Nanomechanical and nano-FTIR analysis of polyester coil coatings before and after artificial weathering experiments

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ABSTRACT

Local heterogeneities can have significant effects on the performance of anti-corrosion coatings. Even small features can act as initiation points for damage and result in corrosion of the substrate material. Analysis methods with high spatial resolution and the ability to collect information relevant to crosslinking and degradation behavior of these coatings are therefore highly relevant. In this work, we demonstrate the utility of nanomechanical AFM measurements and nano-FTIR in investigating the nanoscale mechanical and chemical properties of two polyester coil coating clearcoats before and after weathering. On the nanoscale, weathering led to a stiffer and less deformable coating with less variation in the nanomechanical properties. Chemical degradation was quantified using changes in band ratios in the IR-spectra. Macro and nano-scale measurements showed similar trends with the latter measurements showing larger heterogeneity. Our results demonstrate the usefulness of the described analysis techniques and will pave the way for future studies of local properties in other coating systems and formulations.

1. Introduction

Coating materials designed to withstand aggressive environments are necessary in many applications where metallic substrates that are sensitive to corrosion are used in harsh environments. To be able to compare already available coating formulations and to aid in the development of new ones, it is necessary to understand and assess different degradation and failure modes. This assessment is often done by analyzing and quantifying optical properties of a coating such as gloss and color change [1–3] and mechanical properties when the material is exposed to mechanical and/or thermal stress [1,4,5]. In addition, it is also common to determine barrier properties and corrosion rate using electrochemical impedance spectroscopy [6], or chemical properties through the use of e.g. infrared spectroscopy [3,6,7]. New ways of quantifying chemical and physical changes to predict the performance of coatings is an area of both academic and industrial interest.

Coil coatings are durable and widely used organic coatings applied onto steel and aluminum substrates in highly optimized continuous processes. It is used both to prevent corrosion of the substrate materials as well as for aesthetic reasons, providing colors and textures to the surface. This study focuses on the outermost part of a coil coating, the topcoat, which is designed to protect the underlying parts of the system and remain stable in aggressive environments. A commercial system is often complex, consisting of many components, such as structural agents (to improve the mechanical properties), pigmentation (to add coloration), and diluents (to improve the viscosity and mixing properties of the uncured system). However, to differentiate between different groups of coil coatings it is common to group them by resin and crosslinking agent. Some of the most widely used resin and crosslinking agent combinations are polyester melamine and polyester isocyanate. Polyester isocyanate is

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also called polyurethane (PUR) due to the urethane bonds formed during crosslinking.

The polymer network which provides structural integrity to an organic coating is unlikely to form in an ideal manner on the nanoscale. This can lead to the creation of different heterogeneities that affect coating durability and performance. As shown by molecular dynamic simulations [8,9], crosslinked networks with multifunctional precursors can have a significant number of topological imperfections, such as dangling ends or loops, when formed using crosslinkers with high functionality. Even voids can occur during formation of crosslinked networks, and these can have severe negative consequences for the end-use properties of such materials and their long-term performance and durability.

Initiation of damage on coil coatings has been reported to start at the nanoscale, with only very small regions affected [10,11]. A well-established method of analyzing areas with a resolution at the scale of nanometers is scanning probe microscopy (SPM) [10,12-14]. Basically, SPM techniques are based on a sharp tip at the end of a cantilever that probes a sample surface. By closely monitoring the interactions between the tip and the sample, it is possible to quantify surface properties such as topography, stiffness, as well as elastic properties. Multiple inventions and improvements have advanced the original technique, primarily designed to capture the topography [15]. Two examples with applications in coatings technology include the analysis of mechanical properties on the nanoscale using atomic force microscopy (AFM), as pioneered by Colton and Burnham [16], and nanoscale chemical analysis based on infrared (IR) spectroscopy [17,18].

Quantification of nanomechanical properties is done by monitoring the deflection of the AFM-cantilever as it approaches and deforms a sample surface, whilst controlling the applied mechanical force. Using the resulting deflection and force-position curve is it possible to extract properties such as surface stiffness, maximum material deformation, and apparent surface elastic modulus [19]. By monitoring the distance dependence of attractive tip-sample forces it is possible to distinguish between, e.g., van der Waals, bridging, and capillary interactions. Van der Waals forces are more short ranged than the other two forces mentioned. Bridging attraction caused by loose polymer chains at the surface sticking to the tip, and capillary attraction caused by the formation of an air or vapor condensate have a more complex deflection-position dependence. Bridging attraction often gives rise to a force curve showing saw-tooth features on separation [20,21]. These features are caused by successive losses of polymer attachment points to the tip as the distance between the tip and sample increases [21]. Similarly, capillary forces can also give rise to saw tooth features if the contact line moves across the sample surface but if the three-phase contact line is pinned, a smoothly decaying attraction on separation results in a smoother force curve [22,23]. In addition to the shape of the separation curve, a characteristic discontinuity, with a sudden jump to zero force is typically observed as the capillary breaks [24,25]. These technique advances make it possible to, for example, use an AFM to e.g. determine exact locations of local phases in materials such as electronic semiconductors [26], explore interphases between particles and a polymer matrix in nanocomposites [27], and to quantify local wear properties [28].

FTIR (Fourier transform infrared) spectroscopy is a well-established technique that has been used for assessment of degradation of organic coatings [1,29,30]. It is also relatively easy to quantify the degradation in coil coatings by determining the percentual increase or decrease of relative band ratios [23,30-32]. However, for most IR-based optical spectroscopic methods, the lateral resolution is restricted by the diffraction limit [33,34]. Thus, IR spectroscopy is primarily used for assessment of global degradation. However, local degradation may also have severe negative consequences for coating systems. This makes the recently developed nanoscale infrared analysis group of techniques very promising for coatings science research aiming at understanding nanoscale events. Although there are several ways to acquire nanoscale infrared information a method based on s-SNOM, nano-FTIR spectroscopy, is one of the most well explored [17,35,36]. During nano-FTIR measurements, a laser beam is focused on a noble metal coated AFM tip close to the sample surface, and the backscattered light from the tip is detected. This light contains information on the near field interaction between the tip and the sample, and can be translated into nano-FTIR absorption, which has been shown to closely correlate with macroscale FTIR spectra [17,37].

A few works have been published analyzing heterogeneities caused by coating degradation at the nanoscale. Nguyen et al. 2013 showed the formation and growth of μm and mm scale pits in model coating formulations after accelerated weathering using various combinations of humidity, UV dosage, and elevated temperatures [38]. They proposed the Nguyen-model that suggests that the coatings analyzed are chemically heterogeneous, consisting of hydrophilic domains interdispersed with crosslinked units.

Biggs et al. 2001 investigated the surface roughness on areas of 40 × 40 μm and larger for pigmented polyester melamine systems [13]. They found that the surface roughness increased with longer weathering times. They suggested that the increase was related to removal of the outer coating layer, which in turn exposed hard pigments that became exposed at the surface and even fell out of the coating.

Morsch et al. 2022 examined local oxidation surrounding buried interphases around iron oxide particles in epoxy amide coatings [39]. To achieve this, they used a microtome to prepare thin slices of a coating and quantified carbonyl and imine bands at buried interphases. They concluded that the interphases showed signs of degradation before the bulk material during mild thermal aging. Their results agreed with a commonly reported diffusion limited oxidation mechanism, where reaction initiation and kinetics at the buried interphase are controlled by local oxygen transport. In addition, Morsch et al. 2015 used AFM-IR to map the local degree of curing, as well as local water sorption in epoxy phenolic coatings [40]. They found that regions of higher cross-linking density displayed increased water uptake, which was in line with earlier research showing that higher global water uptake was correlated with a higher amount of free volume found in more highly cross-linked polymer networks.

He et al., 2018 analyzed the effect of curing time and saltwater exposure on nanomechanical and nanowear properties of an acrylic melamine coating [14]. They found that the exposure did not seem to greatly change the nanomechanical or wear properties. They also determined that the samples with a shorter curing time displayed signs of low molecular compounds migrating to the surface after long term saltwater exposure.

The investigation presented here aims at further the understanding of weathering effects on local mechanical properties and chemical effects at the initial stages of degradation in two clearcoat coil coating systems, polyester melamine and polyester isocyanate (PUR). To this end, AFM, Nano-FTIR and ATR-IR (attenuated total reflection IR spectroscopy) were utilized to study the coating before and after xenon arc exposure.

2. Experimental

2.1. Materials

In this work, pigment free coil coating systems based on aromatic polyester and cured using of two different crosslinking agents were prepared and analyzed. The first system contained hexa(methoxymethyl)melamine (HMMM) in a polyester:crosslinker ratio of 85:15. The curing reaction was catalyzed with dodecylbenzenesulfonic acid (DBBSA). The second system was a polyester urethane system, crosslinked with tri-functional caprolactam blocked hexamethylene diisocyanate (HDI) with a cyclic trimer (CT) core at a ratio of 80:20 and catalyzed with monobutyltin oxide. The molecular structures of the two crosslinkers and how they are bonded to the polyester matrix after
crosslinking are shown in Fig. 1. Each HMMM has six available OH-groups whereas each HDI CT has three caprolactam groups that can be displaced during crosslinking.

The systems were applied onto a hot dipped galvanized (HDG) steel panel using a wire rod. Before being coated, the panel was covered with a thin film primer based on polyester/acrylic polymers with melamine crosslinking and ion exchange anti corrosive pigments. Non-weathered reference samples were rinsed with n-heptane and dried in ambient conditions in a fume hood for at least one week before measurements to remove any remains of uncured material and allow for complete evaporation of any remaining heptane.

Additional samples were manufactured in the form of free coating films by wire rod application onto Teflon covered substrates. After curing the resulting films could be removed from the substrate.

Both systems were cured for 34 s to a peak metal temperature (PMT) of between 232 and 249 ºC to achieve high crosslinking without overcuring.

2.2. Accelerated weathering conditions

Accelerated weathering was performed in a Q-sun Xe-3 Xenon arc test chamber equipped with a Daylight-Q filter, providing a light spectrum with relative wavelength intensities designed to mimic that received from the sun. The samples were weathered in accordance with ISO 4892-2 method A cycle number 1 [43]. This recurring cycle consists of 102 min of dry irradiance from a Xe-arc lamp with a Daylight Q filter, followed by 18 min of water spray. During the dry period the black panel temperature was calibrated to 63 ºC, the relative humidity 50 ± 3 %, and the irradiance to a narrowband intensity of 0.51 W/(m² × nm) at a wavelength of 340 nm. This corresponds to approximately 60 W/m² in the wavelength range 300–400 nm, the part of the electromagnetic spectrum meant to simulate UV radiation at ground level. The ambient temperature was kept at 38 ± 3 ºC. FTIR-ATR analysis was performed after 249, 521, 1026, 2078, and 4138 h of exposure. Nanomechanical and nano-FTIR analysis were performed after 2078 h as the degradation was deemed severe enough to be easily quantified, but still low enough to not show any large-scale visual defects. 2078 h is referred to as 2000 h throughout the rest of the text.

2.3. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed in tensile mode on free-standing films using a TA Instruments DMA Q800. The sample geometry was approximately 10 × 9.0 × 0.025 mm. The films were analyzed at a constant frequency of 1 Hz, with the strain set to 0.2 % of the sample length. Initially, the films were equilibrated at −10 ºC for 5 min, after which they were subjected to a temperature ramp with a heating rate of 3 ºC/min up to 70 ºC, or the point at which the sample stiffness decreased to below 100 N/m, the sensitivity level of the instrument. The measurements were performed in triplicates. The glass transition temperature (Tg) was evaluated at the maximum of the loss factor (tan δ) curve, in accordance with Schlesing et al. [44].

2.4. Nanomechanical measurements

Topography and nanomechanical properties were measured at 22 ºC and a relative humidity of approximately 45 % using a JPK NanoWizard 3 (JPK Instruments AG, Germany) AFM system. Measurements were performed in the quantitative imaging mode (QI) mode. A DLC300 probe from Budget Sensors with a measured 46 N/m spring constant and tip outer radius of 15 nm was used. The tip radius was determined via an indirect method where the known elastic modulus of polystyrene was evaluated by applying the DMT (Derjagin, Muller, Toropov) model to compression-decompression force curves [45].

The imaging force used during the measurements was 75 nN. Three 1 × 1 μm areas were examined for each sample at a resolution of 256 × 256 pixels and a dwelling time of 1.2 milliseconds in each pixel.

The vertical deflection of the tip of the AFM cantilever was determined as a function of separation at each pixel during compression and decompression of the surfaces. From the shape of such deflection curves several nanomechanical properties can be calculated as illustrated in Fig. 2. Far away from the surface of the sample, when there is no tip-surface interaction, the deflection is zero. As the tip approaches the sample but before it makes contact, attractive forces pull the cantilever towards the surface, causing negative deflection. As the tip gets closer to the surface, the total force becomes less attractive as repulsive force contributions come into play. The formal contact between the tip and the surface is defined as the position where the deflection has returned

![Fig. 1. Molecular structure of hexa(methoxymethyl)melamine (HMMM) before and after crosslinking into a polyester resin are shown at the top left and top right respectively. Caprolactam blocked hexamethylene diisocyanate (HDI) with a cyclic trimer (CT) before and after crosslinking are shown at the bottom left and bottom right respectively [41,42].](image1)

![Fig. 2. A schematic illustration of the tip-sample force curves recorded on compression (dashed line) and decompression (solid line).](image2)
to zero, even though tip-sample contact may occur before this point. As the force from the cantilever compresses the material the vertical deflection force increases. The stiffness of the material is evaluated as the slope of the deflection curve as it approaches the maximum applied force. The deformation of the material at the maximum force is evaluated as shown in Fig. 3, and it is a measure of how deformable the material is. After the point at which maximum force is reached, the applied force is decreased, and the material starts to decompress. There is often a hysteresis between the compression and decompression curves, which is due to a viscoelastic, rather than elastic, response of the material. The tip-sample adhesive force is defined as the magnitude of the force minimum observed during decompression. After the force minimum is passed, the deflection returns to the zero-point in a manner that depends on the nature of the attractive tip-sample interaction. We note that the tip only deforms the material surface by a few nanometers, and thus the mechanical properties reflect those of the surface region of a few nanometers thickness. In this study each compression-decompression cycle took approximately 1.2 milliseconds, and the measurements were performed at room temperature. This is well below the setup works in tapping mode and provides the surface topography and the nano-FTIR spectra acquisition. AFM tips were acquired from Neaspec, Attocube systems AG and were made of Pt/Ir coated silicon. The nominal tip diameters were approximately 50 nm and the resonance frequencies were 240–380 kHz. The tapping amplitude was kept close to 60 nm during acquisition of nano-FTIR spectra.

The nano-FTIR spectra were acquired using a broadband femtosecond laser with a repetition frequency of 80 MHz, a spectral range of 650–2200 cm$^{-1}$, and an output power of ca. 1 mW. The working range used to acquire spectra was 1100–1800 cm$^{-1}$. Each spectrum was collected using an average of 10 scans and a 9.8 ms integration time per scan at a spectral resolution of 12 cm$^{-1}$. Background normalization of the nano-FTIR spectra were made using a silicon surface test grating TGQ1 from NT-MDT spectrum systems.

Three different areas of 1 × 1 μm on each sample were analyzed, and between three and six spectra were measured on each area on topographically different locations.

### Results and discussion

#### 2.5. FTIR-ATR

FTIR-ATR measurements were performed using a Bruker Vertex 70 spectrometer. The instrument was equipped with a Specac Quest ATR accessory with a replaceable diamond internal reflective element (IRE) with a reflective index of 2.419 and a reflection angle of 45°. For each examined exposure time, three measurements were performed on different sites across the samples. Background spectra were collected using 512 scans and sample measurements were performed using 256 scans, both at a resolution of 4 cm$^{-1}$ in the wavenumber region 380–8000 cm$^{-1}$.

Baseline correction, normalization, as well as peak area and intensity calculations were carried out in Orange Quasar spectroscopy module version 1.7.0 [46,47]. The figures showing the O–H and N–H stretching region are normalized to area of the bands at 2700–3130 cm$^{-1}$, assigned to the stretching of CH$_2$ and CH$_3$ bonds. The figures showing the fingerprint region were normalized to the intensity of the band centered around 1375 cm$^{-1}$, assigned to in-chain CH$_2$ and CH$_3$ deformations, with additional contributions from the triazine ring [48–50]. This band has previously been deemed stable and used to normalize bands in the polymer fingerprint region [34,49]. The overview, showing the entire range 400–4000 cm$^{-1}$ are vector normalized with respect to the entire area under the spectral curve.

#### 2.6. Nano-FTIR

The nano-FTIR spectroscopy analyses were carried out with a scattering-type scanning near-field optical microscope (s-SNOM) from Neaspec, Attocube systems AG (Germany). The AFM microscope part of the setup works in tapping mode and provides the surface topography and the nano-FTIR spectra acquisition. AFM tips were acquired from Neaspec, Attocube systems AG and were made of Pt/Ir coated silicon. The nominal tip diameters were approximately 50 nm and the resonance frequencies were 240–380 kHz. The tapping amplitude was kept close to 60 nm during acquisition of nano-FTIR spectra.

The nano-FTIR spectra were acquired using a broadband femtosecond laser with a repetition frequency of 80 MHz, a spectral range of 650–2200 cm$^{-1}$, and an output power of ca. 1 mW. The working range used to acquire spectra was 1100–1800 cm$^{-1}$. Each spectrum was collected using an average of 10 scans and a 9.8 ms integration time per scan at a spectral resolution of 12 cm$^{-1}$. Background normalization of the nano-FTIR spectra were made using a silicon surface test grating TGQ1 from NT-MDT spectrum systems.

Three different areas of 1 × 1 μm on each sample were analyzed, and between three and six spectra were measured on each area on topographically different locations.

### Results and discussion

#### 3.1. Dynamic mechanical analysis

Results from dynamic mechanical analysis (DMA) allowed for the determination of the viscoelastic properties of the coatings in the form of free-standing films. One representative tan δ plot from each sample is presented in Fig. 3. Storage modulus plots are reported in Fig. S1 in the Supplementary material. The tan δ is the ratio of loss modulus to storage modulus, respectively representing the viscous and the elastic part of the sample’s response to the oscillatory stress. The values of the glass transition temperature ($T_g$), defined as the temperature of the tan δ peak maximum, along with the tan δ peak height are reported in Table 1.

A clear difference in $T_g$(8 °C) was observed for the two formulations. It is evident that the formulation containing HM MMM as the crosslinker resulted in a more rigid material, which can be partly correlated to a higher crosslink density. Additional factors affecting the viscoelastic properties of the two different coating systems are the plausible presence of hydrogen bonding, well-known to exist in polyester–isocyanate coatings, as well as aromatic stacking in polyester melamine coatings, and longer flexible chains in the case of the polyester isocyanate coating system [51,52].

Further conclusions about the macromolecular structure of the crosslinked networks can be deduced from the analysis of the tan δ versus temperature curve (Fig. 3 and Table 1). Lower values of the tan δ peak height, as in the case of the polyester melamine coating system, are associated with lower damping of the material during mechanical oscillations, in the temperature range of the glass transition [53]. This observation is in agreement with the increase in $T_g$, again indicating that segmental motions in the crosslinked network of the polyester melamine are more restricted than in the polyester isocyanate.

Finally, a higher storage modulus (and thus higher stiffness) can be observed for the polyester melamine compared to the polyester isocyanate coating system in the temperature range 20–50 °C. This is shown in the Supplementary Fig. S1.

In summary, DMA indicates that the polyester melamine formulation

### Table 1

<table>
<thead>
<tr>
<th>Coating</th>
<th>$T_g$ (°C)</th>
<th>tan δ peak height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester melamine</td>
<td>44 ± 1</td>
<td>1.34 ± 0.07</td>
</tr>
<tr>
<td>Polyester isocyanate</td>
<td>36 ± 2</td>
<td>1.77 ± 0.03</td>
</tr>
</tbody>
</table>
gave rise to a more rigid crosslinked network as compared to polyester isocyanate. The results corroborate well with previous observations where a higher $T_g$ and lower tan $\delta$ peak height have been related to thermosets with increased rigidity, often exhibiting a higher crosslink density [53–55].

3.2. Nanomechanical measurements

3.2.1. Polyester melamine

AFM maps showing the topography, stiffness, maximum deformation, and adhesion of two areas across the surfaces of the polyester melamine samples are reported in Fig. 4. One area is from the non-weathered reference sample and the other area from the sample exposed to 2000 h of Xe arc weathering. In addition, histograms showing the distribution of these measured properties are shown to the right. Weathering of the samples results in a homogenization of both topography mechanical properties. This can be seen in the topography, stiffness, and deformation histograms in rows 1–3, where exposure causes an increase in relative frequency of the median value and a narrower distribution of values. Qualitatively, the unweathered reference sample shows two distinct domains in the stiffness and deformation maps, with a softer and more easily deformed area on the left side of the maps. There is also an area to the right with lower adhesion correlating with areas of higher stiffness.

Table 2 and Table 3 report the RMS surface roughness, as well as the arithmetic mean stiffness, maximum deformation at 75 nN force, and tip-sample adhesion for three different $1 \times 1 \mu m$ areas, denoted i, ii, and iii for the polyester melamine samples. The standard deviation within
each area as well as the total standard deviation across the three areas are shown. These data confirm that the local (1 × 1 μm²) nanoscale surface roughness, deformation, and adhesion are reduced with weathering whereas the stiffness increases. In polyester urethane systems, an increase in macro-scale stiffness has been attributed to an increase in the amount of hydrogen bonding and formation of polar groups during weathering [56,57]. It is reasonable to assume that similar reasoning could be used to explain an increase in local stiffness. Note that the stiffness and deformation values are closely related, and an increased stiffness is associated with a lower deformation. The variation in stiffness, deformation and adhesion are smaller for the weathered samples, both within each area and between the different areas.

Since the weathering was performed above Tg, we can speculate that the decrease in surface roughness could be caused by flow in the surface of the material to minimize the surface energy. If the temperature was high enough to allow for a certain flow of the material it is also possible that segregation of species with lower surface energy could have contributed to lowering the adhesion. Stiffness, deformation, as well as adhesion would also be affected by the formation of degradation products. Note that since the material deformation was on the nanometer scale, these properties do not necessarily correlate with changes in the bulk of the material.

Biggs et al. 2001 reported an increase in surface roughness with accelerated UV weathering and suggested that this was due to removal of the comparatively soft coating matrix around harder constituents such as pigments [13]. This was said to cause topographical features in the form of protruding pigments as well as valleys where pigments fell out of the coating. In contrast, our data reported in Fig. 4, as well as in Tables 2 and 3 show a decrease in the surface roughness. However, in our case no harder constituents were present in the analyzed clearcoats. Thus, weakening and subsequent removal of material from the coating surface does not expose hard particles. Instead, the weathering homogenizes the surface, at least locally. It is important to note that surface roughness is highly dependent on the size of the measured area. This is illustrated in the RMS surface roughness of area iii of the weathered polyester melamine sample that has an RMS of 1.8 nm, approximately three times higher as compared to the other two areas. In this case the measurement was done in a valley between two hills, as shown in Fig. 5, which significantly increased the RMS. This suggests a variation in sample height over areas larger than the 1 × 1 μm² sites used in this work. It is important to note that the nanomechanical properties were not affected by these height variations, and thus the data from area iii of the weathered sample align with the mean values from the less curved areas i and ii. The valley-like feature could have been removed by image processing, but such operations have been avoided in this work as it can result in artifacts.

We note that a compression and a decompression force curve is measured at each pixel. As the images consists of 256 × 256 pixels we obtain over 65,000 force curves. Inspection of these force curves show two principle cases. The first set of force curves shows no clear discontinuities whereas the other set displays small sudden changes in force with separation. Representative decompression force curves for these two cases both before and after weathering are shown in Fig. 6. The zero-distance position is defined at the point of maximum attraction.

The difference between the force curves recorded before and after weathering provides evidence that xenon arc exposure causes a change in the nature of the attractive tip-sample forces. The decompression curves for the reference sample show larger variation as compared to the weathered areas. This is also shown for the adhesion maps in Fig. 4 that was extracted from such force curves. We note that the range of the attraction is large, 10–12 nm, which is longer than the measurable range of a van der Waals force that does not reach a value of −1 nN until the distance is <1 nm. Further details on how this was calculated can be found in Eq. (S1) and Fig. S2 in the Supplementary material [58]. The long-range attraction we do observe can be caused by either formation of a condensed water capillary between the tip and sample or by bridging polymer chains. The discontinuities in the force curves, as seen at 13 and 17 nm in the red curve at the top right and marked with arrows, are consistent with both explanations. If a water capillary was formed, breakage of the capillary at large enough separation would lead to a sudden return to zero force. Similarly, bridging polymer chains would lead to one or several discontinuities in the force curve as they detach from the tip [20,21,59]. Thus, the nature of the observed long-range attraction cannot be conclusively determined. However, since the measurements were conducted at ambient humidity and with low tip-surface contact times, we find the most probable cause being bridging polymer chains. For the weathered polyester melamine samples the attraction is reduced to about 5 nm, indicating that any bridging polymer chains would be significantly shorter than before weathering. The changes that have occurred at the surface has led to increased stiffness and a decrease of loose and movable polymeric chains.

We note that the range of the attraction, that reflects how far loose polymer chains can be stretched, is about halved by weathering. In contrast, the adhesion force is much less affected as it depends on the interaction between tip and sample in direct contact. Thus, the adhesion force is affected by the tip-sample contact area, which is slightly decreased due to weathering as a result of the increased surface stiffness and reduced deformation.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>RMS surface roughness (nm)</th>
<th>Stiffness (N/m)</th>
<th>Deformation (nm)</th>
<th>Adhesion (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference i</td>
<td>1.3</td>
<td>38.1 ± 5.8</td>
<td>3.8 ± 1.3</td>
<td>20.1 ± 1.8</td>
</tr>
<tr>
<td>Reference ii</td>
<td>1.8</td>
<td>38.2 ± 6.5</td>
<td>3.9 ± 1.0</td>
<td>19.8 ± 1.4</td>
</tr>
<tr>
<td>Reference iii</td>
<td>2.6</td>
<td>45.1 ± 4.9</td>
<td>2.5 ± 0.5</td>
<td>16.6 ± 2.1</td>
</tr>
<tr>
<td>Mean</td>
<td>1.9 ± 0.5</td>
<td>40.5 ± 10.3</td>
<td>3.4 ± 1.6</td>
<td>18.8 ± 3.3</td>
</tr>
</tbody>
</table>

*a Shown in Fig. 4.*

Table 3

<table>
<thead>
<tr>
<th></th>
<th>RMS surface roughness (nm)</th>
<th>Stiffness (N/m)</th>
<th>Deformation (nm)</th>
<th>Adhesion (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weathered i</td>
<td>0.64</td>
<td>46.5 ± 4.3</td>
<td>2.2 ± 0.2</td>
<td>14.1 ± 1.3</td>
</tr>
<tr>
<td>Weathered ii</td>
<td>0.52</td>
<td>46.0 ± 3.7</td>
<td>2.3 ± 0.2</td>
<td>15.5 ± 1.3</td>
</tr>
<tr>
<td>Weathered iii</td>
<td>1.8</td>
<td>47.6 ± 4.7</td>
<td>2.2 ± 0.2</td>
<td>14.8 ± 1.2</td>
</tr>
<tr>
<td>Mean</td>
<td>1.0 ± 0.6</td>
<td>46.6 ± 7.4</td>
<td>2.3 ± 0.3</td>
<td>14.8 ± 2.2</td>
</tr>
</tbody>
</table>

*a Shown in Fig. 4.*
3.2.2. Polyester isocyanate

AFM maps and histograms of areas from the polyester isocyanate samples before and after weathering are shown in Fig. 7. Like for the polyester melamine samples, weathering results in a less rough, stiffer surface with lower deformation and adhesion. The non-weathered reference area displays multiple features with variations in topography, stiffness, deformation, and adhesion. For example, a stiff protrusion with relatively low adhesion can be found at the top right.

Tables 4 and 5 summarizes the RMS and nanomechanical properties of all analyzed areas of the reference and weathered polyester isocyanate samples. Weathering results in less rough, stiffer, and less deformable surfaces for all areas. However, in contrast to Tables 2 and 3 the mean tip-sample adhesion appears to increase with Xe exposure time. This is unexpected as the surface stiffness is larger and the surface deformation smaller for the exposed sample. Thus, the contact area and adhesion would typically be lower for the exposed sample, as observed for polyester melamine. Weathering is known to cause certain changes in chemical composition in polyester isocyanate coatings, as discussed in Section 3.3, but they are unlikely to cause a decrease in adhesion between the AFM tip and the coating. In addition, surface sensitive nano-

FTIR measurements, as discussed in Section 3.4, do not indicate noticeable contamination in the studied area or any distinct chemical regions. Only regions of higher or lower levels of degradation. Therefore, it seems unlikely that the low adhesion for the weathered sample is due to contamination. Instead, the most likely explanation is that roughness on the nm and sub-nm level decrease the tip-sample contact area and thus also the tip-sample adhesion. We note that such local roughness would not be observed in the topography images as the area per pixel, \( \approx 15 \, \text{nm}^2 \), is at least an order of magnitude larger than the local roughness we discuss above. We note that the other nanomechanical properties determined from the force curves are consistent over all investigated areas. This allows us to reject tip damage or material transfer from the sample to the tip as the reason for the low tip-sample adhesion of the unweathered reference sample.

We note that DMA showed that before weathering polyester melamine was stiffer than polyester isocyanate on the macro-scale. The same trend is observed for the surface stiffness reported by AFM. However, weathering largely remove this difference in surface stiffness values for our two sample types. One potential reason is that while the reaction pathways are complex, multiple similar chemical changes occur in both systems. This is further discussed in the following sections.

Representative force curves for the polyester isocyanate are shown in Fig. 8. Here we also notice similar features as for the polyester melamine. Possible discontinuities indicating capillary breakages or bridging polymer chains can be seen at 14 nm before weathering in the top left image, orange curve. After weathering, similar discontinuities can be seen at around 5 nm from the surface in the bottom right light blue curve. A force curve typical of areas with low adhesion, especially prevalent in area i and ii of the reference samples, is shown in red at the top right.

After weathering, polyester isocyanate and polyester melamine samples have similar surface nanomechanical properties. The force curves also look very similar as illustrated with the light and dark blue decompression curves in the bottom part of Figs. 6 and 8. The dark blue curve at the bottom right of Fig. 8 shows a force curve with no clear jumps or discontinuities. The light blue curve in the bottom right shows a distinct jump at around 6 nm separation, which could both be due to either bridging or capillary forces.

3.3. FTIR-ATR

The increase in stiffness and decrease in deformation as well as homogenization of these nanomechanical quantities suggest that weathering could have caused chemical changes at the coating surface. This was further investigated using FTIR analysis.

FTIR-ATR spectra for the polyester melamine sample and before weathering and after various weathering times are shown in Fig. 9. Each spectrum shown is the average from three different locations. Multiple wide peaks, assigned to O–H and N–H stretching vibrations, are centered around 3300 cm\(^{-1}\), which is close to multiple overlapping peaks assigned to CH\(_2\) and CH\(_3\) stretching vibrations around 2900 cm\(^{-1}\).
The large peak at 1720 cm\(^{-1}\) [4,60,61] is assigned to carbonyl C–O stretching. The band centered around 1550 cm\(^{-1}\) is assigned to the quadrant stretching of the triazine ring in the HMMM, as well as contraction of the exogenous N–H bonds, coupled with CH\(_2\) and CH\(_3\) bending vibrations [50,62].

As the weathering time increases, at least three major changes can be observed:  

Fig. 7. Topography, stiffness, deformation, and adhesion for the polyester isocyanate surfaces. From left to right, the columns show maps for a reference surface, maps after 2000 h of Xenon arc chamber exposure, and the distribution of nanomechanical properties of these two areas. The image areas are 1 × 1 μm\(^2\), and the measurements were done in air.

Table 4  
Mean values for roughness and nanomechanical properties in areas i, ii, and iii, for the polyester isocyanate reference sample.

<table>
<thead>
<tr>
<th></th>
<th>RMS surface roughness (nm)</th>
<th>Stiffness (N/m)</th>
<th>Deformation (nm)</th>
<th>Adhesion (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference i</td>
<td>1.66</td>
<td>32.5 ± 3.9</td>
<td>3.9 ± 0.5</td>
<td>20.7 ± 2.9</td>
</tr>
<tr>
<td>Reference ii</td>
<td>0.94</td>
<td>31.0 ± 2.9</td>
<td>3.9 ± 0.5</td>
<td>5.8 ± 1.7</td>
</tr>
<tr>
<td>Reference iii</td>
<td>0.91</td>
<td>33.5 ± 3.5</td>
<td>3.9 ± 0.6</td>
<td>6.2 ± 1.9</td>
</tr>
<tr>
<td>Mean</td>
<td>1.17 ± 0.35</td>
<td>32 ± 6</td>
<td>3.9 ± 1</td>
<td>10.9 ± 4.9</td>
</tr>
</tbody>
</table>

* Shown in Fig. 7.
seen in the spectra. Firstly, a significant increase in intensity of the wide range of O–H and N–H bands around 3300 cm\(^{-1}\) has been assigned to the formation of carboxylic acids, peresters, primary urethanes, acetyl urethanes, and primary amides [60]. This wide band normalized against the CH\(_2\) peaks around 2900 cm\(^{-1}\) has previously been used to quantify the oxidation of the material and has been denoted the photoxidative index, or oxidation index [4,63,64].

Secondly, a decrease in intensity and broadening of the carbonyl band at 1720 cm\(^{-1}\), as normalized against the band around 1375 cm\(^{-1}\), is seen. In similar coating systems, this broadening has been attributed to the formation of anhydrides, carboxylic acids and aldehydes [65,66]. This broadening and formation of polar groups such as carboxylic acids has also been suggested to increase the amount of hydrogen bonding in the system [67-69]. Note that Bauer 1991, found an increase in the carbonyl band after weathering of acrylic melamine [70]. While a reduction in band intensity could occur due to a decrease in the amount of carbonyl bonds it is more likely due to changes of the chemical surroundings of the bonds. Either in terms of interactions between the functional group and its chemical surrounding, or a reaction that entirely changes the nature of the functional group. A smaller shoulder to the carbonyl band is formed around 1780 cm\(^{-1}\). Multiple peaks around this area have previously been connected to coating photo-degradation and has been attributed to peracids, peresters, γ-lactones, and anhydrides [66,71,72]. The increase in intensity of this shoulder was measured and normalized against the peak around 1375 cm\(^{-1}\). Malanowski correlated an increase in total carbonyl band area, caused by both band broadening and the formation of shoulders, with an increase in macro-scale surface hardness in two tested polyester based coil coating formulations [73]. This is consistent with the increase in surface stiffness found in our study.

Thirdly, the decrease in intensity of the band around 1550 cm\(^{-1}\) is sensitive to changes in the methyol groups attached to the triazine rings and has therefore been widely used to follow the degradation process [6,30,69]. The resulting lowering of the band, when normalized to the C–H bands, has been seen to correlate well with crosslink scission [74]. The peak around 1375 cm\(^{-1}\) assigned to in-chain CH\(_2\) and CH\(_3\) deformations, with additional contributions from the triazine ring [48-50] is relatively stable throughout the weathering procedure, and this peak was used to normalize both the band at 1550 cm\(^{-1}\) and the carbonyl band [34,49].

Especially the changes in the O–H and N–H region, as shown in the bottom left corner in Fig. 9, brought on by moisture, UV, and elevated temperatures has been coupled to an increase in hardness and brittleness in polyester melamine coatings [4,5]. Thus, amide and amine groups, visible in the spectral region 3380–3520 cm\(^{-1}\), are formed together with peroxide and polymeric free radicals respectively. Especially the polymeric free radicals might then react amongst themselves, increasing film hardness which is consistent with the nanomechanical measurements. A more comprehensive summary of these degradation reactions, including molecular schematics can be found in the work of Batista et al. [4].

The polyester isocyanate spectra in Fig. 10 show many similarities with the polyester melamine spectra with some notable differences. In the bottom left image displaying the O–H and N–H region, a relatively large peak is visible at 3385 cm\(^{-1}\), even before weathering. This peak has been assigned to hydrogen-bonded N–H stretching vibrations [60]. Further, instead of a single strong band around 1720 cm\(^{-1}\), two distinct but overlapping bands related to the carbonyl groups can be seen in the bottom right part of Fig. 10. The bands centered around 1720 cm\(^{-1}\) and 1685 cm\(^{-1}\), have both been assigned to the carbonyl C=O bond stretching. The former band is assigned to free C=O stretching whereas the second is assigned to C=O stretching in the urea groups, N-(C=O)-N [41,49,67]. A band centered around 1523 cm\(^{-1}\), assigned to amide II group vibration, –CO–NH–, in the crosslinker can also be seen [72]. The stable band around 1375 cm\(^{-1}\) from the polymer in-chain backbone, also visible in IR-spectra of the polyester melamine, is present. Like the polyester melamine the growth of the O–H bands around 3300 cm\(^{-1}\) were used to assess degradation. In addition, the changes in carbonyl bands and the amide II band were also quantified. The broadening and changes in absorbance of the carbonyl bands, and the decrease of the amide II band has previously been used to follow the oxidation in the urethane N–H groups and loss of urethane structures [56,60,74,75].

IR spectral changes associated with UV and moisture induced degradation are well documented for polyester melamine- and polyester urethane-based coil coatings [4,30,64,72]. More specifically, the degradation indexes were calculated according to:

\[
D = \frac{P_{\text{ref}} - P_{\text{exp}}}{P_{\text{ref}}} \times 100
\]

where \(D\) is the degradation index, \(P_{\text{ref}}\) is the normalized band area or

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Exposed}^i & \text{Exposed}^ii & \text{Exposed}^iii & \text{Mean} \\
\text{RMS surface roughness (nm)} & 0.77 & 0.57 & 0.57 & 0.63 \pm 0.09 \\
\text{Stiffness (N/m)} & 45.6 \pm 3.6 & 44.8 \pm 4 & 44.1 \pm 3.4 & 44.8 \pm 6.4 \\
\text{Deformation (nm)} & 2.4 \pm 0.2 & 2.4 \pm 0.2 & 2.5 \pm 0.2 & 2.4 \pm 0.3 \\
\text{Adhesion (nN)} & 18.8 \pm 1.5 & 17.8 \pm 1.4 & 18.5 \pm 1.5 & 18.4 \pm 2.5 \\
\hline
\end{array}
\]

\(^{a}\) Shown in Fig. 6.

**Table 5**

Mean values for roughness and nanomechanical properties for areas i, ii, and iii, for the weathered polyester isocyanate sample.
intensity of a certain band from the non-weathered reference sample and $P_{\text{exp}}$ is the normalized band area or intensity of a weathered sample. Note that in contrast to some similar calculations $[3]$, a negative sign is added to lead to negative index-values for a decrease in peak intensity and a positive values for an increase. The peroxide, carbonyl, and crosslinker indexes were calculated using the band intensities whereas the oxidative index was calculated using peak areas. The reason is the very wide and overlapping bands included in the oxidative index. To compensate for the overlap between broad region of $O$–$H$ and $N$–$H$ vibrations with the $C$–$H$ bands, the latter region was removed from the former when calculating the oxidation index as shown in Fig. 11. An illustration showing how peak intensities for carbonyl vibrations are calculated are shown in Fig. S3. Note that a band intensity is defined using the height of the band with respect to a band-specific baseline, not the absorbance value. A complete list of the baselines and peaks used during the calculations can be found in Table S1 and Table S2 in the Supplementary material. Degradation indexes are calculated for Xe arc exposures up to 2000 h.

It is worth noting that the depth from which it is possible to acquire information using ATR is limited by Eq. (2) $[33]$.

$$d_p = \frac{\lambda}{2\pi n_1 \sin(\theta) - \left(\frac{\text{A}}{\text{B}}\right)^2}$$

where $d_p$ is the depth of penetration (defined as the depth where the IR electric field strength is $1/e$ of that at the surface), $\lambda$ is the wavelength of incident radiation, $\theta$ is the angle of incidence, $n_2$ is the refractive index of the sample, and $n_1$ the refractive index of the internal reflection element. Using the parameters from Section 2.5 and assuming the refractive index of the organic coatings to be 1.5, a typical value for polymers in the infrared region, the depth of penetration can be estimated $[34,52]$. Using 3200 cm$^{-1}$ (3125 nm), the approximate location of the peaks used to calculate the oxidative index, the depth of penetration is 0.6 $\mu$m. At 1600 cm$^{-1}$ (6250 nm), close to both the crosslinker and carbonyl degradation indexes, the penetration depth is approximately 1.3 $\mu$m.

The degradation indexes as a function of time, up to 2000 h, are shown in Figs. 12 and 13. Note that for some data points the error bars are smaller than the symbol size. In general, the polyester melamine and isocyanate systems show a similar behavior. The oxidative index, calculated from the area of the wide $O$–$H$ band centered around 3300 cm$^{-1}$, and the peroxide index, calculated from the increase in intensity of the shoulder of the carboxyl bands located at 1780 cm$^{-1}$ both
increase. Thus, oxidation reactions occur in both coatings, and species associated with photodegradation are formed [4,60,63,66,71,72]. For the polyester melamine coating, the carbonyl index decreases, as measured from the intensity (band height with respect to baseline) of the carbonyl band around 1720 cm$^{-1}$. A shift to lower wavenumbers, and subsequent decrease in band intensity, has been connected to the formation of hydrogen bonds [68,76]. In contrast, the two polyester isocyanate carbonyl indexes show an increase in the intensity around 1680 cm$^{-1}$ and a decrease in the 1720 cm$^{-1}$ bands. This has been suggested to be due to formation of polyurea and a decrease of polyurethane components [2]. The crosslinking indexes, quantifying the degradation by showing the decrease of the 1550 cm$^{-1}$ band and the amide band at 1530 cm$^{-1}$ for the polyester melamine and polyester isocyanate respectively, both decreases. However, the crosslinker index for the polyester isocyanate is relatively stable for the first 500 h before the peak intensity starts to decrease.

3.4. Nano-FTIR

FTIR-ATR measurements collected data over macroscopic areas, with the sampling area being limited by the IR-beam focus and the area of the ATR crystal. The interchangeable ATR Specac Quest accessory has a diamond crystal with a diameter of approximately 1 mm. In addition, the optical properties of the diamond and the sample result in an information depth of about 1 μm in the fingerprint region of the spectra. In contrast, the nano-FTIR sampling area probes a much smaller surface area: the lateral resolution is limited by the sample tip diameter, which in this setup is approximately 50 nm, and an information depth in the order of tens to a hundred nm [35,37]. Thus, nano-FTIR probes the surface chemistry on a much more local scale.

Topography and nano-FTIR spectra of the polyester melamine sample before and after 2000 h of xenon arc weathering are shown in Fig. 14. For the sake of comparison, a spectrum from the same sample and weathering conditions obtained using FTIR-ATR is shown above the nano-FTIR spectra. These spectra were rescaled to show similar intensities as the nano-FTIR spectra and are shown as gray dotted lines. Overall, the nano-FTIR spectra correlated well with FTIR-ATR data, and the general features of the spectra are very similar. Notably the three bands previously used to quantify coating degradation are well-defined: the band around 1720 cm$^{-1}$ assigned to carbonyl groups, the band around 1550 cm$^{-1}$ assigned to multiple functional groups and used to follow the decrease in crosslinker functionality, as well as the stable band around 1375 cm$^{-1}$ assigned to the carbon backbone structure. The exact band definitions are shown in Table S3. A noteworthy difference between the nano-FTIR and FTIR-ATR spectra is that there are two additional peaks in the former, one located at 1650 cm$^{-1}$, and one
a shoulder on the right side of the carbonyl peak, around 1695 cm\(^{-1}\). These wavenumbers are marked in Fig. 14. The band around 1650 cm\(^{-1}\) has previously been used to confirm the presence of H–O–H bending vibrations in metal/coating interfaces [77]. This makes water adsorbed to the coating surface a possible explanation to these bands. The much smaller depth and thus higher surface sensitivity of the nano-FTIR measurements would explain why these bands did not show up in the FTIR-ATR measurements. The observations of these potential water bending vibrations at relatively high wavenumbers, at around 1650 cm\(^{-1}\), rather than at lower wavenumbers, closer to 1600 cm\(^{-1}\), suggests that water is adsorbed to the coating surface [48,78,79]. The band at around 1650 cm\(^{-1}\) decreases in width and intensity after weathering. This would point towards a lower water uptake at the outermost part of the surface after weathering for the polyester melamine coating. This is consistent with APM-results that suggested that weathering led to reduced length of weakly attached loose chains as well as higher stiffness, and that areas with lower crosslinking, and more loose chain ends, tend to be more hydrophilic in polyester melamine samples [4].

The shoulder located around 1695 cm\(^{-1}\) could potentially be assigned to one of multiple different carbonyl stretching bonds. It is very likely that the polyester resin consists of polymer chains with slight differences in their backbone structures, for example density and location of aromatic groups. This has an effect on the miscibility of the individual chains and has the potential of leading to phase segregation [80]. Therefore, it is possible that segregation of different phases has led to a thin layer with a difference in backbone chemistry at the surface of the coating, not caught by the FTIR-ATR measurements with larger penetration depths. Since the surfaces of the unexposed reference samples were washed before measurements, and that the shoulders are still present after weathering, this surface layer seems to be stable. This would indicate that it is not a film on top of an otherwise perfectly homogeneous coating but rather a part of the coating itself.

It is worth noting that, owing to how the weak molecular vibrational resonances are detected, a low intensity repeating wave pattern can sometimes be seen in nano-FTIR spectra [17,81]. This could be misinterpreted as individual bands. However, as the location of the bands were relatively stable across multiple sample areas, it is more likely that the bands are caused by actual chemical features rather than instrumental artifacts.

Another noticeable feature is that there are variations in the spectral

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![Fig. 11. Peak definitions in the wavelength region 3800–2450 cm\(^{-1}\) for the polyester melamine samples before and after 2000 h of Xe arc weathering. The orange striped area is dominated by C–H stretching and used for normalization whereas the growing blue area represents the increase of O–H bonds due to oxidation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 12. Degradation indexes of the polyester melamine coating as a function of weathering time.](image)

![Fig. 13. Degradation indexes of the polyester isocyanate coating as a function of weathering time.](image)
intensities. If the entire spectral region is equally affected, it is most likely a topological effect. For example, the light blue spectrum from the weathered sample has a slightly lower overall intensity. This spectrum was collected from a local protrusion as seen on the corresponding topographical map.

Peak intensities for the carbonyl band at around 1720 cm\(^{-1}\) and the band around 1550 cm\(^{-1}\), used to quantify degradation, were calculated similarly as for the FTIR-ATR spectra. Normalization in each spectrum was performed using the carbon chain backbone band located at 1375 cm\(^{-1}\). To avoid effects of band shoulders only present in the nano-FTIR spectra with a variation in both position and relative intensity, band definitions were slightly altered as compared to the macro scale FTIR spectra. The exact band definitions can be seen in Table S3 in the Supplementary material. The spread in calculated band ratios was noticeable for both the reference and weathered samples and clearly hints at local chemical differences. However, the variation leads to very large standard deviations and makes calculation of degradation indexes problematic. Due to this, the normalized band intensities before (top) and after (bottom) weathering are shown in Fig. 15. Both the variation between each analyzed area and the variations between the different areas (named i, ii, and iii for each sample) can be seen. As to the change in band ratios, similar trends are present in both Fig. 15 and the macro scale FTIR-ATR results in Fig. 12. The normalized band around 1550 cm\(^{-1}\), used to assess degradation associated with the crosslinker, changes noticeably. The mean value decreases from slightly above 1 to around 0.75. This is close to the 30 % reduction seen in FTIR-ATR.

Fig. 14. Topography and nano-FTIR spectra from an unexposed reference surface (top) and the weathered (bottom) polyester melamine samples. The locations where the nano-FTIR spectra were acquired across the 1 × 1 μm sample area are marked with color-coded points. Each colored point corresponds to the nano-FTIR spectra of the same color. The dotted line in each image is the corresponding FTIR-ATR spectrum rescaled to the same absorbance as observed in the nano-FTIR measurements.

Fig. 15. Normalized 1550 and 1720 cm\(^{-1}\) bands intensities for the nano-FTIR measurements of the three 1 × 1 μm\(^2\) areas of the polyester melamine samples. Normalization in each spectrum was performed using the carbon chain backbone band located at 1375 cm\(^{-1}\).

Fig. 16. Topography and nano-FTIR spectra from the reference (top) and weathered (bottom) polyester isocyanate samples. The locations where the nano-FTIR spectra were acquired across the 1 × 1 μm sample area are marked with color-coded points. Each colored point corresponds to the nano-FTIR spectra of the same color. The dotted line in each image is the corresponding FTIR-ATR spectrum rescaled to the same absorbance as observed in the nano-FTIR measurements.
Fig. 17. Normalized 1530, 1690, and 1722 cm$^{-1}$ band intensities for the nano-FTIR measurements of the three 1 × 1 μm$^2$ areas of the isocyanate samples. Normalization in each spectrum was performed using the carbon chain backbone band located at 1375 cm$^{-1}$.
4. Conclusions

AFM-based nanomechanical measurements, DMA, FTIR-ATR measurements and s-SNOM nano-FTIR measurements were used to study the effect of UV-light and moisture on the degradation of polyester melamine and polyurethane coil coatings. Over small areas both coatings are uniform with around 1 nm RMS roughness over 1 × 1 μm measurement areas. A higher nanomechanical surface stiffness in the polyester melamine system before weathering was correlated with a higher macro-scale surface stiffness in the polyester melamine system before weathering. Nanomechanical properties over the 1 μm × 1 μm measurement areas. Weathering increases the surface stiffness and reduces the deformation caused by the AFM tip in both systems. A tendency towards reduction of adhesive forces between the AFM tip and sample as well as qualitative analysis of nanomechanical force curves suggest a reduced number and length of stretchable polymer chains at the coating surface.

Chemical changes (e.g., alterations of crosslinker/polyester bonds, chain scission, and formation of degradation products) were quantified using infrared spectroscopy. One of the most significant changes brought on by weathering was an increase in the amount of polar groups such as hydroxyls and peracids. This finding is consistent with the observed increase in local stiffness, as polar groups allow for formation of hydrogen bonds and stronger molecular interactions between chains in the polymeric network.

On the macro-scale, the chemical changes caused by weathering were assessed using FTIR-ATR and more locally, in the 50–100 nm scale, and with higher surface sensitivity, using nano-FTIR. Both methods showed similar trends in terms of the spectral changes occurring due to weathering. The variations observed in nano-FTIR spectra obtained at different analysis areas are larger than the variations over larger surface areas as reported by FTIR-ATR spectra. This suggests local variations in the surface chemical composition, even though weak band intensities make quantification of these variations difficult. However, average values for a decrease in band intensities associated with loss in cross-link hydrolysis, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 449–453, https://doi.org/10.1021/ie00115a014.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2024.108355.

References


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