Supporting Information

Minimizing corrosion of outdoor metalworks using dispersed chemically-stabilized nanoclays in PVDF latex coatings

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SURFACE CHARACTERIZATION BY RAMAN SPECTROSCOPY

The Raman spectral features of LAPc and LFPc, when compared to unmodified clay (LNa), each have distinctive characteristic vibrations in Figure S1 confirming their presence: (1) a carbonyl stretching band at 1718 cm$^{-1}$ ($\nu$C=O) for LAPc or (2) the trifluoromethyl mode at 749 cm$^{-1}$ ($\nu$C-F$_3$) for LFPc. Other characteristic frequencies include aliphatic vibrations from methylene asymmetric ($\nu_{\text{as}}$ C-H$_2$) and symmetric ($\nu_{\text{s}}$ C-H$_2$) stretching at 2945 and 2900 cm$^{-1}$, where the intensities of these bands were blue shifted for LFPc due to the dense electronegativity of the fluorinated tail ($\nu_{\text{as}}$ C-H$_2$=2955 and $\nu_{\text{s}}$ C-H$_2$=2920 cm$^{-1}$). In-chain methylene motions are responsible for a number of C-H deformation modes present from 1462-1221 cm$^{-1}$. Peaks indicative of the tetrahedral structure of the silicate include the unmodified clay LNa’s characteristic peak at 683 cm$^{-1}$ (Si-O$_4$ stretch) and various metal-oxide vibrations found lower than 600 cm$^{-1}$ including peaks at 482 cm$^{-1}$ (Si-O) and 360 cm$^{-1}$ (Mg-O).

Figure S1. Raman spectra of functionalized clays, where M-O-Si denotes the Mg-O-Si and Si-O-Si combination stretching vibrations.

The hydroxyl region of the nanoclays (4000-2800 cm$^{-1}$) was described in the main text by Figure 2. The hydrophilicity ratios discussed in the main text can be found below in Table S1. The spectra of LA and LF (not shown) contained a peak at 832 cm$^{-1}$ corresponding to an out-of-plane C-H deformation band indicative of unreacted silane linkages and upon cation exchange these bands disappeared. We have previously reported similar observations from FTIR spectra of these materials.\(^1\)
Table S1. Physical properties of clays described by Raman, WAXD, and TGA

|               | Free H₂O | Si-O₄ | ζ (mV) | 2θ (°) | d₀₀₁ (nm) | Δ d₀₀₁ (nm) | Adsorbed H₂O (%w/w) |
|---------------|----------|-------|--------|--------|-----------|-------------|---------------------|
| LNa           | 528.5    | 1416.9| 0.373  | 6.97   | 1.57      | 0.37        | 12.1               |
| LAPc          | 819.2    | 2805.5| 0.292  | 5.1    | 1.74      | 0.82        | 6.45               |
| LFPc          | 578.2    | 3027.2| 0.191  | 5.84   | 1.51      | 0.59        | 7.00               |

The increase observed in d₀₀₁ spacing was calculated relative to the dry unit cell (0.92 nm)

S2  WIDE-ANGLE X-RAY DIFFRACTION AND THERMO-GRAVIMETRIC ANALYSIS

The wide-angle diffraction (WAXD) patterns in Figure S2 of dry Laponite before and after modification showed an increase in the interlayer gallery or basal spacing (d₀₀₁) of the clay upon functionalization. Sodium Laponite is an amorphous nanoclay and, without modification, exists as an average of 3-5 stacked platelets in its bulk form with no long-range order. As such, the WAXD spectra show broad peaks at most angles that subsequently mask some of the characteristic 00ℓ patterns, such as d₀₀₂ and d₀₀₄. The broad d₀₀₁ peaks for LNa at 6.97 2θ indicate: (1) random disordered stacking of the clay and (2) expansion of the gallery space by ~0.3 nm, the tumbling radius of water, suggesting the presence of a layer of water trapped between platelets.

Modification of clays expanded the gallery space (observed by a shift of d₀₀₁ to lower angles) to 1.74 nm for LAPc and 1.51 nm for LFPc, with their net changes listed in Table S1. Given the lateral cross-section of the siloxane is close to 0.5 nm, the basal expansion is likely related to the lateral height of excess silane intercalated between platelets in a monolayer fashion where both ends are touching the clay surface. Furthermore, an expansion greater than the length of the cationic chain, or 0.61 nm for LAPc nanoclay, may indicate an interdigitated bilayer arrangement of Pc in the gallery space. Typically this expansion bears little influence on the...
particle’s behavior in a solvent. It is of note when initially dispersed in water, organo-clays LA and LF did not exfoliate fully until blended with the same peptizing agent as LNa (tetrasodium pyrophosphate, TSPP). Lack of exfoliation and expansion of the gallery space led us to consider silane attachment to multiple clay platelets as others have reported. However, we consider this possibility to be unlikely due to steric hindrance of the siloxane since the distance between oxygen atoms on the silicon head group can be as much as 0.3 nm.

Figure S3. TGA profiles of nanoclays before and after covalent modification are overlaid in (a) with mass loss (solid lines) and respective first derivatives (dashed lines) to highlight the region indicating decomposition of small organic molecules from the silicate nanoclays from 200 - 600 °C. The amount of water lost from the unmodified LNa clay (b) was compared to that of the organically modified nanoclays LA (c) and LF (d).

Thermal gravimetric analysis of covalently modified clays LA and LF was compared to unmodified clay LNa. Thermograms by mass loss and their first derivative plots are shown in Figure S3 where three main phases of degradation upon heating of LNa can be observed. These phases indicate: (1) loss of adsorbed water on the particle surface from 50-330 °C and equal to 12.1% mass, (2) loss of interlayer water in gallery space from 330-600 °C where approximately 2.5% mass loss occurred and (3) the onset of hydroxyl degradation at 600 °C. Modified clays exhibited four main phases, the first of which from 50-170 °C was also due to bulk water loss and indicated 6.5% and 7% water content in the clay structure for LA and LF, respectively. This was less water than released by unmodified clay LNa. A decrease in hydrophilicity after
modification should correspond to a decrease in surface charge and was confirmed by zeta
potential measurements, listed in Table S1. The calculated number of surface-bound water
molecules per Laponite unit cell (MpU=#molecules/# clay unit cell) was 7.1 MpU for LNa, 5.1
MpU for LA, and 4.5 MpU for LF. The second decomposition phase in LA and LF from 150-320
°C indicated a significant amount of silane was adsorbed to the surface of the clay due to the
lower temperature of degradation than the covalently bound molecules observed in the third
region from 320-600 °C. Using the mass lost in each phase, relative percentage of molecules
adsorbed as opposed to covalently bound were 23% for LA and 35% for LF.

These data combined provide insight into the physical changes the clays undergo from
modification. From thickness and unit cell values obtained during WAXD analysis, it was
estimated that there are 1,050 unit cells per Laponite platelet. This number compared well to
another work that used surface adsorption and titrations to derive an accessible hydroxyl density
of 0.36 mmol –OH/g clay. Given the dry conditions of the synthesis, platelets were likely
suspended in small stacks of 3 discs (on average) in anhydrous toluene with broken edge
hydroxyls available for grafting. Utilizing the measured coordinates by XRD in combination
with the empirical formula of the unit cell, each 3-disc stack would have approximately 730
silanols available for attachment along the disc edges and thermal gravimetry data provided a
value of 907 accessible hydroxyl groups.

**S3 ATTACHMENT EFFICIENCY ESTIMATED BY X-RAY PHOTOELECTRON SPECTROSCOPY**

Integration of regions Na 1s, Si 2p, Mg 2s, Li 1s, and O 1s peaks in the XPS scan of LNa
confirmed the empirical formula of the clay’s unit cell (Figure S4). High resolution scans of clay
LF showed peaks at 688, 683 and 102 eV that correspond to the binding energy of F 1s and Si 2p
orbitals, and were fit with a Lorentzian peak shape for quantitation. The two peaks in the F 1s
scan are due to organic C-F bonds in the silane molecule and the metallic Si-F bonds from a
small amount of direct fluorination of the silicate - which is likely a byproduct of the sample and
X-ray beam interaction. The peak ratio of fluorine from the peak at 688 eV to silicon at 102 eV
indicated that on average each 25 nm discoid had 690 FOTES molecules on its surface. Using
the number of accessible hydroxyl groups calculated in S2, a grafting efficiency of 228% was
obtained for the LF nanoclay. TGA analysis of LF showed a gravimetric decrease upon heating
and quantitatively revealed that 35% of the FOTES molecules were merely physisorbed to the
clay surface. When the number of FOTES molecules per clay stack was adjusted by -35%, the
result is 148% covalent grafting efficiency of the docking sites or on average 1.5 FOTES
molecules/accessible hydroxyl. Although some have reported individual silanes covalently
bridging multiple clay sheets, the geometric constraints of these molecules make that scenario
unlikely. Our grafting efficiency of 1.5 suggests that cross-linking reactions between silane
molecules occurred, resulting in an average of 1-2 molecules bound per “docking” site.
Figure S4. XPS full scan of Laponite clay modified with FOTES (LF, purple) and expansions of Fluorine 1s and Silicon 2p regions used in quantitation. Peaks used in peak fitting of data are shown with dashed blue lines overlapping the spectrum. Unmodified clay (LNa, yellow) is shown for comparison. The KLL lines are Auger emissions (Auger lines were not used in quantitation).

S4  CIRCUIT ELEMENT TRENDS IN IMPEDANCE ANALYSIS OF PCN’S

The capacitance of a protective film can be thought of as a material’s ability to store charge across a select area. A capacitor in parallel with a resistor representing the coating generally corresponds to the coating capacitance, \( C_{\text{coat}} \), of the entire film and the pore resistance, \( R_{\text{pore}} \), or the average open path through the coating to the substrate. Thus the product of the two elements is the time constant, \( T_{\text{coat}} = R_{\text{pore}} C_{\text{coat}} \) and can represent the shortest (minimum) relaxation time for an ion to travel from the bulk solution through the coating to the metal interface. The high frequency CPE(R) pair dominated the EIS spectra of these films from approximately \( 1 \times 10^6 \) Hz and therefore \( C_{\text{coat}}, R_{\text{pore}}, \) and \( T_{\text{coat}} \) can be assumed to represent the bulk of the protective coating. Based on the general formula for a planar capacitor (Equation 1), capacitance can increase due to: (1) change in permittivity from increased porosity, (2) change in permittivity from uptake of higher \( \varepsilon \) liquid into the material matrix, (3) increase in surface area of the plate, and (4) decrease in film thickness – distance between plates.

\[
C = \frac{\varepsilon_0 \varepsilon_m A}{d}
\]

(1)
Although the data was fit with models containing constant phase elements in place of capacitors, each value was converted to effective capacitance in Farad using the Brugg equation (Eq. 2):

\[
C = \frac{(CPE \times R)^{1/2}}{R}
\]

EIS spectra acquired of films before and during weathering were fit to a circuit model with two CPE/Resistor pairs in parallel: \(CPE_{\text{coat}}(R_{\text{pore}})CPE_{\text{di}}(R_{\text{ct}})\), until failure expanded the circuit model with another RC pair: \(CPE_{\text{perc}}(R_{\text{perc}})CPE_{\text{coat}}(R_{\text{pore}})CPE_{\text{di}}(R_{\text{ct}})\), both shown in Figure 5d. The equivalent for a failed coating was only observed for PVDF without clay and with the LNa composite after 3500 hours of QUV weathering. Additionally, EIS spectra were normalized with the cell constant \((k=14.62 \text{ cm}^2)\) so that all values presented with units in Farads (F) are F/cm² and Ohms (Ω) are Ω·cm².

### 4.1.1 Coating capacitance

An evolution of \(C_{\text{coat}}\) can be observed in Figure 5c, where each coating experienced a decrease in capacitance after the first weathering cycle. Capacitance of films with modified clay materials were higher after exchange with phosphoryl choline, as expected from the hydrophilic nature of the cation and increased water sorption seen in the Raman data. After 1000 hours of weathering, all films containing clay began to increase in capacitance. The highest final \(C_{\text{coat}}\) after 4500 h of QUV-B was observed for the PVDF film without clay, 1.78 nF, followed by 0.794 nF for LAPc, 0.684 pF for LNa, and the lowest was 0.427 pF for LFPc. Recalling the ways in which a capacitor can increase in value, the most likely contributions after weathering include decreasing film thickness and increased permittivity, as the area is relatively unchanged and the films were analyzed after a UV exposure cycle where little water remained in the film. Changes in film thickness were measured with a tri-gloss meter, and the largest decrease was observed for the coatings with the highest capacitance: PVDF lost 37% of its total film thickness and LAPc lost 43%. In contrast, the coating with LFPc had the lowest capacitance and underwent the smallest change in film thickness of -23% and similarly LNa lost 29.4%.

### 4.1.2 Film resistance

The term film resistance is useful to describe a film having number of pore channels that ions may travel through more quickly than they may through a film lacking such pores. The resistance of the full intact film (\(R_{\text{coat}}\)) is assumed to have a value much greater than the pore resistance and is not typically observed by experimental methods. Plotted for each coating over time in Figure 7, \(R_{\text{pore}}\) had decreased from its maximum value in all composites by 2000 hours of QUV-B weathering. Coatings without clay (PVDF only) and those with LNa showed partitioning of the film at advanced weathering times, which was represented by a new time constant for a percolation layer, as shown in Figure 5d. The final film resistances after 4500 hours QUV-B weathering were highest for the coating with LFPc (\(R_{\text{pore}} = 442 \text{ MΩ}\)), followed by LAPc (\(R_{\text{pore}} = 87.1 \text{ MΩ}\)), then LNa (\(R_{\text{perc}}= 27.4 \text{ MΩ}\) and \(R_{\text{pore}} = 183 \text{ MΩ}\)) and latex resin without nanoclay (\(R_{\text{perc}} = 0.373 \text{ MΩ}\) and \(R_{\text{pore}} = 1.85 \text{ MΩ}\)). The film with LFPc maintained a film resistance above 1 GΩ after 3500 hours of weathering and as thus was considered exceptional protection.
In general, it can be assumed that the resistance of the film drops as ion transport rises due to chemical degradation of the film (increased material permittivity). Resistance is not only related to a material’s ability to transport charge, but also directly proportional to path length (here film thickness) and inversely proportional to area (here working electrode area). The observed decreases in film thickness may explain the later drop in $R_{pore}$ upon extended weathering, but this is in direct opposition to the initial observed increases up until 1500 hours. Accelerated weathering methods typically have a long UV step at an elevated temperature above the MFFT (here the UV step is run at 60 °C when MFFT$_{FMA}$ = 12 °C) and we hypothesize that these steps serve as continued annealing to provide limited repair for films retaining their flexibility throughout weathering. This maintained annealing drives out water from the film, promotes close packing and limited reorganization, all that decrease permittivity of the coatings.

4.1.3 Time constants
The combined product of capacitance and resistance of a protective coating can also be considered the relaxation time of the film after polarization and provides an average time for charge transport through the film to the metal surface. The initial time constant of the films studied here did not follow the same trend as $C_{coat}$ nor $R_{pore}$ and are ordered from shortest to longest: PVDF without clay (2.2 ms), LAPc (33.0 ms), LNa (144.7 ms), and LFPc (185.5 ms). After 4500 hours of weathering, $T_{coat}$ decreased and is ordered from shortest to longest as follows: PVDF (0.0059 ms), LNa (18.7 ms), LAPc (69.2 ms), and LFPc (188.7 ms). Given the very small capacitances of these films in the pico- to nano- Farad range, the magnitude of the resistive components have a greater contribution in determining the time and is thus more closely related to the permittivity (or resistivity or in-phase behavior) of the dielectric being studied.

S5 Film degradation by ATR-FTIR and TF-XRD
Surface analysis by ATR-FTIR of weathered composites in Figure 6 showed significant erosion of the acrylic component of the latex coating with simultaneous enrichment of all PVDF associated vibrations. Coating surfaces are particularly sensitive to photodegradation and typically a loss of film thickness during weathering corresponds to a simultaneous decrease in barrier properties. In Figure 5 we observed an increase in barrier properties over time from EIS data, up to 3500 hours in the case of LFPc, even after the film had lost substantial thickness. Since PVDF is well known to have a temperature-dependent crystalline structure, it was hypothesized that an increase in the number of impenetrable crystalline domains had occurred at the PVDF-rich surface of the film, ultimately increasing barrier properties.

Thin-film XRD spectra in Figure S5 were obtained to investigate both the amount and quality of the composite films remaining after 3500 of weathering. The characteristic diffraction peaks of PVDF are shown for a weathered composite containing LF in (b), where reflections of the TGTG’ form of PVDF produced peaks at 18.7°, 19.8°, and 26.5° 2θ. Since only an amorphous scattering halo can be clearly observed for PVDF (non-weathered), any sharpening of the aforementioned peaks would indicate an increase in the number and uniformity of PVDF
crystalline domains.\textsuperscript{7} These same peaks were also present in spectra (a) acquired using a thin-film geometry, which allowed for in-situ investigation of the entire bulk film. A decreased intensity for each sample spectrum upon weathering confirmed loss of film thickness and sharpening of the d\textsubscript{110} peak at 18.7 2\(\Theta\) indicate an increase in PVDF crystallinity. The grazing-incidence data was acquired in a surface-sensitive geometry, and showed less overlap between the non-weathered and weathered films, another indication of increased PVDF crystallinity at the surface of the coating. Furthermore, the appearance of low-angle peaks at 4.2 and 6.3 2\(\Theta\) in Figure S5b correspond to the d\textsubscript{001} spacings of Laponite, as discussed in previous sections. While these types of peaks would typically be unwanted in a composite (they indicate long-range stacking of pillars, as opposed to exfoliated discoids), the LF composite was the only film that showed diffraction peaks of nanoclay in-situ at any point in this study. Appearance of these peaks for the sample with LF as opposed to the other films indicated surface enrichment of not only PVDF but also the nanoclay, as chemical modification with FOTES may have increased particle retention in the coating.

\textbf{Figure S5.} Diffraction spectra of PVDF-Laponite composites weathered by QUV for 3500 hours with (a) Thin-Film spectra showing increased PVDF crystallinity at 18.7 and 19.8 2\(\Theta\) after weathering and (b) Grazing Incidence (0.5°) of non-weathered PVDF compared to PVDF+LF showing both surface enrichment of modified clay LF with d\textsubscript{001} spacings at 4.2° and 6.3° 2\(\Theta\) as well as increased PVDF crystallinity with reflections at 18.7° (d\textsubscript{020}), 19.8° (d\textsubscript{110}), and 26.5° (d\textsubscript{021}) 2\(\Theta\).
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