0.286				
	0.2855				
	0.285				
	0.285				
	0.2835				
	0.283				
	0.282				
Avg.	0.2863	0.2838	0.2808	0.2748	0.2773
Stdev	0.0028	0.0017	0.0020	0.0041	0.0009
Error Bars	0.0008	0.0008	0.0008	0.0017	0.0004
c)	1160cm-1				
	Unexposed	4hr	6hr	8hr	12hr
	0.351	0.347	0.344	0.335	0.332
	0.347	0.3415	0.342	0.333	0.331
	0.347	0.3415	0.338	0.33	0.331
	0.345	0.34	0.336	0.33	0.329
	0.345	0.344	0.336	0.326	0.328
	0.345	0.34	0.332	0.322	0.327
	0.344				
	0.343				
	0.343				
	0.343				
	0.34				
	0.339				
	0.339				
Avg.	0.3439	0.3423	0.3380	0.3293	0.3297
Stdev	0.0033	0.0025	0.0040	0.0043	0.0018
Error Bars	0.0009	0.0012	0.0016	0.0018	0.0007

APPENDIX C

Statistical Calculations

Table C1: Black REC SKP Statistical Comparison

The data below represents the Paired Students T-Test comparison between different treatments. The exposures being compared are denoted by a header (ex. 4 vs 6) showing that the 4 hour is being compared to the 6 hour exposure. This is done by taking the sections in Table B1 and solving for the difference between the 2 sections (D) and the difference squared (D²) for two different exposure times at a given peak. The t-values calculated using these differences is used to calculate a p-value. If the p-value is below .05 then the two data sets are likely not equal to each other (shown in green).

	4 vs 6		6 vs 0		6 vs 8		8 vs 12	
Section	D	D ²	D	D ²	D	D ²	D	D ²
1	0.0529	0.0028	0.0564	0.0032	0.1195	0.0143	0.2663	0.0709
2	0.1008	0.0102	0.0219	0.0005	0.1404	0.0197	0.2654	0.0704
3	0.0783	0.0061	0.0469	0.0022	0.1214	0.0147	0.2790	0.0778
4	0.0000	0.0000	0.1218	0.0148	0.0731	0.0053	0.2700	0.0729
5	0.0971	0.0094	0.0610	0.0037	0.1177	0.0139	0.2701	0.0730
6	0.0772	0.0060	0.0450	0.0020	0.1220	0.0149	0.3048	0.0929
7	-0.0025	0.0000	0.1225	0.0150	0.0975	0.0095	0.2870	0.0823
8	0.0520	0.0027	0.1150	0.0132	0.0988	0.0098	0.2803	0.0785
9	0.0642	0.0041	0.0634	0.0040	0.1253	0.0157	0.2884	0.0832
Sum	0.5200	0.0413	0.6539	0.0587	1.0158	0.1178	2.5114	0.7021
T	4.61769		5.829813		17.06298		65.02358	
P	0.001715		0.000392		1.41E-07		3.48E-12	

Table C2: Clear REC SKP Statistical Comparison

Here the work function data from one exposure time is compared to another using the Paired Students T-Test. The exposures being compared are denoted by a header (ex. 4 vs 6) showing that the 4 hour is being compared to the 6 hour exposure. This is done by taking the sections in Table B2 and solving for the difference between the 2 sections (D) and the difference squared (D²). The t-values calculated using these differences is used to calculate a p-value. If the p-value is below .05 then the two data sets are likely not equal to each other (shown in green).

4 vs 6	D	D ²	6 vs 8	D	D ²	8 vs 12	D	D ²
1	-0.0439	0.001924	1	0.1454	0.021150	1	0.0020	0.000004
2	-0.0152	0.000230	2	0.1145	0.013110	2	-0.0061	0.000037
3	-0.0129	0.000166	3	0.0711	0.005049	3	0.0013	0.000002
4	-0.0254	0.000646	4	0.1217	0.014806	4	0.0666	0.004440
5	0.0014	0.000002	5	0.0795	0.006328	5	0.0479	0.002291
6	0.0063	0.000040	6	0.0615	0.003779	6	0.0169	0.000285
7	-0.0364	0.001323	7	0.1040	0.010806	7	0.1070	0.011445
8	0.0024	0.000006	8	0.0785	0.006155	8	0.0843	0.007113
9	0.0060	0.000036	9	0.0613	0.003761	9	0.0556	0.003088
10	0.0661	0.004365	10	0.0676	0.004568	10	0.0727	0.005281
11	0.0877	0.007689	11	0.0617	0.003809	11	0.0411	0.001692
12	0.1451	0.021050	12	0.0130	0.000170	12	0.0216	0.000465
13	0.0803	0.006443	13	0.0228	0.000521	13	0.1022	0.010443
14	0.0987	0.009746	14	0.0379	0.001438	14	0.0425	0.001802
15	0.1601	0.025622	15	0.0108	0.000116	15	-0.0171	0.000293
16	0.0899	0.008078	16	-0.0123	0.000151	16	0.0689	0.004748
17	0.1124	0.012635	17	-0.0269	0.000721	17	0.0534	0.002854
18	0.1440	0.020747	18	-0.0268	0.000720	18	-0.0077	0.000060
Sum	0.8667	0.1207	Sum	0.9853	0.0972	Sum	0.7529	0.0563
T	2.9964		T	4.6056		T	4.6420	
P	0.008116		P	0.000252		P	0.000233	

Table C3: Black REC Raman Statistical Comparison

Raman vibration band data from one exposure time is compared to another for five different peaks 1730cm⁻¹ (a), 1600cm⁻¹ (b), 1440cm⁻¹ (c), 1350cm⁻¹ (d), and 1260cm⁻¹ (e) using the Paired Students T-Test. This is done by taking the sections in Table B3 and solving for the difference between the 2 sections (D) and the difference squared (D²) for two different exposure times. The t-values calculated using these differences is used to calculate a p-value. If the p-value is below .05 then the two data sets are likely not equal to each other (shown in green). The red highlight signifies that the results were not statistically different.

a.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	-220	48400	21	441	41	1681	57	3249
	-202	40804	21	441	43	1849	34	1156
	-202	40804	22	484	6	36	43	1849
	-94	8836	-80	6400	1	1	10	100
	-63	3969	-53	2809	-29	841	-18	324
	-69	4761	-48	2304	-29	841	10	100
Sum	850	147574	117	12879	33	5249	136	6778
T	4.7085		1.0375		0.4232		2.0423	
p	0.0053		0.3470		0.6897		0.0966	
b.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	210	44100	152	23104	23	529	131	17161
	178	31684	159	25281	33	1089	130	16900
	163	26569	106	11236	76	5776	88	7744
	288	82944	49	2401	58	3364	97	9409
	316	99856	22	484	82	6724	75	5625
	353	124609	-12	144	47	2209	75	5625
Sum	1508	409762	476	62650	319	19691	596	62464
T	7.850164		2.754401		5.57		9.527041	
p	0.000539		0.0401		0.002563		0.000216	

Table C3 Continued: Black REC Raman Statistical Comparison

c.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	285	81225	91	8281	120	14400	96	9216
	254	64516	93	8649	130	16900	80	6400
	193	37249	117	13689	43	1849	126	15876
	35	1225	284	80656	-12	144	117	13689
	11	121	154	23716	-98	9604	81	6561
	12	144	131	17161	-71	5041	140	19600
Sum	790	184480	870	152152	112	47938	640	71342
T	2.542362		4.925216		0.48		10.53521	
p	0.051745		0.004378		0.65315		0.000133	
d.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	239	57121	174	30276	0	0	164	26896
	212	44944	170	28900	19	361	141	19881
	203	41209	126	15876	48	2304	160	25600
	258	66564	74	5476	52	2704	137	18769
	247	61009	104	10816	86	7396	82	6724
	286	81796	70	4900	65	4225	81	6561
Sum	1445	352643	718	96244	270	16990	765	104431
T	19.36747		6.450953		3.54		8.411064	
p	6.77E-06		0.001332		0.016513		0.000389	
e.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	188	35344	82	6724	67	4489	100	10000
	146	21316	85	7225	97	9409	110	12100
	127	16129	120	14400	70	4900	96	9216
	142	20164	125	15625	53	2809	87	7569
	150	22500	129	16641	87	7569	46	2116
	143	20449	137	18769	76	5776	74	5476
Sum	896	135902	678	79384	450	34952	513	46477
T	17.85158		11.75978		11.85		9.156919	
p	1.01E-05		7.82E-05		0.00008		0.00026	

Table C4: Clear REC FT-IR Statistical Comparison

FT-IR peak intensity data from one exposure time is compared to another for three different peaks 1720cm⁻¹ (a), 1227cm⁻¹ (b), and 1160cm⁻¹ (c), using the Paired Students T-Test. This is done by taking the sections in Table B4 and solving for the difference between the 2 sections (D) and the difference squared (D²). The t-values calculated using these differences is used to calculate a p-value. If the p-value is below .05 then the two data sets are likely not equal to each other (shown in green). The red highlight signifies that the results were not statistically different.

a.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	0.0130	0.0002	0.0000	0.00000	0.0070	0.00005	0.0030	0.00001
	0.0110	0.0001	0.0030	0.00001	0.0060	0.00004	0.0030	0.00001
	0.0100	0.0001	0.0070	0.00005	0.0050	0.00003	0.0000	0.00000
	0.0130	0.0002	0.0040	0.00002	0.0070	0.00005	-0.0030	0.00001
	0.0057	0.0000	0.0113	0.00013	0.0090	0.00008	-0.0030	0.00001
	0.0122	0.0001	0.0078	0.00006	0.0090	0.00008	-0.0060	0.00004
Sum	0.0649	0.0007	0.0331	0.00026	0.0430	0.00032	-0.0060	0.00007
T	9.5696		3.3798		10.9574		-0.6742	
p	0.0000		0.0181		0.0001		0.5301	
b.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	0.0080	0.00006	0.0000	0.00000	0.0040	0.00002	0.0010	0.00000
	0.0060	0.00004	0.0020	0.00000	0.0040	0.00002	0.0000	0.00000
	0.0057	0.00003	0.0020	0.00000	0.0060	0.00004	-0.0010	0.00000
	0.0040	0.00002	0.0030	0.00001	0.0050	0.00003	-0.0020	0.00000
	-0.0010	0.00000	0.0090	0.00008	0.0060	0.00004	-0.0040	0.00002
	0.0000	0.00000	0.0080	0.00006	0.0110	0.00012	-0.0090	0.00008
Sum	0.0227	0.00015	0.0240	0.00016	0.0360	0.00025	-0.0150	0.00010
T	2.598234		2.696799		5.64		-1.69192	
p	0.048353		0.042948		0.00244		0.151446	
c.	D	D ²	D	D ²	D	D ²	D	D ²
	0 vs 4	0 4 ^2	4 vs 6	0 4 ^2	6 vs 8	0 4 ^2	8 vs 12	0 4 ^2
	0.0040	0.00002	0.0030	0.00001	0.0090	0.00008	0.0030	0.00001
	0.0055	0.00003	-0.0005	0.00000	0.0090	0.00008	0.0020	0.00000
	0.0055	0.00003	0.0035	0.00001	0.0080	0.00006	-0.0010	0.00000
	0.0050	0.00002	0.0040	0.00002	0.0060	0.00004	0.0010	0.00000
	0.0010	0.00000	0.0080	0.00006	0.0100	0.00010	-0.0020	0.00000
	0.0050	0.00002	0.0080	0.00006	0.0100	0.00010	-0.0050	0.00003
Sum	0.0260	0.00013	0.0260	0.00017	0.0520	0.00046	-0.0020	0.00004
T	6.162591		3.265342		14.10		-0.27735	
p	0.001637		0.022313		0.00003		0.79265	