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Experimental and Computational Studies of Structure-Property Relationships in Flat-flex Cable  
Adhesives and UV-cured Thiol-ene Resins

By

CHRISTINA A. FOX  
DISSERTATION

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in

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in the

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of the

UNIVERSITY OF CALIFORNIA

DAVIS

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2026



# **Experimental and Computational Studies of Structure-Property Relationships in Flat-flex Cable Adhesives and UV-cured Thiol-ene Resins**

## **Abstract**

This dissertation examines the chemical, structural, and performance evolution of two technologically important polymer systems: high-performance flat-flex cable assemblies used in aerospace and defense applications, and UV-cured thiol-ene resins for volumetric additive manufacturing. This work integrates experimental characterization with multiscale computational modeling to identify the molecular mechanisms that govern degradation, reactive transformation, and macroscopic property development.

For flat-flex cable assemblies, accelerated aging, high potential breakdown testing, peel testing, and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were used to quantify the evolution of dielectric, mechanical, and chemical properties under humid thermal conditions. These measurements were used to develop kinetic and mechanistic models linking polymer chemical change to performance decay. To extend this framework, atomistic simulations were performed using density functional tight binding (DFTB), steered molecular dynamics, conformational sampling with the conformer-rotamer ensemble sampling tool (CREST), and density functional theory (DFT). This workflow enabled identification of likely degradation products, reconstruction of aged vibrational spectra, and evaluation of electronic descriptors associated with dielectric failure. Together, these studies establish a molecular-scale basis for understanding how site-specific hydrolysis and local sequence architecture drive loss of adhesion and insulation performance in cable adhesive systems.

For thiol-ene materials, this dissertation develops a reactive force field based on ReaxFF to study photo-initiated radical polymerization and to rationalize experimentally observed mechanical behavior. The force field was parameterized against DFT reference data, including geometries, bond energies, atomic charges, and reaction energies to provide a chemically consistent description of reactive network formation. The resulting model enables mechanistic interpretation of polymerization behavior and evaluation of thiol-ene resins as candidate materials for volumetric additive manufacturing.

Overall, this dissertation demonstrates the value of combining experiment with predictive simulation to resolve the thermodynamics, kinetics, and structure-property relationships that control polymer performance. By connecting molecular reactivity to engineering-scale behavior, this work provides a framework for understanding degradation in adhesive cable materials and reactive network formation in photopolymer resins.

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# Chapter 1

## Introduction

Polymer-enabled technologies often fail or succeed based on chemical process that occur at length and time scales that are difficult to access directly. In service, polymers may undergo slow reactions such as hydrolysis, oxidation, and network rearrangement that progressively alter molecular structure, redistribute local polarity, and change interfacial bulk properties. These molecular-scale transformations can ultimately manifest as engineering-level outcomes including dielectric breakdown, loss of material cohesion, and changes in stiffness or toughness. Developing predictive lifetime and performance models therefore requires methods that can both quantify how materials evolve under realistic stressors and identify the underlying reaction pathways responsible for that evolution.

This dissertation addresses that need by integrating targeted experimental measurements with multiscale molecular modeling to connect reactivity, structure, and performance in two polymer systems of technological importance. For humid-thermal aging of flat-flex cable assemblies, accelerated aging experiments combined with electrical, mechanical, and spectroscopic characterizations provide quantitative time-resolved observables that can be interpreted using kinetic and mechanistic models. Complementary atomistic simulations are used to propose chemically plausible degradation products, relate predicted vibrational signatures to measured ATR-FTIR changes, and evaluate electronic descriptors linked to dielectric failure. For UV-cured thiol-ene resins, reactive force field development enables simulation of photo-initiated radical network formation at scales inaccessible to electronic-structure dynamics, while retaining chemical consistency through parameterization to DFT reference data. Together, these

approaches provide a unified framework for translating molecular reaction mechanisms into experimentally measurable property evolution, supporting both lifetime prediction for cable materials and rational design of photopolymer resins for additive manufacturing.

## 1.1 Accelerated Aging Experiments

Accelerated aging (AA) experiments are used to estimate the service life of a material or assembly without waiting for real-time aging results.<sup>1</sup> The central premise of AA is that many physical and chemical degradation processes proceed at rates that increase predictably with increasing temperature. For thermally activated chemical degradation, the mathematical basis is commonly expressed using the Arrhenius relation through an acceleration factor ( $AF$ ):

$$AF = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{\text{Ref}}} - \frac{1}{T} \right) \right], \quad (1.1.1)$$

where  $E_a$  is the effective activation energy,  $R$  is the ideal gas constant,  $T_{\text{Ref}}$  is the reference temperature (operation or storage temperature), and  $T$  is the accelerated aging temperature.<sup>1</sup> The acceleration factor is then used to define an effective age ( $A_{\text{eff}}$ ), as:

$$A_{\text{eff}} = t_{\text{AA}} \cdot AF, \quad (1.1.2)$$

where  $t_{\text{AA}}$  is the duration of the accelerated aging exposure.<sup>1</sup>

For an idealized single-step chemical reaction,  $E_a$  corresponds to the activation barrier for that reaction. In practical materials systems, degradation typically reflects multiple coupled pathways, so  $E_a$  is more appropriately interpreted as effective activation energy representing the net temperature sensitivity of overall degradation processes.<sup>2</sup> Key limitations of the Arrhenius-based lifetime extrapolation include over-acceleration, where the AA temperature induces degradation mechanisms that would not occur under reference conditions, and non-linear

degradation, where the apparent rate changes over time. In addition, the Arrhenius model does not explicitly account for non-thermal stressors such as humidity, higher-energy radiation (for example, ultraviolet light), or mechanical wear.<sup>1, 2</sup>

When additional stressors are important, Arrhenius-type models are often extended with additional terms. For example, the Peck model<sup>3</sup> is commonly used to incorporate humidity effects by defining a humidity-inclusive acceleration factor,  $AF_H$ :

$$AF_H = \left( \frac{RH}{RH_{\text{Ref}}} \right)^n \cdot \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{\text{Ref}}} - \frac{1}{T} \right) \right], \quad (1.1.3)$$

where  $RH$  and  $RH_{\text{Ref}}$  are the accelerated aging and reference relative humidity values, respectively, and  $n$  is the humidity exponent.

In this work, accelerated aging is not interpreted solely through an Arrhenius or Peck acceleration factor. Instead, lifetime implications are assessed by directly linking changes in material performance to the kinetics of underlying chemical transformations, as inferred from the appearance or disappearance of molecular vibrational features over the course of the aging exposure. As a mechanistic interpretation of  $E_a$ , Arrhenius-type acceleration follows from the temperature dependence of reaction rate constants. For an elementary step, the rate  $r$  is written in terms of a rate constant  $k(T)$  and a concentration dependence. For example, for a single reactant  $A$ ,

$$r = -\frac{d[A]}{dt} = k(T)[A]^n, \quad (1.1.4)$$

where  $[A]$  is concentration and  $n$  is the reaction order. The temperature dependence of  $k$  is commonly modeled by the Arrhenius equation,

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right), \quad (1.1.5)$$

where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy (effective activation energy when multiple pathways contribute),  $R$  is the ideal gas constant, and  $T$  is temperature in Kelvin. Under accelerated aging conditions, increasing  $T$  increases  $k(T)$ , thereby increasing the rates of chemical transformations that drive material property loss.

When degradation is tracked experimentally through the growth or decay of infrared (IR) absorbance bands associated with specific functional groups, the spectroscopic signal can be related to concentration through Beer-Lambert behavior (Equation 1.2.3). If an absorbance feature  $A_{IR}(t)$  is proportional to the concentration of a reactant or product, the time-dependent spectra provide a direct proxy for reaction progress and therefore reaction kinetics. In the simplest case of apparent first order behavior,

$$\begin{aligned} A &\rightarrow B, \\ \text{Rate} &= -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A], \\ [A] &= [A]_0 e^{-kt}, \\ [B] &= [B]_\infty (1 - e^{-kt}). \end{aligned} \quad (1.1.6)$$

By estimating  $k$  from the time evolution of band intensities at multiple temperatures and fitting  $\ln(k)$  versus  $1/T$ ,

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}, \quad (1.1.7)$$

an apparent  $E_a$  can be extracted from the slope, providing a quantitative link between observed spectroscopic change and the effective activation energy that underpins acceleration in AA experiments.

## 1.2 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy is used to probe molecular vibrational structure. When IR radiation interacts with a material, specific chemical bonds absorb energy and undergo vibrational motions. These vibrations involve changes in the bond lengths and/or angles, and for IR-active modes, produce a change in the molecular dipole moment that is detected spectroscopically.<sup>4</sup>

Functional groups exhibit characteristic absorption bands associated with fundamental vibrational motions. For a non-linear molecule containing  $N$  atoms, there are  $3N - 6$  normal modes.<sup>5</sup> A normal mode is IR-active only if the vibration induces a change in the molecular dipole moment. Consequently, symmetric vibrations are often weak or absent in IR spectra, and in molecules possessing a center of symmetry, vibrations that are symmetric with respect to the inversion center are IR-inactive.<sup>5</sup>

In the mid-IR region ( $4000$  and  $400\text{ cm}^{-1}$ ),<sup>4</sup> two broad classes of vibration are typically distinguished: stretching vibrations ( $\nu$ , dominated by changes in bond lengths) and bending vibrations (dominated by changes in bond angles). Bending vibrations may be in-plane ( $\delta$ ) or out-of-plane ( $\pi$ ).

Many characteristic vibrational frequencies can be approximated using a harmonic oscillator model based on Hooke's law, where the frequency depends on the reduced mass,

$$\mu = \frac{m_A m_B}{m_A + m_B} , \quad (1.2.1)$$

and the force constant (bond strength),  $k$ . The fundamental frequency  $\nu$  is:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} , \quad (1.2.2)$$

where  $c$  is the speed of light.<sup>4</sup> Vibrational spectra are typically reported in wavenumbers  $\bar{\nu}$  ( $\text{cm}^{-1}$ ), using  $\bar{\nu} = \nu/c$ . Because bending motions generally require less energy than stretching motions, bending bands often appear at lower wavenumbers. Because frequency increases with bond strength, double and triple bonds typically appear at higher wavenumbers. Local chemical environments (for example, hydrogen bonding or nearby electronegative groups) can alter effective bond strength and shift band positions.<sup>4, 5</sup> This sensitivity of band position and intensity to the chemical environment makes IR spectroscopy a powerful tool for characterizing material chemistry and tracking chemical change.

Band intensity depends primarily on the magnitude of the dipole change associated with the vibration and the concentration of the absorbing species.<sup>6</sup> Strong absorptions are commonly associated with polar functional groups (for example, carbonyl C=O).<sup>5</sup> The measured absorbance  $A$  is related to concentration  $c$  via the Beer-Lambert law:<sup>7</sup>

$$A = \varepsilon \cdot l \cdot c , \quad (1.2.3)$$

where  $\varepsilon$  is the molar absorptivity and  $l$  is the effective path length.

Modern FTIR instruments collect data using an interferometer (commonly a Michelson interferometer)<sup>5</sup> to generate an interferogram containing information across many wavelengths simultaneously. The interferometer utilizes a beam splitter to divide coherent IR light into two

paths. Mirrors reflect the light back to the beamsplitter where it recombines and interacts with the sample. By altering the distance of one of the mirrors from the beam splitter, the wavelengths in each path eventually recombine out of phase, causing destructive interference in some wavelengths, thus controlling the wavelength of light interrogating the sample.<sup>7</sup> A Fourier transform<sup>8</sup> converts the interferogram,  $I(\delta)$ , from the optical path distance domain to a spectrum,  $B(\bar{\nu})$ , in the frequency (wavenumber) domain:

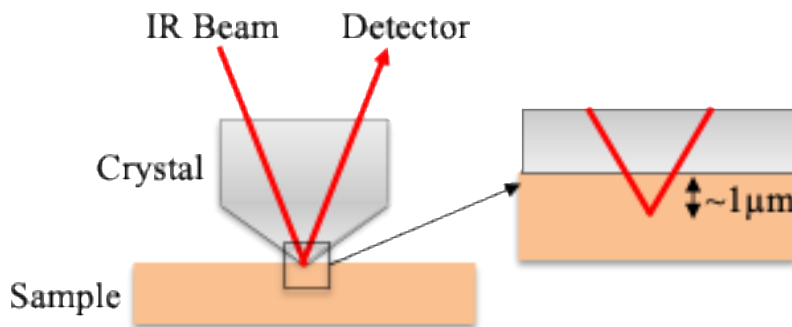
$$B(\bar{\nu}) = \int_{-\infty}^{+\infty} I(\delta) \cos(2\pi\bar{\nu} \delta) d\delta, \quad (1.2.4)$$

where  $\delta$  is the optical path difference.

In attenuated total reflectance (ATR), IR radiation is directed into a high-refractive-index crystal in intimate contact with the sample. The beam undergoes total internal reflection within the crystal, generating an evanescent field that extends a short distance into the sample.<sup>4, 8</sup> If the sample contains vibrational modes resonant with the evanescent field, energy is absorbed, attenuating the reflected beam measured at the detector. ATR is therefore a near-surface technique with a typical penetration depth on the order micrometers. The penetration depth  $d_p$ , which defines the effective path length, is given by:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - (n_2/n_1)^2}}, \quad (1.2.5)$$

where  $\lambda$  is the wavelength,  $n_1$  and  $n_2$  are the refractive indices of the ATR crystal and sample, respectively, and  $\theta$  is the angle of incidence. **Figure 1.1** is a schematic of the total reflectance phenomenon and interaction of the evanescent wave with a sample.



**Figure 1.1.** A schematic of total reflectance depicting an IR beam interacting with a crystal and sample generating an evanescent wave. Adapted from Abidi.<sup>4</sup>

## 1.3 Statistical Analysis

### 1.3.1 Principal Component Analysis

Principal component analysis (PCA) is a multivariate statistical method that reduces dimensionality of large datasets by transforming the original variables into a smaller set of orthogonal (uncorrelated) variables called principal components (PCs).<sup>9</sup> PCA identifies linear combinations of the original variables that capture the maximum variance in the data, with PC1 explaining the largest fraction of variance, followed by PC2, PC3, and so on. For spectroscopic datasets, the input is typically a matrix  $X$  in which rows correspond to samples and columns correspond to variables (for example, absorbance values at each wavenumber).

A standard PCA workflow includes: 1) mean centering, 2) covariance matrix calculation, 3) eigenvalue decomposition, and 4) projection into principal component space.<sup>10,11</sup> Mean centering is performed by subtracting the mean  $\mu$  of each variable:

$$Z = X - \mu , \quad (1.3.1)$$

where  $Z$  is the centered data matrix.<sup>11</sup> In spectroscopic applications, mean centering corresponds to subtracting the average spectrum from each individual sample spectrum, emphasizing deviations from the ensemble mean.<sup>12</sup> The covariance matrix  $C$  is then computed as:

$$C = \frac{1}{n-1} Z^T Z, \quad (1.3.2)$$

where  $n$  is the number of observations and  $Z^T$  is the transpose of  $Z$ .<sup>9-11</sup> The principal components are obtained from the eigenvalue decomposition of  $C$ :

$$|C - \lambda I| = 0,$$

$$(C - \lambda I)v = 0, \quad (1.3.3)$$

where  $\lambda$  are eigenvalues,  $v$  are eigenvectors, and  $I$  is the identity matrix.<sup>11</sup> Eigenvectors define the directions of the new axes (PCs), and eigenvalues quantify the variance captured along each PC.<sup>9-11</sup> Finally, the centered data are projected onto the leading  $k$  components:

$$Y = ZV_k, \quad (1.3.4)$$

where  $V_k$  is the matrix of the top  $k$  eigenvectors.<sup>11</sup>

Retaining only the leading eigenvectors preserves the dominant patterns in the data while discarding lower-variance dimensions that often correspond to measurement noise. PCA produces two outputs that are particularly useful for interpretation: scores and loadings. Scores (the rows of  $Y$ ) represent each sample in the rotated PC coordinate system, enabling visualization of clustering or trends among samples. Loadings (the eigenvectors in  $V_k$ ) quantify how strongly each original variable contributed to a PC, and in spectroscopic applications they can identify specific spectral bands associated with the largest sources of variance.<sup>12</sup>

### 1.3.2 Monte Carlo Uncertainty Quantification

Monte Carlo (MC) uncertainty quantification is a simulation-based approach that propagates uncertainty in input parameters through a computational framework to estimate the resulting uncertainty in model predictions.<sup>13</sup> The method proceeds by sampling uncertain inputs repeatedly (often thousands of times) from specified probability distributions, evaluating the model for each sample, and using the resulting ensemble of outputs to estimate confidence intervals of predictive contributions.<sup>13, 14</sup> This approach is particularly valuable for complex and non-linear models, where analytic uncertainty propagation is impractical.<sup>13, 14</sup>

One MC strategy used in conjunction non-linear least squares modeling is to generate many plausible parameter sets based on fitted parameter values and their associated standard errors.<sup>14</sup> The model is then evaluated for each parameter set to produce a distribution of predicted outcomes. For time-dependent, non-linear models, this produces a distribution of predicted values at every time point, where the spread of the distribution reflects model uncertainty.

For a model  $Y = g(X)$ , the MC procedure generates  $N$  independent parameter sets  $X$  by sampling from parameter probability density functions.<sup>13</sup> A probability density function (PDF) describes the likelihood that a continuous random variable takes on particular values. In the non-linear least squares approach, parameter errors are assumed to follow a normal distribution, and therefore the Gaussian PDF is used:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}, \quad (1.3.5)$$

where  $\mu$  is the mean parameter value and  $\sigma$  is the parameter standard deviation.<sup>13</sup> For each MC draw, sampled parameters are passed through the model ( $Y = g(X)$ ), generating an ensemble of

predictions ( $Y$ ). Aggregating predictions across all samples yields an empirical distribution of model outputs from which means, credible intervals, and time-dependent uncertainty bands can be computed.<sup>13</sup> When model predictions are time-dependent, this process produces an uncertainty distribution at each time point, enabling quantitative comparison between predicted trends and experimental measurements.<sup>14</sup>

## 1.4 Density Functional Theory

Density functional theory (DFT)<sup>15-17</sup> is a quantum mechanical framework for computing electronic structure and molecular properties by using electron density, rather than the many-electron wavefunction, as the primary variable to determine the total energy of a system.<sup>18</sup> DFT is widely applied across chemistry, materials science, and biology because it provides a first principles description of matter that is broadly consistent with experimental observations while remaining computationally amenable for systems beyond reach of the exact wavefunction methods.<sup>19-25</sup>

Using the Born-Oppenheimer approximation,<sup>26</sup> electronic motion is treated with fixed nuclear positions and described by the time-independent Schrödinger equation:<sup>27</sup>

$$\left[ \frac{h^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(r_i) + \sum_{i=1}^N \sum_{i < j} U(r_i, r_j) \right] \psi = E\psi, \quad (1.4.1)$$

where  $m$  is the electron mass,  $h$  is Planck's constant,  $r$  is the position vector,  $E$  is total energy and  $\psi$  is the many-body electronic wavefunction.<sup>18</sup> The kinetic energy of electrons is represented by the first term, electron-nuclear interactions by the second term, and electron-electron interactions by the third. Because the wavefunction depends on the coordinates of all electrons,

the dimensionality grows rapidly with system size, making direct solution impractical for all but very small systems.

Kohn and Sham<sup>28</sup> introduced a reformulation in which the central quantity is the electron density  $\rho(r)$ , which depends only on three spatial coordinates. The electron density can be written in terms of single-electron orbitals as:

$$\rho(r) = 2 \sum_i \psi_i^*(r) \psi_i(r), \quad (1.4.2)$$

where the asterisk denotes conjugation, and the term inside the summation is the probability that an electron in wavefunction  $\psi_i(r)$  is located at position  $(r)$ . This reduction from the many-electron wavefunction to the electron density dramatically simplifies the problem while retaining the ability to compute ground-state properties. The Kohn-Sham equation<sup>28</sup> equations are expressed as:

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r), \quad (1.4.3)$$

where  $\varepsilon_i$  are orbital energies,  $\phi_i(r)$  are the Kohn-Sham orbitals,  $V(r)$  is the electron-nuclear potential,  $V_H(r)$  is the Hartree potential describing Coulombic repulsion between an electron and the total electron density, and  $V_{XC}(r)$  is the exchange-correlation potential. Here  $\phi$  is used to describe the single electron wavefunction, while  $\psi$  is used to describe the true, many-body wavefunction. The equation contains three potentials,  $V(r)$ ,  $V_H(r)$ , and  $V_{XC}(r)$ .  $V(r)$  also appeared in Equation 1.4.1 and describes the interaction energy between an electron and all nuclei. The Hartree potential,  $V_H(r)$ , defines the Coulombic repulsion between a single electron and the total electron density of the system. The final potential,  $V_{XC}(r)$ , describes exchange and

correlation contributions to the single electron equations. Because  $V_{XC}(r)$  is not known exactly, approximations are required, and these approximations define the class of functional used.<sup>18</sup>

One approximation class is the local density approximation (LDA),<sup>29-30</sup> which leverages the special case of the uniform electron gas for which exchange-correlation is known exactly. In LDA-type approaches the exchange-correlation potential at each spatial point is approximated using the exchange-correlation potential of a uniform electron gas evaluated at the local density. Generalized gradient approximation (GGA) functionals improve upon LDA by incorporating both the local electron density and its gradient  $\nabla\rho(r)$ .<sup>30</sup> Common GGA examples include Perdew-Wang (PW91)<sup>31</sup> and Perdew-Burke-Ernzerhof (PBE)<sup>32</sup>. Meta-GGA functionals further incorporate the kinetic energy density  $\tau(r)$  of the Kohn-Sham orbitals:

$$\tau(r) = \frac{1}{2} \sum_{occupied\ states} |\nabla\phi_i(r)|^2. \quad (1.4.4)$$

An example of a non-empirical meta-GGA functional is Tao-Perdew-Staroverov-Scuseria (TPSS).<sup>33</sup>

In this work, hybrid (hyper-GGA) functionals were used, which mix exact exchange with semi-local exchange-correlation terms and are therefore inherently non-local.<sup>30</sup> The exact exchange energy density can be written as:

$$E_{exchange}(r) = \frac{1}{2n(r)} \int d^3r' \frac{|\sum_{occupied\ states} \phi_i^*(r')\phi(r)|^2}{|r - r'|}. \quad (1.4.5)$$

A common hybrid functional is B3LYP,<sup>34-38</sup> expressed as

$$V_{XC}^{B3LYP} = V_{XC}^{LDA} + \alpha_1(E_{exchange} - V_X^{LDA}) + \alpha_2(V_X^{GGA} - V_X^{LDA}) + \alpha_3(V_C^{GGA} - V_C^{LDA}). \quad (1.4.6)$$

Here  $V_X^{GGA}$  and  $V_C^{GGA}$  correspond to the Beck 88 exchange<sup>34</sup> and Lee-Yang-Parr correlation<sup>35</sup> components, and the  $\alpha$  parameters are empirically determined.<sup>30</sup> To improve the description of non-covalent interactions, Grimme’s D3 dispersion correction,<sup>39</sup> which uses Becke-Johnson damping, can be employed.

Practical DFT calculations also require a basis set, which defines the set of functions used to expand molecular orbitals.<sup>18</sup> Gaussian-type orbitals (GTOs)<sup>40</sup> are widely used in molecular quantum chemistry, and the choice of basis set balances accuracy against computational cost.<sup>18</sup> In this work, the 6-31G(d)<sup>41</sup> basis set was used as a computationally modest choice for the molecular sizes considered. In this notation, “6” denotes the number of Gaussian primitives used for inner-shell orbitals, “31” indicates a split-valence double-zeta description of valence orbitals, and “(d)” indicates the inclusion of polarization functions.<sup>18</sup>

#### 1.4.1 Vibrational Frequency Calculations

Vibrational frequency calculations determine normal mode frequencies and associated spectroscopic intensities from a converged electronic structure geometry. In Gaussian16,<sup>42</sup> a frequency calculation begins with an estimate of the Hessian matrix  $H_{i,j}$  typically derived from the final approximated Hessian of the optimized geometry. The Hessian matrix is a  $3N \times 3N$  matrix containing force constants associated with second derivatives of the energy with respect to nuclear coordinates.<sup>18</sup> In the harmonic oscillator approximation, higher order (anharmonic) terms are neglected, and the Hessian elements are defined as:

$$H_{i,j} = \frac{\partial^2 E}{\partial x_i \partial x_j}, \quad (1.4.7)$$

where  $i$  and  $j$  index Cartesian degrees of freedom.<sup>17, 18</sup> The eigenvalues of the Hessian matrix

relate to effective force constants and reduced masses, and the vibrational frequencies are computed as:

$$\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i}. \quad (1.4.8)$$

Infrared intensities reflect how the molecular dipole moment changes as nuclei move along a normal coordinate. Accordingly, the IR intensity is proportional to the squared derivative of the dipole moment with respect to the normal mode coordinate.

$$I_{IR} \propto \left| \frac{\partial \mu}{\partial Q_k} \right|^2. \quad (1.4.9)$$

## 1.5 Density Functional Tight Binding

While DFT provides a first-principles description of the ground-state electronic structure, the computational cost of repeatedly solving the Kohn-Sham equations becomes prohibitive for very large systems. Density Functional Tight Binding (DFTB) addresses this limitation by introducing a controlled approximation to DFT that greatly improves computational efficiency while retaining an electronic description of bonding. DFTB achieves this primarily by using pre-calculated Hamiltonian and overlap integrals stored in Slater-Koster files,<sup>43</sup> avoiding expensive integral evaluations during simulation. These look-up tables contain the distance-dependent Hamiltonian and overlap information for each pair of atom types (for example, C–C and C–O), where Hamiltonian integrals describe interaction energies and overlap integrals describe the spatial overlap of atomic orbitals.<sup>44</sup>

DFTB is derived by expanding the Kohn-Sham energy around a reference density constructed as a superposition of atomic densities and expanding the exchange-correlation contributions.<sup>45</sup> In the third-order formulation used here, the total energy is expressed as

$$E_{\text{DFTB}} = E_{\text{BS}} + E_{\text{Coul}} + E_{\text{Rep}} + E_{\text{Disp}}, \quad (1.5.1)$$

where  $E_{\text{BS}}$  is the electronic band-structure energy,  $E_{\text{Coul}}$  accounts for the Coulombic energy associated with charge fluctuations,  $E_{\text{Rep}}$  is a short-range repulsive term, and  $E_{\text{Disp}}$  is a dispersion correction to long-range van der Waals interactions. The band-structure energy is computed from the occupied orbitals using a non-self-consistent Hamiltonian  $\hat{H}_0$ :

$$E_{\text{BS}} = \sum_i n_i \langle \psi_i | \hat{H}_0 | \psi_i \rangle, \quad (1.5.2)$$

where  $n_i$  is the occupation number of orbital  $i$ , and orbitals are expanded as linear combinations of pre-defined atomic orbitals:

$$\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}, \quad (1.5.3)$$

with  $C_{\mu i}$  as molecular orbital coefficients (it describes how much of an atomic orbital  $\mu$  is present in molecular orbital  $i$ ).<sup>44</sup> Electrostatic contributions are captured by the charge-fluctuations term.

In the third-order formulation, a damping function  $\gamma_{AB}$  is used to soften short-range electrostatics, and improve treatment of close contacts and proton transfer behavior:<sup>44, 45</sup>

$$E_{\text{Coul}} = \frac{1}{2} \sum \gamma_{AB} \Delta q_A \Delta q_B. \quad (1.5.4)$$

The repulsive term is computed from pairwise potentials:

$$E_{\text{Rep}} = \sum_{A < B} V_{AB}(R_{AB}), \quad (1.5.5)$$

where  $V_{AB}$  is a spline-fitted function defined for each  $A$ - $B$  atom pair and stored in Slater-Koster parameterization, and  $R_{AB}$  is the internuclear distance.<sup>44, 45</sup> Long-range dispersion is treated with an empirical correction, here using Grimme D3 with Becke-Johnson damping:<sup>39</sup>

$$E_{\text{Disp}}^{\text{D3}} = \sum_{A \neq B} \left( s_6 \frac{C_6^{AB}}{R_{AB}^6} f_{d,6}(R_{AB}) + s_8 \frac{C_8^{AB}}{R_{AB}^8} f_{d,8}(R_{AB}) \right), \quad (1.5.6)$$

where  $C_6^{AB}$  are dynamic coefficients that change based on the coordination number of the atoms,  $s_6$  and  $s_8$  are global scaling factors that are pre-fitted for the specific method, and  $f_d$  is the damping function for short atomic distances.<sup>44, 45</sup>

### 1.5.1 Molecular Dynamics and Steered-Molecular Dynamics

While the dispersion correction ensures that the static snapshot of molecules includes critical van der Waals forces, the true efficiency of the DFTB method is observed when going from single points to molecular dynamics calculations. Because DFTB can calculate forces substantially faster than standard DFT, it enables high-level observation of a system evolution over time. In this work, a dynamic system is simulated over thousands of steps to observe chemical reactions.

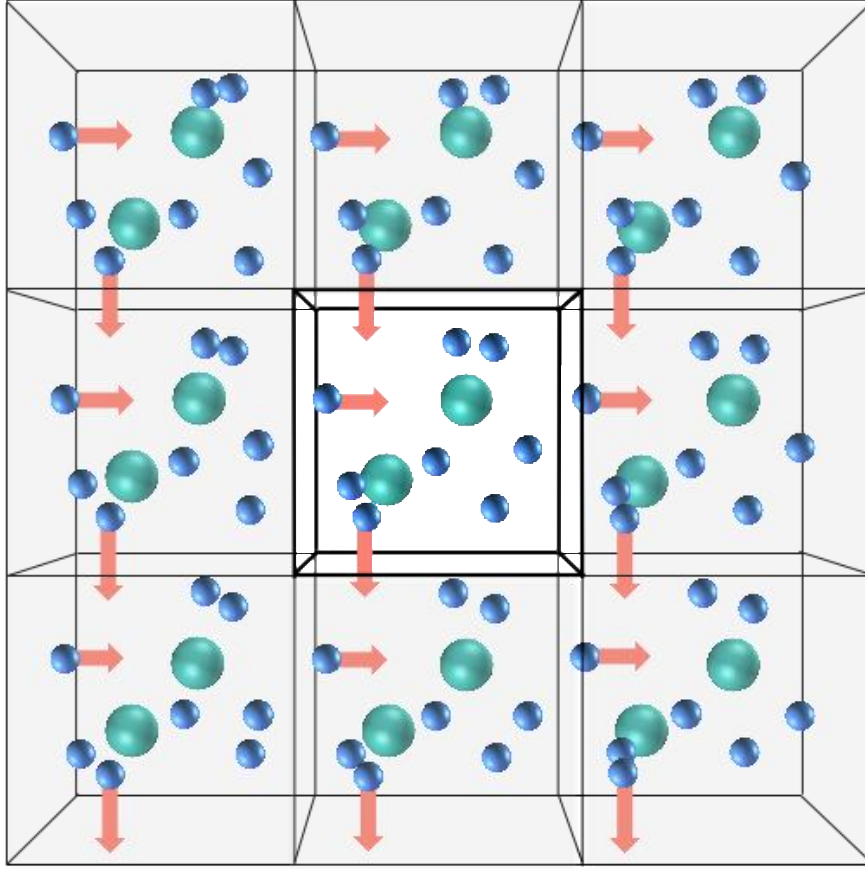
Molecular dynamics (MD) simulations model the time evolution of an atomistic system by numerically integrating Newton's equations of motion. Forces on atoms are obtained from the negative gradient of the potential energy, and positions and velocity are updated iteratively using a chosen integrator and timestep. Common integration algorithms are the Velocity Verlet,<sup>46</sup> Position Verlet,<sup>47</sup> and Leapfrog Verlet.<sup>48</sup> In this work, the Velocity Verlet<sup>46</sup> integrator was used because it is stable, time-reversible, and provides good energy conservation for many systems.<sup>45</sup> In Velocity Verlet<sup>46</sup> positions are propagated using current velocities and accelerations, an intermediate half-step velocity is computed, then forces are re-evaluated at the new positions to update velocities to the full step. Initial velocities are assigned based on a Maxwell-Boltzmann distribution at the target temperature. The updated relations can be expressed as

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2$$

$$v\left(t + \frac{1}{2}\Delta t\right) = v(t) + \frac{1}{2}a(t)\Delta t$$

$$v(t + \Delta t) = v\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}a(t + \Delta t)\Delta t. \quad (1.5.7)$$

To represent bulk materials and reduce finite-size effects, period boundary conditions (PBC) are commonly employed, in which the simulation box is replicated infinitely in all directions and particles leaving one face re-enter through the opposite face with the same velocity. **Figure 1.2** depicts a visual representation of a PBC.



**Figure 1.2.** A three-dimensional representation of a periodic boundary condition (PBC) where there is an infinite lattice containing identical copies of a simulation cell surrounding the center cell and particles leaving one side of a simulation box reappear on the opposite side.

The thermodynamic constraints of an MD stimulation are determined by its ensemble. In the microcanonical NVE ensemble, the number of particles  $N$ , volume  $V$  and total energy  $E$  are conserved such that:  $E_{\text{total}} = KE + PE = \text{constant}$ , where  $KE$  and  $PE$  are kinetic and potential energy, respectively.<sup>48</sup> In the canonical NVT ensemble, the temperature is regulated with a Nose-Hoover thermostat<sup>51</sup> by modifying the equations of motion:

$$\frac{dr}{dt} = \frac{p_i}{m_i},$$

$$\frac{dp_i}{dt} = F_i - \xi p_i, \quad (1.5.8)$$

$$\xi = \frac{1}{Q} \left[ \sum \frac{p_i^2}{m_i} - (3N + 1)k_B T_{\text{target}} \right],$$

where  $p_i$  is the atomic momentum ( $p = mv$ ) non-relativistic,  $\xi$  is the thermostat variable,  $Q$  is the thermostat mass which determines the inertia of the heat bath,  $k_B$  is Boltzmann's constant, and  $T_{\text{target}}$  is the target temperature. The first equation calculates atom velocity (how its position changes with time) and the second equation calculates the net force acting on the atom (how momentum changes with time).<sup>48</sup> In the isothermal-isobaric NPT ensemble, pressure is regulated using a barostat that permits volume changes (for example Parrinello-Raham<sup>49</sup> or Berendsen methods<sup>50</sup>).

While equilibrium MD is valuable for observing natural dynamics, chemical reactions and other rare events often occur on timescales much longer than typical simulations. Steered molecular dynamics (SMD)<sup>52</sup> addresses this limitation by applying an external, time-dependent bias potential that drives the simulation along a selected coordinate. A common implementation applies a moving harmonic potential

$$V_{\text{bias}}(R, t) = \frac{k}{2} [R - R_0(t)]^2 \quad (1.5.9)$$

where  $k$  is the spring constant,  $R$  is the steered coordination, and  $R_0(t)$  is the time-dependent restraint center, often moved at a constant speed  $v$  from an initial equilibrium value.<sup>52</sup> The pulling force is evaluated at each step from displacement between the instantaneous coordinate and the moving restraint center.<sup>52</sup> The cumulative work performed along the trajectory can be calculated discretely as:

$$W_n = \sum_{i=1}^n F_i \cdot v \cdot \Delta t . \quad (1.5.10)$$

A key motivation for monitoring work in SMD is its connection to free energy differences.

Under NVT conditions, the characteristic thermodynamic potential is the Helmholtz free energy  $\Delta F$ , and the Jarzynski relation<sup>53, 54</sup> provides a route to estimate  $\Delta F$  from an ensemble of non-equilibrium work:

$$e^{-\frac{\bar{W}}{k_B t}} = e^{-\frac{\Delta F}{k_B t}} . \quad (1.5.11)$$

When SMD is performed with consistent pulling parameters ( $v$  and  $k$ ), relative work or free-energy estimates can be used to qualitatively compare reaction pathways, where larger values indicate less favorable transformations under the applied steering protocol.

## 1.6 Conformational-Rotamer Ensemble Sampling Tool

SMD can be effective for exploring a reaction coordinate when the relevant sites and pathways are known, but in large molecules, the most reactive site or most stable structure is not always obvious. In addition, molecules at ambient conditions may have many stable geometries separated by small energy differences. The Conformational Rotamer Ensemble Sampling Tool (CREST)<sup>55-57</sup> addresses these challenges by automatically exploring the conformational space and identifying low-energy conformers using the extended Tight Binding (xTB)<sup>57, 57</sup> framework.

Like DFTB, xTB uses a tight-binding energy model, but xTB also incorporates inductive polarization effects. In the Geometry Frequency Non-covalent Second-order xTB (GFN2-xTB)<sup>58</sup> method used here, higher-order multipole electrostatic (dipoles and quadrupoles) interactions are included in the Coulombic energy term:

$$E_{Coul} = \frac{1}{2} \sum_{A,B} \sum_{l,l'} q_{A,l} \gamma_{AB,ll'} q_{B,l'} , \quad (1.6.1)$$

where  $l = 0$  corresponds to monopole (charge-charge) terms and  $l > 0$  corresponds to multipole contributions. Unlike DFTB's Slater-Koster tables, GFN2-xTB uses element-specific parameters that were fit to reference data from the PBEh-3c functional.<sup>59</sup>

CREST uses the iterative Meta-Dynamics with Genetic Crossing (iMTD-GC) algorithm<sup>56</sup> to drive a molecule out of local minima to discover new conformers. In this approach, a bias potential is applied based on root-mean-square deviation (RMSD) between the current structure and a set of reference structures representing previously identified conformers.<sup>56</sup> The bias potential can be expressed as:

$$V_{bias}(RMSD) = \sum_k h_k \exp\left(-\frac{RMSD(R, R_k)^2}{2\alpha^2}\right), \quad (1.6.2)$$

where  $h_k$  sets the energy scale of the bias and  $\alpha$  controls the range of the repulsion in RMSD space. After the molecule is pushed into a new structural configuration, xTB relaxes the structure to the nearest local minimum, and structures are retained if they are distinct from the existing conformer set. Genetic Crossing then combines features from low-energy conformers by mixing atomic coordinates, which can improve identification of the global minimum.<sup>56</sup>

Because CREST operates within xTB, it can incorporate implicit solvation models. In such models, the total energy is written as the gas-phase electronic energy plus a solvation energy term:

$$E_{Total} = E_{Gas} + \Delta G_{Solv} . \quad (1.6.3)$$

The solvation free energy represents the work done to create a cavity in the solvent and van der

Waals interactions, collectively they are represented by  $\Delta G_{nonpolar}$ , and the change in electrostatic potential  $\Delta G_{Elec}$ :<sup>45</sup>

$$\Delta G_{Solv} = \Delta G_{Elec} + \Delta G_{nonpolar}. \quad (1.6.4)$$

The xTB approach typically uses Analytical Linearized Poisson-Boltzmann (ALPB)<sup>60</sup> or Generalized Born Surface Area (GBSA)<sup>61, 62</sup> solvation models. In this work, the ALPB<sup>60</sup> model was used, which describes the electrostatic contribution as:

$$\Delta G_{Elec} = -\frac{1}{2} \left(1 - \frac{1}{\epsilon}\right) \frac{1}{1 + \beta} \sum_{i,j}^N \frac{q_i q_j}{f_{GB}(r_{ij}, R_i, R_j)} \quad (1.6.5)$$

where  $\epsilon$  is the dielectric constant of the solvent,  $q_i q_j$  are the atomic partial charges,  $\beta$  is an ALPB correction factor<sup>60</sup> to account for the finite size of solute in a dielectric medium (the GBSA model does not account for this),  $f_{GB}(r_{ij}, R_i, R_j)$  is the a smoothing function  $f_{GB} = \sqrt{r_{ij}^2 + R_i R_j \exp(-r_{ij}^2 / 4 R_i R_j)}$ , and  $R_i, R_j$  are the atomic Born radii.<sup>60</sup> The non-polar term is represented as:

$$\Delta G_{nonpolar} = \sum_i^N \gamma_i A_i \quad (1.6.6)$$

where  $A_i$  is the exposed surface area of atom  $i$  and  $\gamma_i$  is atomic surface tension coefficient (a semi-empirical parameter).<sup>60</sup>

The combined use of CREST/xTB conformer sampling, DFTB-based molecular dynamics and higher-level DFT vibrational calculations provides a practical workflow to explore reaction pathways, screen conformal landscapes of candidate products, and generate computed IR spectra for comparison with experiment.

## 1.7 Reactive Force Fields

DFT and DFTB provide electronic-structure-based methods to investigate reaction pathways and dynamics, but there is also a separate class of approaches that simulate reaction using reactive force fields. Conventional classical force fields treat bonds as fixed and therefore cannot represent bond breaking and formation. Reactive force fields overcome this limitation by incorporating bond-order formalisms that allow chemical connectivity to evolve dynamically during molecular dynamic simulations. ReaxFF<sup>63, 63</sup> is a widely used reactive force field that achieves reactivity by defining continuous relationships between bond order and bond length, allowing bond energies to smoothly decrease toward zero as atoms separate and enabling transitions among single, double, and triple bonding.

In ReaxFF the system energy is represented as a sum of bonded and non-bonded terms:

$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{angle}} + E_{\text{lone-pair}} + E_{\text{dihedral}} + E_{\text{electrostatic}} + E_{\text{vdW}} \quad (1.7.1)$$

where  $E_{\text{bond}}$  is bond energy,  $E_{\text{angle}}$  is valency angle energy,  $E_{\text{dihedral}}$  is dihedral angle energy, and  $E_{\text{over}}$ ,  $E_{\text{under}}$ , and  $E_{\text{lone-pair}}$  are energetic penalties of bond interactions accounting for over-coordination, under-coordination and breaking up a lone pair of electrons.<sup>63, 63</sup> Non-bonded interactions include van der Waals  $E_{\text{vdW}}$  and Coulombic contributions  $E_{\text{electrostatic}}$ .

Bonded interactions are bond order dependent and bond orders are computed for all atom pairs as sum of contributions associated with  $\sigma$ ,  $\pi$  and  $\pi\pi$  bonding:

$$\begin{aligned} BO_{ij} &= BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \\ &= \exp \left[ p_{bo1} \cdot \left( \frac{r_{ij}}{r_0^{\sigma}} \right)^{p_{bo2}} \right] + \exp \left[ p_{bo3} \cdot \left( \frac{r_{ij}}{r_0^{\pi}} \right)^{p_{bo4}} \right] + \exp \left[ p_{bo5} \cdot \left( \frac{r_{ij}}{r_0^{\pi\pi}} \right)^{p_{bo6}} \right] \end{aligned} \quad (1.7.2)$$

where  $r_0$  represents the equilibrium bond distance and  $p_{bo}$  are empirical parameters specific to the atom types.<sup>63, 63</sup> Each contribution is typically expressed as an exponential decay function of interatomic distance and controlled by empirical parameters specific to the interacting atom types. Because many energetic terms depend on bond order, ReaxFF naturally couples bonding, angles, torsions and coordination penalties. However, the resulting parameter space is large, and robust application to new chemistries generally requires careful parameterization and validation.<sup>65</sup>

A defining feature of ReaxFF is its treatment of electrostatics via partial charges. Rather than defining fixed charges, ReaxFF commonly uses an electronegativity equalization (EEM/QEq) procedure to compute charges that respond to local environment.<sup>63</sup> At each update, each element is assigned an electronegativity and a chemical hardness, and the optimal charges are those that equalize the chemical potential across atoms while penalizing large charge fluctuations. These charges are then used in the Coulombic energy term  $E_{electrostatic}$ , enabling charge redistribution to occur as bonds break and form.<sup>63</sup> This capability improves the qualitative realism of polarization and charge transfer, and is computationally inexpensive, but the accuracy of predicted charges and reaction energies remains dependent on the selected parameter set and chosen charge equilibration settings in the simulation.

A typical ReaxFF force field contains several hundred parameters and while a significant fraction of parameters can be transferred from previously optimized force fields, often 100 or more parameters require optimization to achieve high quality production simulations.<sup>65</sup> ReaxFF parameterization typically relies on training to quantum mechanical reference data, including energies, geometries, and charges for representative structures and reaction intermediates.<sup>65</sup> There are a variety of semi-automated parameterization methods that can be implemented to

facilitate the optimization of a reactive FF for a given system, though all require user monitoring, interpretation and input.<sup>64-67</sup> Each parameter is assigned a weight that dictates its level of importance to the optimization routine. Optimization is often posed as a minimization of a weighted penalty function comparing ReaxFF predictions to training targets:

$$P = \sum_i^{Training\ Set} \left( \frac{V_{i,Train} - V_{i,Reax}}{\omega V_{i,Train}} \right)^2 \quad (1.7.3)$$

where  $V_{i,Train}$  is a property from the training set (for example, a bond energy),  $V_{i,Reax}$  is the corresponding ReaxFF prediction,  $\omega$  is the inverse weight assigned to that property.<sup>67</sup> Although ReaxFF can simulate reactive dynamics at substantially lower cost than DFT or DFTB, its predictive capability is constrained by parameter quality, transferability limits across chemical systems, and the practical challenge that adjusting one subset of parameters can degrade performance in others due to strong coupling of energy terms.<sup>65</sup>

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## Chapter 2

### 2      **Hygrothermal Aging Effects on Polyimide and Acrylate-Based Adhesive Materials in High-Performance Flat-flex Cable Assemblies**

*My contribution to this work included conducting accelerated aging experiments, ATR-FTIR spectroscopy data collection, all data and statistical analysis, and writing. This chapter originally appeared in the literature as:*

C.A. Fox, H.E. Reinstein, B.R. Foley, N.T. Liesen, M.P. Kroonblawd, A.M. Maiti, R. Faller, R.H. Gee. Hygrothermal aging effects on polyimide and acrylate-based adhesive materials in high-performance flat-flex cable assemblies. *Polymer Degradation and Stability*. 2026 May; 247, 112005.

#### **Abstract**

Flat-flex assemblies are widely used across a diverse range of technologies, including consumer electronics, automotive systems, aerospace and defense applications, and medical devices, due to their compact form factor and flexibility. However, environmental stressors like temperature and humidity are known to degrade performance over time, though the main mechanisms for degradation remain unknown. In this work, we examined the aging behavior of copper/polyimide/adhesive laminate systems under varying temperature and humidity conditions, focusing on material degradation and its effects on mechanical and dielectric properties. Results show that peel strength and breakdown voltage decrease with exposure time, temperature, and humidity; spectroscopic characterization revealed that the adhesive, and not the polyimide, is the weak link in the material stack-up. The adhesive, identified as a butyl acrylate-acrylonitrile (BA-AN) copolymer, exhibited age-related spectral changes that correlated with

exposure severity and duration. Hydrolysis at BA ester and AN nitrile groups was identified as the primary degradation mechanism, producing amides, acids, and alcohols. We developed a mechanistic model that connects kinetic parameters for BA-AN spectral band decay to peel strength and breakdown voltage, and implicates hydrolysis at the AN moiety, not BA, in performance decrements. Modeling predictions at ambient conditions indicate faster decline in peel strength than dielectric strength at early times, followed by plateauing of both properties at longer times. These findings provide critical insights into laminate aging mechanisms and highlight the importance of addressing BA-AN degradation to improve the long-term reliability of these systems in high-humidity environments.

## 2.1 Introduction

Flat-flex cables are widely utilized in high-voltage applications due to their compact design, flexibility, and durability that makes them suitable for a variety of applications including aerospace, defense, and advanced electronics.<sup>1-3</sup> These cables are often constructed as copper-clad laminates, which include copper conducting strips laminated with a polymeric insulator material with high thermal stability and dielectric strength. Copper-clad laminates fabricated by Dupont™ are often bonded using a combination of polymeric materials: poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline) (PMDA-ODA), known for its high dielectric strength and thermal stability,<sup>4-7</sup> and an acrylate-based adhesive, which provides mechanical integrity and adhesion between layers (**Figure 2.1**).<sup>8-9</sup> Despite their robust construction, the long-term reliability of flat-flex cables is influenced by environmental factors that can induce material degradation, particularly in humid conditions. While these materials are engineered to withstand challenging operating conditions, environmental stressors such as humidity and heat can accelerate their degradation, potentially compromising the electrical performance and mechanical reliability of the cables over time.

Understanding the aging mechanisms of these polymeric materials is therefore critical for ensuring long-term functionality and safety of high-voltage systems.

Previous studies have demonstrated that the individual polymers used in flat-flex cables are susceptible to degradation when exposed to humid environments, leading to changes in their mechanical, chemical, and electrical properties. For instance, PMDA-ODA is known to absorb nominally 3.5 wt.% water<sup>8, 10, 11</sup> and undergo hydrolysis and oxidative degradation under prolonged exposure to moisture and elevated temperatures, which can result in reduced dielectric strength and mechanical integrity.<sup>12, 13</sup> Similarly, acrylate-based adhesives are prone to chemical changes such as hydrolysis and chain scission, which can weaken adhesion and alter their overall performance.<sup>14–16</sup> However, the specific contributions of each polymeric material to the aging behavior of flat-flex cables remain poorly understood, particularly in the context of high-voltage applications where dielectric and mechanical properties are critical.

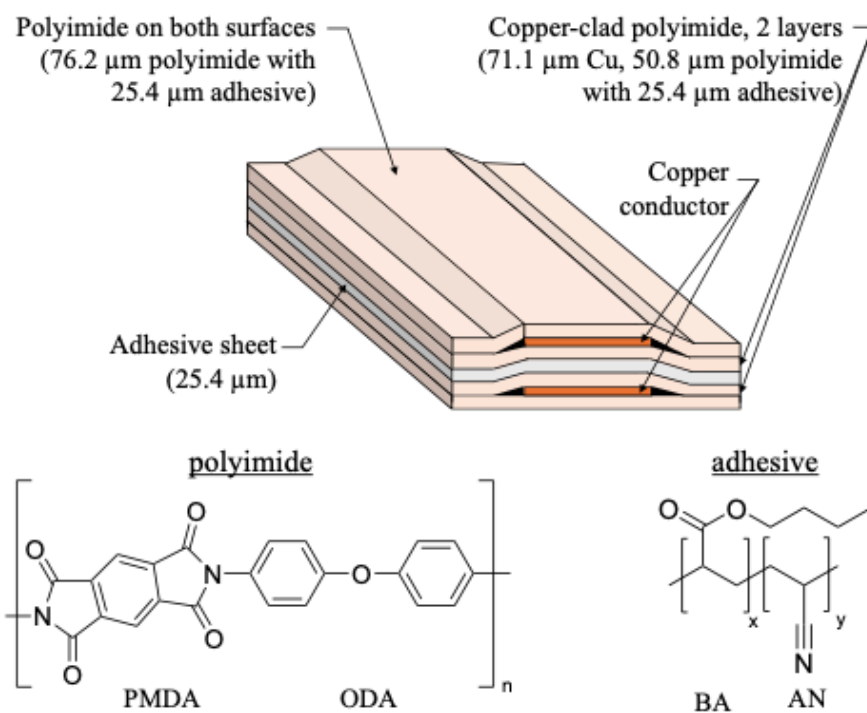
To address these gaps, this study investigates the aging mechanisms of flat-flex cables subjected to accelerated aging in controlled humid environments. Accelerated aging protocols were employed to simulate long-term exposure conditions, enabling the evaluation of age-induced changes within a practical timeframe. High potential testing was conducted to assess the dielectric properties of aged cables, providing insights into the electrical performance. Additionally, peel testing was performed to quantify changes in adhesion strength, which is a key indicator of mechanical reliability.<sup>16</sup>

The challenges of materials characterization in these systems add complexity to understanding their aging responses. For example, PMDA-ODA, a widely used material in electronic applications, is insoluble in all solvents but concentrated sulfuric acid.<sup>17</sup> Similarly, the as-fabricated acrylate-based adhesive is a B-stage polymer (i.e., partially crosslinked), which fully

crosslinks on lamination and consequently also precludes dissolution.<sup>9</sup> Thus, traditional solution-based analytical techniques are impractical for characterizing these materials. Internal flat-flex cable materials are also not easily separated in the full-up assembly, meaning that their interactions and degradation mechanisms cannot be fully understood through isolated testing. Instead, it is necessary to age and characterize cable materials *in situ*, as close contacts between the different polymers and metals in the assembled cable likely influence how each material ages and responds to environmental stressors such as heat and humidity. To further elucidate the chemical mechanisms underlying changes to peel and dielectric strength, we adopted attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy to analyze the polymeric materials inside peeled cables and track vibrational signatures indicative of chemical degradation over exposure time. As will be discussed at length below, we also applied ATR-FTIR to the adhesive layer of unaged flat-flex cables to chemically identify the acrylate adhesive as poly(butyl acrylate-co-acrylonitrile) (BA-AN). This identification provides a foundation for understanding the chemical changes observed during aging and their relationship to performance degradation.

The primary objectives of this study are twofold: (1) to determine which polymeric material—PMDA-ODA or BA-AN—is primarily responsible for the observed changes in dielectric properties and adhesion strength, and (2) to identify the chemical mechanisms driving the degradation of these materials under humid conditions. This work builds upon existing literature on polymer degradation in high-voltage applications,<sup>10, 18–28</sup> while offering new insights into the specific aging mechanisms of flat-flex cables. By integrating electrical, mechanical, and spectroscopic analyses, this research provides a comprehensive understanding of the aging behavior of flat-flex cables. The findings are expected to inform material selection, design optimization, and predictive maintenance strategies for high-voltage systems, ultimately

enhancing their reliability and operational lifespan. Furthermore, the identification of degradation pathways and their impact on cable performance will also contribute to the development of more resilient materials and improved environmental resistance for future applications.



**Figure 2.1.** (Top) Three-dimensional representation of the flat-flex cable material assembly and material stack-up, illustrating the layered structure comprising 3 materials: polyimide (light orange), adhesive (gray), and copper (dark orange). (Bottom) Chemical structures of the constituent materials: polyimide, poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline) (PMDA-ODA) used as the polyimide dielectric, and poly(butyl acrylate-*co*- acrylonitrile) (BA-AN) used as the adhesive layer.

## 2.2 Methods

### 2.2.1 Materials

Flat-flex cables were assembled from single-sided Pyralux® LF Copper-Clad Laminate, Coverlay and Bondply, and Sheet Adhesive which were purchased from Dupont™. A schematic of the flat-flex cable material stack-up and the chemical structures of PMDA-ODA and BA-AN are presented in **Figure 2.1**. To fabricate flat-flex cables, the following materials were laminated together under controlled conditions of 1.79 MPa (260 psi) at 177 °C for 1 hour:

- **Single-sided Pyralux® LF Copper-Clad Laminate:** Two layers, each consisting of 71.1 µm Cu, 25.4 µm adhesive, and 50.8 µm polyimide.
- **Coverlay and Bondply:** Two layers, each composed of 76.2 µm polyimide and 25.4 µm adhesive.
- **LF Sheet Adhesive:** A single layer of 25.4 µm adhesive.

The polyimide used in these assemblies is Kapton® HN, which has a well-characterized chemical structure: poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline) (PMDA-ODA).<sup>8</sup> The Pyralux® LF adhesive is a material for which the chemical structure is not disclosed by the manufacturer and is partially cured prior to delivery.<sup>9</sup> Its chemical structure was determined through ATR-FTIR spectroscopy (refer to Section 2.4.1) and identified as poly(butyl acrylate-*co*-acrylonitrile) (BA-AN). Additionally, replicate Sheet Adhesive samples were pressure cured under identical conditions (1.79 Mpa (260 psi) at 177 °C for 1 hour) and subsequently analyzed using dynamic vapor sorption (DVS; see Section 2.2.8) and differential scanning calorimetry (DSC; see Section 2.2.7) to evaluate their water vapor sorption and thermal properties.

### 2.2.2 Accelerated Aging

Flat-flex cables were subjected to hygrothermal conditioning in environmental chambers (Associated Environmental Systems) equipped with Watlow controllers for precise temperature and humidity regulation. The aging conditions, including temperature (°C), relative humidity (% RH), and exposure duration (days) are summarized in **Table 2.1**. Upon completion of the specified aging durations listed in **Table 2.1**, two cables were removed from the environmental chambers and allowed to equilibrate to ambient temperature and humidity for 2 hours prior to subsequent testing. Unaged cables, stored under laboratory conditions throughout the study, served as the baseline for comparison against aged cables.

**Table 2.1.** Summary of flat-flex cable aging conditions, including values for temperature (°C), relative humidity (% RH), and exposure duration (days)

| Temperature<br>(°C) | Relative Humidity<br>(% RH) | Duration<br>(days)                   |
|---------------------|-----------------------------|--------------------------------------|
| 70                  | 70                          | 14, 28, 42, 56, 70, 84, 98, 112, 140 |
| 70                  | 40                          | 182, 273                             |
| 70                  | 25                          | 126, 182, 399                        |
| 40                  | 70                          | 30, 63, 93, 156, 276, 365            |
| 25                  | 70                          | 182, 427, 714                        |

### 2.2.3 Dielectric Strength Tests

A custom high potential dielectric tester was designed and fabricated to evaluate the localized dielectric breakdown voltage of flat-flex cables. The tester applied a high potential between the outer polymeric layers and inner copper conducting strips of flex-flex cables at a

specific location. The setup consisted of a grounded brass conductor plate equipped with two brass grounding pins that contacted the polyimide dielectric on opposite sides of the cable (**Figure S2.1a**). To prepare the cables for testing, the ends were stripped back approximately 5 mm to expose the copper conductor strips. These exposed strips were connected to a Fluke 80K-40 high voltage probe and powered by either a 35 or 40 kV power supply. Voltage was increased linearly at a rate of 1000 V/s using a National Instruments DAQmx analog I/O device and data acquisition module controlled by LabVIEW software. A Fluke 199C Scopemeter was integrated into the system to capture the voltage data. All tests were conducted under uncontrolled laboratory temperature and humidity conditions.

Dielectric breakdown voltage was defined as the maximum voltage observed on the voltage versus time curve. The analog voltage controller introduced oscillations during the ramp process, creating discrete 100 V steps at a frequency of 10 steps per second (**Figure S2.1b**). Breakdown voltage was determined by averaging the voltage data within the final discrete step before a rapid voltage drop occurred, which is characteristic of dielectric breakdown. The standard deviation of the voltage data within this step was also calculated to quantify variability.

After initial testing under the 70 °C/70% RH and the 70 °C/40% RH conditions, the 35 kV power supply was replaced with a 40 kV power supply to accommodate higher voltage requirements. All aged breakdown voltage data were normalized relative to the unaged baseline data collected with the same power supply. Breakdown voltages are reported as relative values ( $V/V_0$ ), where  $V_0$  represents the unaged baseline voltage. The reported error reflects the propagated standard deviation of the normalized values.

#### 2.2.4 Peel Strength Tests

Peel strength tests were conducted on flat-flex cables to measure adhesion strength between layers. T-peel tests were performed using a TestResources 100 Series universal testing machine (Model DG250) equipped with G56K-BP Grips and controlled by Newton™ Universal Software. The tests were conducted at a constant speed of  $8.3 \times 10^{-4}$  m/s (50 mm/min). Peel strength was calculated as the constant load per unit width, determined from the flat, stable portion of the force versus extension curve. All tests were conducted under uncontrolled laboratory temperature and humidity conditions.

As the cables aged, the force-displacement data exhibited increased noise and a reduction in the length of the flat portion of the curves. To ensure consistency across samples, peel strength values were calculated by averaging forces over the same displacement range for all tested samples (an example curve is shown in **Figure S2.2**). Errors are reported as one standard deviation of the forces within this displacement range. Peel strength values for aged cables were normalized relative to the peel strength of unaged cables and are expressed as relative values ( $N/mm / N/mm_0$ ), where  $N/mm_0$  represents the peel strength of unaged cables.

#### 2.2.5 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Polyimide and adhesive materials on unaged and aged peeled cables were evaluated by ATR-FTIR spectroscopy to identify chemical changes in the individual materials. Spectroscopic data were collected using a Bruker Hyperion FTIR microscope equipped with a 20X GaAs ATR objective and controlled by Bruker OPUS 7.2 software. Infrared light reflected from a 100  $\mu$ m sample area was captured by a HgCdTe detector over the spectral range 400-6000  $\text{cm}^{-1}$ . Each acquisition point averaged 64 scans, and a total of four acquisition points were collected for each

material. A single spectrum was generated by averaging the data from all four acquisition points. All spectroscopic measurements were performed under uncontrolled ambient temperature and laboratory humidity.

#### 2.2.6 Principal Component Analysis (PCA)

PCA was applied to the ATR-FTIR data set for aged and unaged polyimide and adhesive materials using Origin(Pro) Version 2023b. PCA is a statistical tool that performs linear combinations of variables (in this case, ATR-FTIR absorbance values) to identify the maximum variance within the dataset, represented by principal components. PCA loadings indicate the contribution of specific variables (absorbance bands) to the principal component, while PCA scores represent individual data points (spectra from specific cables) in a rotated coordinate system defined by the principal components. This approach allowed identification of absorbance bands associated with the largest variations in the data (from PCA loadings) and relationships between spectra from specific cables (from PCA scores).

#### 2.2.7 Differential Scanning Calorimetry (DSC)

DSC characterization was performed using a TA instruments Discovery DSC Model 250 operating in non-modulated mode with Tzero™ DSC technology, which utilizes power compensation for precise thermal measurements. Approximately 5 milligrams of cured adhesive were placed in hermetically sealed pans with pinholes to allow controlled gas exchange. The samples were analyzed under nitrogen purge flow, with the temperature ramped at a constant rate of 3 °C/minute, covering a range from -80 to 100 °C.

## 2.2.8 Dynamic Vapor Sorption (DVS)

Dynamic water vapor sorption isotherms were measured using *in situ* gravimetry on a cured BA-AN adhesive sample (27.56 x 26.57 x 0.0254 mm and 0.0176 g). The sample was cured prior to analysis using the same conditions noted in Section 2.2.1. Measurements were performed using a Hiden Isochema IGAsorp equipped with a microbalance ( $\pm 0.05 \mu\text{g}$ ) and temperature ( $\pm 0.01 \text{ K}$ ) and humidity controllers ( $\pm 0.01\%$  RH regulation accuracy,  $\pm 1\%$  RH calibration accuracy). Humidified nitrogen was delivered at a flow rate of  $4.167 \text{ cm}^3\text{s}^{-1}$  by blending dry and saturated nitrogen streams. Isotherms were collected at 40, 50, 60, and  $70^\circ\text{C}$  over a range of 0–90% RH, with % RH increased in 5% steps. At each humidity step, the sample was allowed to reach equilibrium, as evidence by a plateauing of the mass, or a minimum of 30 minutes. Both adsorption and desorption branches were measured to assess hysteresis. The measurements and analysis described herein pertain to the bulk adhesive properties, as interface effects between different materials in the stack-up are negligible for the dynamic vapor sorption behavior observed.

Sorption data were analyzed using the dual-mode model described in Foley et al.<sup>29</sup> yielding mobile species described by Henry's ( $H_m$ ) and pooling ( $p_m$ ,  $n_m$ ) sorption parameters and immobile, non-diffusing species described by Langmuir ( $L_i$ ,  $b_i$ ) sorption parameters. Nonlinear least squares fitting was performed using MATLAB. Dynamic vapor sorption measures the total sorbed equilibrium concentration ( $c_m + c_i$ ) and effective diffusivity ( $D_{\text{eff}}$ ) as a function of temperature and relative humidity. The Henry's mobile ( $H_m$ ) and pooling ( $p_m$ ,  $n_m$ ), and immobile Langmuir ( $L_i$ ,  $b_i$ ) parameters are fit simultaneously with the diffusion parameters ( $D$ ) to equilibrium vapor concentrations and effective diffusivity data ( $D_{\text{eff}}$ ) using Equation 2.1. These parameters describe the vapor's sorption uptake equilibrium and dynamics in BA-AN

$$D_{\text{eff}} = \frac{H_m + p_m a^{n_m - 1}}{\frac{b_i L_i}{(1 + b_i a)^2} + H_m + p_m n_m a^{n_m - 1}}$$

$$c_m = H_m + p_m a^{n_m} \quad (2.1)$$

$$c_i = \frac{b_i a}{1 + b_i a} L_i$$

where  $a$  is thermodynamic activity of water (% RH expressed as a fraction),  $c_m$  and  $c_i$  are the mobile and immobile equilibrium vapor concentrations, and  $n_m$  and  $b_i$  are fitted parameters.

Model assumptions and limitations are discussed in Foley et al.<sup>29</sup>

### 2.2.9 Monte Carlo Uncertainty Quantification

Monte Carlo uncertainty quantification was employed to rigorously assess the impact of experimental variability on model parameter estimates and predictions for the mechanistic model described in Section 2.5, thereby providing statistically robust confidence intervals for all reported results. For each  $N = 1000$  iterations, synthetic datasets were generated by resampling measured values (peel strength or breakdown voltage, and  $k'$ ) from normal distributions defined by their experimentally determined means and standard deviations. The mechanistic model was then fitted to each synthetic dataset using non-linear least-squares regression (nlsLM function in R). This process yielded distributions of  $\alpha$  and  $\beta$  parameter estimates, from which 95% confidence intervals were determined using the percentile method. The standard deviation of model predictions across all iterations was used to estimate propagated uncertainty for each data point.

## 2.3 Macroscale Tests: Cable Dielectric and Peel Strength

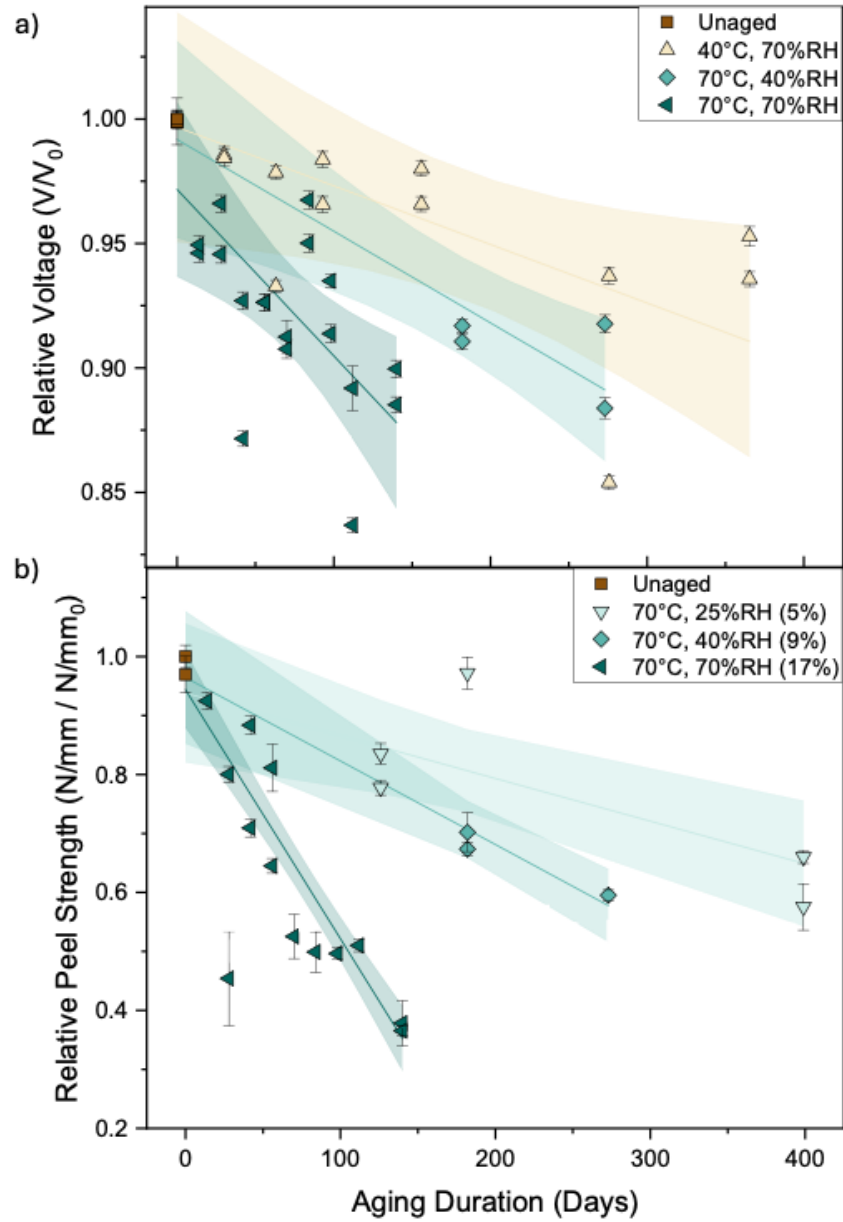
### 2.3.1 Results

Dielectric and peel strength tests were employed to investigate macroscopic, age-induced changes in flat-flex cables. High potential dielectric breakdown tests assess the dielectric strength of an insulating material, defined as the voltage required to force current through the material. These tests were conducted by gradually increasing the voltage until the insulator failed and allowed current to pass through it. Breakdown voltage depends on several factors, including the thickness of the insulating material (thinner dielectric films can withstand higher voltages),<sup>20, 30-32</sup> temperature (higher temperatures reduce breakdown voltage),<sup>33</sup> surface conditions (defects or debris can concentrate electric fields, causing premature breakdown),<sup>34</sup> and humidity during testing (higher humidity decreases dielectric strength).<sup>10, 18, 20, 22, 35, 36</sup>

Peel strength tests measure the force required to separate bonded materials at a constant rate, providing insights into the strength of adhesive bonds. T-peel tests are specifically used to evaluate adhesion between flexible bonded materials, such as flat-flex cables. Peel strength is influenced by factors such as substrate properties,<sup>37</sup> adhesive characteristics,<sup>38-40</sup> testing parameters,<sup>41</sup> environmental conditions,<sup>42</sup> and effects of aging.<sup>43</sup> In this study, dielectric strength tests were performed approximately mid-way along the cable's length, followed by T-peel tests conducted 24 hours later.

Both dielectric and peel strength tests revealed qualitatively similar trends in performance degradation over time. Specifically, both properties decreased with extended exposure to aging conditions. **Figure 2.2** illustrates linear fits to the data as a function of aging duration, with only conditions showing statistically significant linear trends displayed ( $p < 0.05$ ; see **Figure S2.3**

for complete data). Notably, cables aged at 25 °C/70% RH did not exhibit statistically significant reductions in either dielectric or peel strength, even when aged up to two years. Furthermore, the slopes of the linear fits increased with higher specific humidity (**Table 2.2**), demonstrating that both performance metrics are influenced by moisture. However, the slopes for peel strength were approximately 4-6 times larger than those for breakdown voltage, indicating that aging has a more pronounced impact on peel strength compared to dielectric properties.



**Figure 2.2.** Breakdown voltage (a) and peel strength (b) data, normalized to the values for unaged cables, plotted as a function of aging duration under various environmental conditions. Specific humidity values for each condition are provided in the parenthesis. Error bars indicate one standard deviation of the measured data. Solid lines represent linear fits to the data, while shaded bands (color-coded to match each aging condition) denote the 95% confidence interval (CI) for the linear fits.

**Table 2.2.** Summary of slopes, intercepts, and statistical p-values for linear fits of breakdown voltage and peel strength as functions of aging duration under specific aging conditions. Data is excluded for conditions without statistically significant linear trends. Errors are reported as the standard error for the corresponding values.

| <b>Relative Breakdown Voltage vs Aging Duration</b>       |                            |                 |                      |
|-----------------------------------------------------------|----------------------------|-----------------|----------------------|
| Aging Condition                                           | Slope ( $\times 10^{-5}$ ) | Intercept       | P-value <sup>†</sup> |
| 40°C, 70%RH                                               | $-20 \pm 7$                | $0.99 \pm 0.01$ | 0.03                 |
| 70°C, 40%RH                                               | $-37 \pm 7$                | $0.99 \pm 0.01$ | 0.007                |
| 70°C, 70%RH                                               | $-67 \pm 2$                | $0.97 \pm 0.02$ | 0.004                |
| <b>Relative Breakdown Peel Strength vs Aging Duration</b> |                            |                 |                      |
| Aging Condition                                           | Slope ( $\times 10^{-5}$ ) | Intercept       | P-value <sup>‡</sup> |
| 70°C, 25%RH                                               | $-70 \pm 20$               | $0.94 \pm 0.04$ | 0.004                |
| 70°C, 40%RH                                               | $-180 \pm 50$              | $1.0 \pm 0.1$   | 0.03                 |
| 70°C, 70%RH                                               | $-420 \pm 30$              | $0.93 \pm 0.03$ | <0.0001              |

<sup>†</sup> p-values for 25 °C, 70 %RH and 70 °C, 25 %RH were 0.15 and 0.97, respectively

<sup>‡</sup> p-values for 25 °C, 70 %RH and 40 °C, 70 %RH were 0.4 and 0.7, respectively

Peel strength is commonly used to evaluate the stability of adhesive materials; however, approximately 15% of the flat-flex cables tested exhibited remnants of PMDA-ODA on the peeled cable arms. ATR-FTIR spectroscopy confirmed these remnants to be PMDA-ODA. This suggests the locus of failure was in the PMDA-ODA layer rather than the adhesive. **Figure S2.4** illustrates representations of T-peel testing and potential failure modes. Structural failure within PMDA-ODA was observed when aged at 70 °C /70% RH for 14, 70, 84, 98 and 112 days, 70 °C/40% RH for 273 days, and 70 °C /25% RH for 182 days. In contrast, the remaining 85% of flat-flex cables exhibited cohesive failure within the adhesive layer. Peel force measurements were consistently lower—and in some cases significantly lower—for PMDA-ODA failures

compared to adhesive failures under identical conditions (**Table S2.1**). Notably, PDMA-ODA failures occurred only in cables aged at 70 °C with 25% or higher relative humidity, and no such failures were observed at lower temperature, even after extended exposure times. However, the age-dependence of PDMA-ODA failure remains unclear. The most aggressively aged cables (140 days at 70 °C/70% RH) exhibited cohesive failure within the adhesive layer. Further, ATR-FTIR analysis revealed that PMDA-ODA from the peeled cable arms was chemically indistinguishable from unaged PMDA-ODA (**Figure S2.5**), suggesting that any age-induced changes were below the detection limit of ATR-FTIR or primarily physical in nature. It is also plausible that inconsistencies in the initial cut influenced the material in which the failure propagated.<sup>40</sup>

### 2.3.2 Discussion

A peel test study by Kinloch and Yuen<sup>28</sup> on copper laminates containing PMDA-ODA and acrylic-based adhesive layers demonstrated similar failure modes to those observed in this study. Laminates composed of polyimide films with “low-thermal history” fractured within the PMDA-ODA layer, while those with “high-thermal history” fractured within the adhesive layer during peel testing.<sup>28</sup> Kinloch and Yuen observed cohesive failure in cases where the adhesive failed, consistent with the results of flat-flex cable peel tests.<sup>28</sup> Additionally, they reported that peel strengths were highly scattered but systematically lower for laminates that fractured within the polyimide layer compared to those that failed within the adhesive layer,<sup>28</sup> a trend also observed in this study (**Table S2.1**). Although no chemical analysis of “low-” or “high-thermal history” PMDA-ODA films was provided, Kinloch and Yuen hypothesized that “low-thermal history” material were only partially imidized, while “high-thermal history” materials were fully imidized.<sup>28</sup>

Infrared spectroscopy can monitor the extent of imidization using characteristic bands of the poly(amic acid) precursor.<sup>44</sup> This band can also be used to evaluate hydrolysis via de-imidization.<sup>45</sup> We applied ATR-FTIR spectroscopy and noted the absence of such bands in aged PMDA-ODA from flat-flex cables (**Figure S2.5**), which suggests that structural failure is unlikely due to as-fabricated partial imidization or age-induced hydrolysis. However, Pyrde demonstrated that even thoroughly cured PMDA-ODA undergoes nominal hydrolysis in humid environments, accounting for approximately 1% of the total imide concentration.<sup>45</sup> The source of the hydrolysis—whether from the PMDA imide ring or an anhydride end group—remains unclear. Although low-level hydrolysis may be below the detection limit of ATR-FTIR spectroscopy, the resulting ring opening and chain scissioning could significantly alter the material's mechanical and dielectric properties. Kim et al. similarly observed no changes in the IR signatures of PMDA-ODA aged at 85 °C and 85% RH environment but attributed adhesion loss on metal surfaces to low-level imide ring hydrolysis.<sup>46</sup> Wu and Denton also found no evidence of chemical changes in PMDA-ODA aged under similar conditions but credited bulk morphological changes for the observed decrease in bulk resistivity.<sup>23</sup> While ATR-FTIR analysis did not reveal detectable age-induced chemical changes in PMDA-ODA, future work will employ more sensitive surface analytical techniques, such as X-ray photoelectron spectroscopy, to investigate subtle chemical modifications resulting from hygrothermal aging.

PMDA-ODA is known to absorb approximately 3.5 wt.% water,<sup>8, 10, 11</sup> which can alter its dielectric response properties. Increased humidity has been shown to raise the dielectric constant, impacting the material's insulating performance.<sup>22</sup> Li et al. investigated the dielectric strength of PMDA-ODA subjected to high temperatures (450–480 °C, near the material degradation temperature)<sup>8</sup> and immersed in water. They observed a decrease in dielectric strength due to

water exposure, attributed to the formation of ionic side groups that promoted conduction. However, drying completely reversed the dielectric strength decrements, demonstrating that moisture uptake did not result in permanent physical changes to the PMDA-ODA polymeric structure.<sup>18</sup> This indicates that, in the absence of chemical changes, moisture uptake is reversible and does not strongly influence insulating properties at ambient temperatures.

Beyond chemical stability, physical aging of PMDA-ODA may also contribute to embrittlement through changes in chain relaxation and local orderliness. Over time, physical aging can reduce molecular mobility and increase local ordering, which in turn diminishes the material's ability to dissipate stress, making it more susceptible to brittle fracture.<sup>47</sup> This interpretation is supported by peel test results from this study, where fracture propagation was observed within the PMDA-ODA layer, indicating bulk mechanical failure rather than interfacial or adhesive layer failure. Such embrittlement mechanisms are consistent with the cohesive failure modes reported by Kinloch and Yuen,<sup>28</sup> who found that laminates with “low-thermal history” polyimide films fractured within the PMDA-ODA layer and exhibited systematically lower peel strengths. These findings suggest that physical aging and associated morphological changes in PMDA-ODA may play a role in the long-term mechanical reliability of flat-flex cable assemblies.

While potential physical changes to aged PMDA-ODA in flat-flex cables cannot be ruled out, the lack of evidence for chemical changes does indicate that the material is robust at the conditions studied. This finding may implicate other materials, such as the adhesive, in the observed degradation of dielectric strength over time.

Adhesives, while primarily designed for bonding applications, are increasingly utilized for their insulating properties in specialized applications such as electronics, thermal

management, and barrier systems.<sup>24</sup> Acrylate-based adhesives, in particular, are widely used in electrical tapes due to their high dielectric strength and stable insulating performance across a broad temperature range.<sup>26</sup> Crosslinked adhesives are especially advantageous in flexible electronics, where thermal stability and electrical insulation are critical. The crosslinked network reduces ionic mobility within the adhesive matrix, enhancing dielectric properties and preventing electrical conduction.<sup>27</sup> Acrylate-based crosslinked adhesives are commonly employed in flexible printed circuit boards due to their high dielectric strength and long-term stability.<sup>25</sup> The crosslinked adhesive used in flat-flex cables has a reported volume resistivity of  $10^{14} \text{ } \Omega/\text{cm}$ ,<sup>9</sup> indicating excellent dielectric properties that likely contribute to the overall dielectric breakdown voltage results observed in this study. Thus, adhesive degradation may influence a cable's breakdown voltage regardless of the apparent stability of the primary PDMA-ODA insulator.

Copper conducting strips within flat-flex cables may also contribute to the degradation of acrylate-based adhesives and alter the mechanical and dielectric properties of polyimides. Under hygrothermal conditions, copper ions can diffuse into adjacent polymeric layers, catalyzing hydrolysis and oxidative degradation.<sup>48, 49</sup> This process accelerates chain scission, reducing the adhesive's mechanical integrity and bonding strength.<sup>48, 49</sup> Such degradation compromises adhesion between the copper and polyimide layers, potentially leading to delamination and mechanical failure. Importantly, peel test results from this study indicate that mechanical failure predominantly arises from bulk adhesive degradation rather than interfacial effects at the copper-adhesive boundary. Therefore, while copper ion migration may contribute to interface-specific degradation, our focus remains on the bulk adhesive properties, which are most relevant to the observed failure modes.

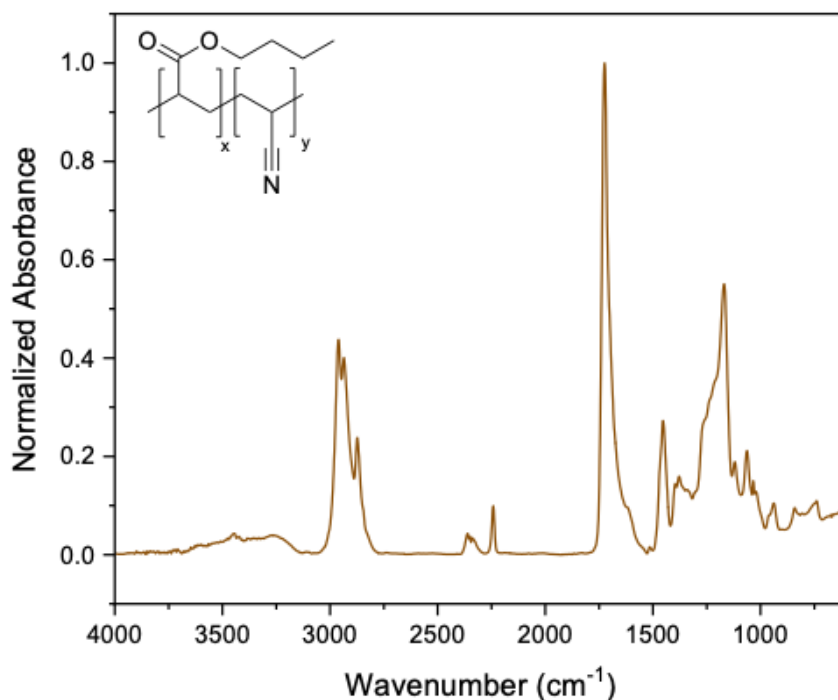
Additionally, copper ions can form conductive pathways within the polymer layers, causing localized electrical breakdown under high-voltage conditions.<sup>48, 50</sup> The extent of copper migration and its contribution to cable degradation remains unclear; however, the combined effects of copper and water on degradation chemistry of the individual polymeric components and conductive path formation can significantly compromise the overall performance and reliability of the cable laminate. While we acknowledge the potential significance of copper migration in these degradation processes, we do not explore this phenomenon in detail. Understanding and mitigating copper migration remains an open problem for ensuring the long-term stability of flat-flex cables, particularly in environments prone to moisture and heat.<sup>48</sup>

## 2.4 Microscale Tests: DVS and ATR-FTIR Spectroscopy

### 2.4.1 Unaged Adhesive Structure

The chemical structure of the flat-flex cable adhesive was identified as poly(butyl acrylate-*co*-acrylonitrile) (BA-AN) through ATR-FTIR spectroscopy analysis of the adhesive from within an unaged cable that was previously peel tested (**Figure 2.3**). A summary of the band assignments for the adhesive is provided in **Table 2.3**. Weak, broad bands between 3100-3600 cm<sup>-1</sup> were attributed to O-H stretching ( $\nu$ ) of absorbed water, with specific bands near 3612, 3560, 3420 and 3255 cm<sup>-1</sup> corresponding to monomeric, dimeric, clustered, and bulk water, respectively.<sup>51</sup> The band at 3444 cm<sup>-1</sup> was identified as an overtone of  $\nu$ C=O. The absence of features between 3100 and 3000 cm<sup>-1</sup> suggests that the adhesive lacks aromatic or olefinic (sp<sup>2</sup> hybridized) functionality within the detection limits of the instrument, indicating minimal residual vinyl end groups. Bands between 2800–2900 cm<sup>-1</sup> correspond to C-H stretching vibrations, confirming the presence of both CH<sub>2</sub> and CH<sub>3</sub> groups. Specifically,  $\nu_{as}$ CH<sub>3</sub> and  $\nu_s$ CH<sub>3</sub> were observed at 2960 and 2873 cm<sup>-1</sup>, respectively, and  $\nu_{as}$ CH<sub>2</sub> at 2931 cm<sup>-1</sup>.<sup>52</sup> A

medium-intensity H-C-H bending ( $\delta$ ) mode appeared slightly downshifted from its standard position at  $1460\text{ cm}^{-1}$ , suggesting the presence of polar groups. The weak band at  $2243\text{ cm}^{-1}$  was characteristic of  $\text{C}\equiv\text{N}$  stretching in nitriles.<sup>53-55</sup> The sharp band between  $1800$  and  $1650\text{ cm}^{-1}$ , coupled with strong bands between  $1200$ - $1100\text{ cm}^{-1}$ , indicates ester ( $\text{COOR}$ ) functionality. Weak bands near  $1396$  and  $1379\text{ cm}^{-1}$  were attributed to methylene and methyl deformations on the BA pendant.<sup>52</sup> The adhesive structure showed a 95% Hit Quality Index match to a 1:1wt.% BA-AN spectrum from the Bio-Rad Laboratories Database<sup>56</sup> (**Figure S6**), but the specific monomer ratio  $x:y$  was not conclusively determined.



**Figure 2.3.** Representative normalized ATR-FTIR spectrum of the cured, unaged adhesive. The adhesive spectrum closely matches that of a BA-AN copolymer (see inset structure).

**Table 2.3.** Summary of adhesive band frequencies, associated functional groups, tentative spectral assignments, and corresponding references for the cured, unaged adhesive.

| Frequency (cm <sup>-1</sup> ) | Relevant Functional Groups                           | Tentative Assignments <sup>†</sup>                                             | References |
|-------------------------------|------------------------------------------------------|--------------------------------------------------------------------------------|------------|
| 3612, 3560, 3420, 3255        | absorbed water (monomeric, dimeric, clustered, bulk) | $\nu$ O-H                                                                      | 51, 52, 57 |
| 3444                          | carbonyl ester (BA)                                  | $\nu$ C=O overtone                                                             | 51, 52, 57 |
| 2960, 2935, 2873              | methyl, methylene                                    | $\nu_{as}$ CH <sub>3</sub> , $\nu_s$ CH <sub>2</sub> , $\nu_s$ CH <sub>3</sub> | 58         |
| 2243                          | nitrile (AN)                                         | C $\equiv$ N                                                                   | 53         |
| 1724                          | carbonyl ester (BA)                                  | $\nu$ C=O                                                                      | 52         |
| 1452                          | methyl, methylene                                    | $\delta_{as}$ C-H                                                              | 52, 53     |
| 1396                          | methylene (BA)                                       | $\delta$ C-H                                                                   | 52         |
| 1379                          | methyl (BA)                                          | $\delta_s$ C-H                                                                 | 52         |
| 1200–1284                     | alkyl (backbone), methylene (BA), ester (BA)         | $\delta$ C-H (wag, twist)                                                      | 52, 57     |
| 1168                          | ester (BA)                                           | $\nu_s$ C-O-C                                                                  | 52, 53, 57 |
| 1118, 1064                    | alkyl (backbone and butyl)                           | $\nu_{as}$ and $\nu_s$ C-C-C                                                   | 52         |
| 1034, 1022, 960, 939          | alkyl (backbone)                                     | $\nu$ C-C-C                                                                    | 52         |
| 841, 806                      | alkyl (BA)                                           | $\nu$ C-C-C                                                                    | 52         |
| 739, 658                      | alkyl                                                | $\delta$ C-H (rock)                                                            | 52         |

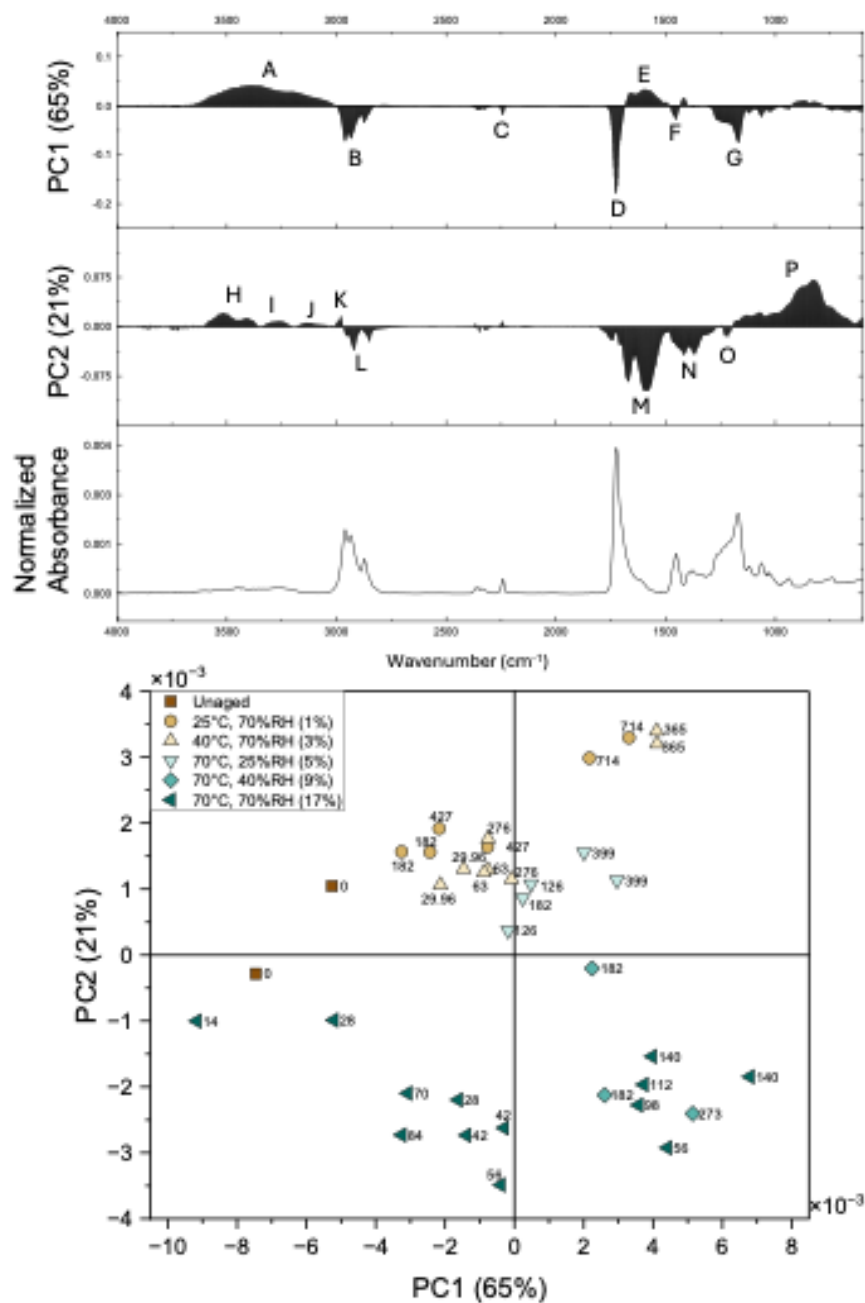
<sup>†</sup> 'a' and 'as' denote symmetric and asymmetric modes, respectively

## 2.4.2 Aged Adhesive Characteristics

Adhesive exposed by peeled cable arms was analyzed using ATR-FTIR spectroscopy to assess chemical changes after exposure to various environmental conditions. Unlike PMDA-ODA, which showed no detectable chemical changes (**Figure S2.5**), the adhesive exhibited significant alterations in vibrational bands after aging. Principal component analysis (PCA) was applied to the data across all aging conditions and durations to identify spectral bands (from PCA loadings) associated with the largest variations in the data and to explore relationships between

spectra collected from specific cables (from PCA scores). The first five principal components (PCs), which accounted for 95% of the total variance, were evaluated as a function of aging duration, temperature, humidity, breakdown voltage, and peel strength. Only the first two PCs, representing a cumulative 86% of the total variance, were statistically correlated to specific aging conditions (temperature, humidity, time) and/or macroscale performance test results. PC1 and PC2 accounted for 65 and 21% of the variance in adhesive ATR-FTIR spectra, respectively. **Figure 2.4** displays PC loadings and scores with lettered band designations (details and tentative assignments are summarized in **Table 2.4**). **Figure S2.7** shows loadings for PCs 3–5, while **Table S2.2** lists statistical parameters for linear regressions of PCs 3–5 to aging conditions and performance metrics.

Positive and negative signed regions of individual bands in the PC loadings indicate the direction of variance according to the PC scores. For instance, the adhesive spectrum from a cable aged for 140 days at 70°C and 70% RH had the largest PC1 score, and the corresponding PC1 loadings showed a larger A region and smaller D region compared to adhesive from a cable aged for 14 days under the same conditions, which had a lower PC1 score. Qualitative trends in PC1 scores suggest that within a given aging condition, longer durations tend to increase positive PC1 loadings bands and decrease negative PC1 loadings bands. Additionally, PC2 scores indicate that adhesive spectra associated with low-temperature, low-moisture aging environments tend to exhibit positive PC2 scores, while spectra from higher-temperature, higher-humidity environments tend toward negative PC2 scores. This suggests that positive PC2 loading bands are associated with low-temperature, low-moisture conditions, while negative PC2 bands correspond to higher-temperature, high-humidity environments. In what follows, we interpret these PC loadings to identify plausible chemical changes and reactions that accompany aging.



**Figure 2.4.** (a) Loadings for PC1 (65% of the total variance) and PC2 (21% of the total variance) plotted as a function of wavenumber. Spectral regions associated with each principal component are labeled A through P. (b) Parametric plot of PC1 and PC2 scores for all aging conditions. Scores are grouped by aging condition (symbol type), with aging duration (in days) indicated next to each score.

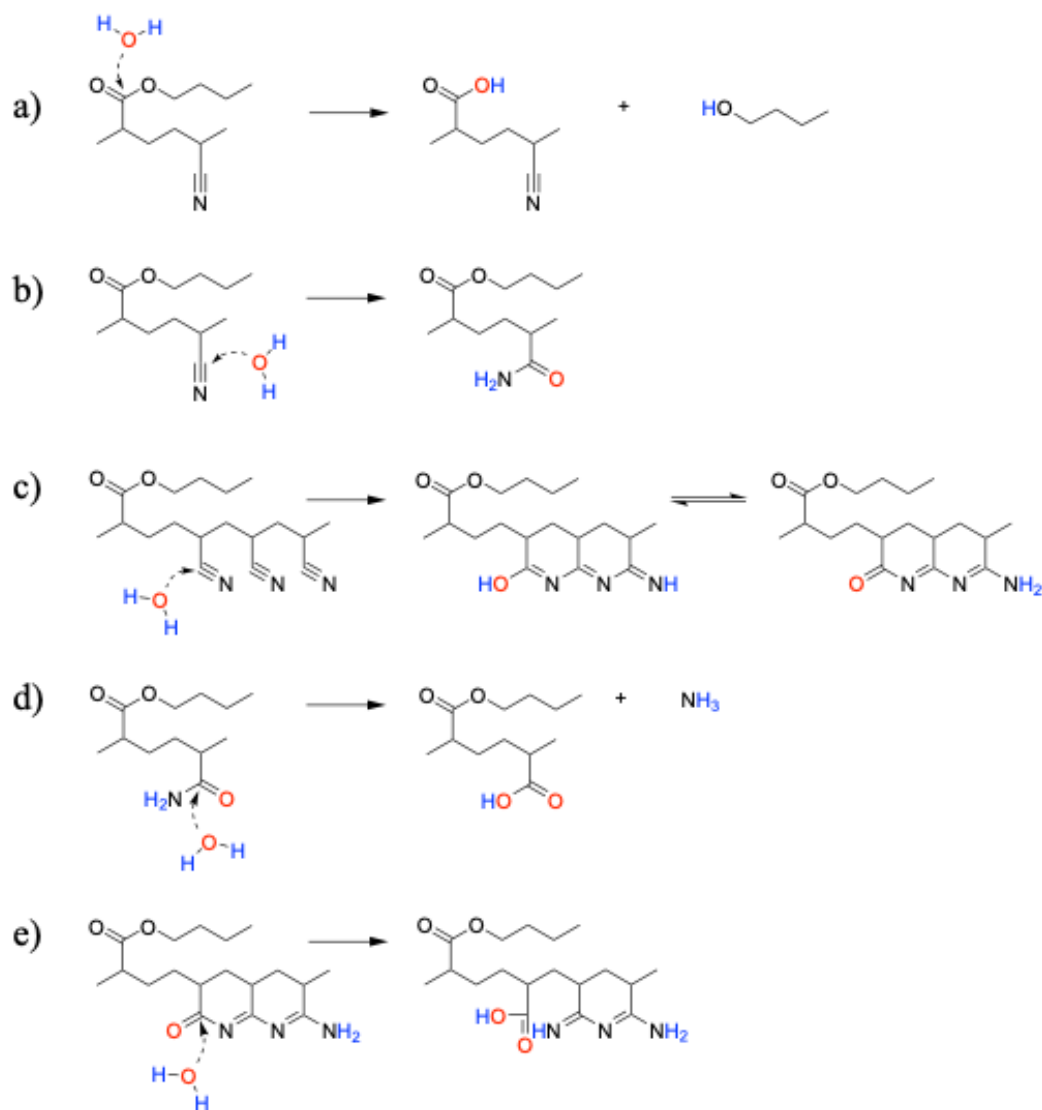
**Table 2.4.** Summary of spectral regions associated with PC1 and PC2, detailing frequencies of major features within each region, relevant functional groups corresponding to specific frequencies, and tentative assignments for these vibrational modes.

| PC1 Bands       |                               |                                         |                                                                                |                    |
|-----------------|-------------------------------|-----------------------------------------|--------------------------------------------------------------------------------|--------------------|
| Spectral Region | Frequency (cm <sup>-1</sup> ) | Primary Functional Groups               | Tentative Assignments <sup>†</sup>                                             | References         |
| A               | 3388                          | alcohol, carboxylic acid, amide A       | $\nu$ O-H (H-bonds & intramolecular) $\nu_{as}$ N-H                            | 54, 50–62          |
|                 | 3204                          | alcohol, carboxylic acid, amide A       | $\nu$ O-H, $\nu_s$ N-H                                                         | 54, 61–65          |
| B               | 2960, 2931, 2873              | methyl, methylene                       | $\nu_{as}$ CH <sub>3</sub> , $\nu_s$ CH <sub>2</sub> , $\nu_s$ CH <sub>3</sub> | 52, 58             |
| C               | 2243                          | nitrile                                 | $\nu$ C≡N                                                                      | 53–55              |
| D               | 1726                          | carbonyl (ester)                        | $\nu$ C=O                                                                      | 52, 54, 59, 63, 65 |
| E               | 1658                          | carbonyl (amide I), amide II, amidine   | $\nu$ C=O, $\nu$ C=N, $\delta$ N-H                                             | 54, 62, 64, 66–69  |
|                 | 1590                          | amide II, amidine                       | $\delta$ N-H                                                                   | 62, 64, 67, 69     |
| F               | 1454                          | methyl, methylene                       | $\delta_{as}$ C-H                                                              | 52                 |
| G               | 1257                          | methylene (BA attached to O)            | $\delta$ C-H (wag)                                                             | 52                 |
|                 | 1236                          | alkyl (backbone), ester                 | $\delta$ C-H, $\nu_{as}$ C-O-C, $\nu$ C-O                                      | 52                 |
|                 | 1168                          | ester                                   | $\nu_s$ C-O-C, $\nu$ C-O                                                       | 52                 |
| PC2 Bands       |                               |                                         |                                                                                |                    |
| Spectral Region | Frequency (cm <sup>-1</sup> ) | Primary Function Groups                 | Tentative Assignments                                                          | References         |
| H               | 3517                          | alcohol                                 | $\nu$ O-H (H-bond intermolecular)                                              | 51, 61, 74         |
|                 | 3409                          | acid, alcohol                           | $\nu$ O-H (acid-OH bonded to alcohol- OH)                                      | 61                 |
| I               | 3268                          | acid, alcohol                           | $\nu$ O-H                                                                      | 61, 68             |
| J               | 3135                          | acid                                    | $\nu$ O-H                                                                      | 61, 65             |
|                 | 3060                          | alkene                                  | C=C stretch                                                                    | 74, 75             |
| K               | 2981                          | methyl                                  | $\nu_{as}$ CH <sub>3</sub>                                                     | 52                 |
| L               | 2954, 2919, 2850              | methyl, methylene                       | $\nu_{as}$ CH <sub>3</sub> , $\nu_s$ CH <sub>2</sub> , $\nu_s$ CH <sub>3</sub> | 52, 54, 59, 63, 65 |
| M               | 1739                          | carbonyl (ester)                        | C=O                                                                            | 52, 54, 59, 63, 65 |
|                 | 1672                          | amide I, amidine                        | $\nu$ C=O, $\nu$ C=N                                                           | 62, 69             |
|                 | 1595                          | amide II, amidine, alkene               | $\delta$ N-H                                                                   | 62, 64, 67, 69, 75 |
| N               | 1487–1246                     | methyl, methylene                       | $\delta$ C-H                                                                   | 52                 |
| O               | 1194–1244                     | ester (BA), methylene (BA and backbone) | $\nu$ C-O-C, $\delta$ C-H (wag, twist)                                         | 52, 53, 57         |
| P               | 1000–1126                     | acid, alcohol                           | $\nu$ COH                                                                      | 65, 68             |
|                 | 800–1000                      | acid, alcohol, alkene                   | $\delta$ O-H <sub>out-of-plane</sub> , $\delta$ C=C-H                          | 65, 68, 74, 75     |
|                 | 746                           | alkene                                  | $\delta$ C=C-H                                                                 | 74, 75             |

<sup>†</sup> 'a' and 'as' denote symmetric and asymmetric modes, respectively

### 2.4.3 Potential Adhesive Degradation Reactions

Several key indicators of chemical degradation are captured by the negative regions of PC1 loadings, which represent the loss of specific vibrational modes over exposure time. Specifically, the B, C, D, and G regions correspond to  $\nu\text{C-H}$ ,  $\nu\text{C}\equiv\text{N}$  (nitrile),  $\nu\text{C=O}$  (ester), and  $\delta\text{C-O}$  (ester) modes, respectively. These observations point to chemical reactions occurring at the pendant groups on both copolymer moieties in BA-AN. Conversely, the positive direction of bands in the A and E regions corresponds to new vibrational modes associated with degradation products formed through reactions involving nitrile and ester functional groups. Simple hydrolysis reactions of BA-AN pendant groups, resulting in their conversion to acid, alcohol and amide functionalities (**Figure 2.5a, b**), can explain the vibrational modes captured by PC1 loadings. Region A features broad bands centered at 3388 and 3204  $\text{cm}^{-1}$ , attributed to  $\nu\text{O-H}$ ,<sup>59–61, 62</sup> and  $\nu\text{N-H}$  stretching modes.<sup>62, 64</sup> Region E contains bands centered at 1658 and 1590  $\text{cm}^{-1}$ , corresponding to amide I ( $\nu\text{C=O}$ ) and amide II ( $\delta\text{N-H}$ ) modes, respectively.<sup>62, 64, 67, 69</sup>



**Figure 2.5.** Possible hydrolysis reactions involving BA-AN pendant functional groups: (a) hydrolysis of a BA ester pendant group yielding an acid and alcohol; (b) hydrolysis of an AN nitrile pendant group forming an amide (simple mechanism); (c) hydrolysis of an AN nitrile pendant group within an AN polymer block leading to conjugated amidine sequences and isomerism to a secondary amide (as proposed by Litmanovich et al.<sup>66</sup>); (d) hydrolysis of the amide group (formed from reaction b) resulting in acid formation; (e) hydrolysis of conjugated amidine sequences (formed from reaction c) leading to acid formation (as proposed by Litmanovich et al.<sup>66</sup>)

An alternative hydrolysis mechanism for poly(acrylonitrile) proposed by Litmanovich et al. suggests the formation of conjugated amidine sequences (**Figure 2.5c**).<sup>66</sup> The distinguishing band for the conjugated amidine structure ( $\nu\text{C}=\text{N}$  at  $1658\text{ cm}^{-1}$ ) overlaps with those from amides and other aged BA-AN vibrational modes, making it difficult to confirm amidine formation using ATR-FTIR spectroscopy alone. The presence of conjugated amidine structures in degraded BA-AN would require the adhesive to exhibit block copolymer characteristics, specifically repeating stereoregular, isotactic AN units. Such repeat units would likely manifest in crystalline regions.

Minagawa et al. demonstrated that isotactic poly(acrylonitrile) exhibits 40–50% crystallinity,<sup>76</sup> while Hobson et al. reported ~30% crystallinity in atactic poly(acrylonitrile).<sup>77</sup> In contrast, Kawasaki et al. determined that stereoregular, isotactic poly(n-butyl acrylate) is amorphous at room temperature due to steric hindrance from the n-butyl groups, which obstruct lattice formation.<sup>52</sup> This suggests that any crystallinity in BA-AN likely originates from AN monomer units.

Differential scanning calorimetry (DSC) analysis of unaged BA-AN revealed evidence of crystallinity, including an endothermic melt peak centered at  $47\text{ }^{\circ}\text{C}$  (**Figure S2.8**). The DSC cooling cycle showed an inflection indicative of the glass transition ( $T_g$ ), occurring nominally  $10\text{ }^{\circ}\text{C}$  below the crystalline melt. However, the absence of a recrystallization peak during cooling and no further crystalline melt during reheat suggests that crystallization is a slow process. Additionally, the thermogram did not show distinct  $T_g$  features for each monomer type, indicating that unaged BA-AN is not extensively block polymerized but is likely a random copolymer with a low degree of stereoregular, isotactic AN repeat units. While it is unlikely that

conjugated amidine sequences are present in significant quantities in aged BA-AN, their existence cannot be ruled out.

There are indications that PC1 captures secondary effects and reactions following the initial hydrolysis of BA-AN functional groups. For instance, the negative direction of B bands associated with C-H stretching suggests potential diffusion and possible evaporation of butanol resulting from BA hydrolysis. Such secondary effects may significantly impact adhesive degradation and flat-flex cable performance but are not clearly distinguished in ATR-FTIR spectroscopy. Furthermore, no positive band can be definitively attributed to  $\nu\text{C=O}$  from acid formation. The overlapping C=O stretching bands from acid and ester groups<sup>54, 63, 65</sup> suggest that more ester functionality may have been lost than acid functionality formed, potentially indicating additional reactions leading to the loss of carbonyl functionality.

The broad bands represented by PC2 loadings are more challenging to interpret without further information on the adhesive's chemical degradation mechanisms, particularly in the region below  $2000\text{ cm}^{-1}$ . However, trends in PC2 loadings provide insight into potential degradation chemistry. PC2 bands above  $3000\text{ cm}^{-1}$  (denoted as H, I and J regions) are all in the positive direction and can be attributed to  $\nu\text{O-H}$ <sup>54, 59–61, 63</sup> and/or  $\nu\text{N-H}$ .<sup>62, 64</sup> If the bands originated from NH stretching due to AN-nitrile hydrolysis, PC2 loadings would be expected to show the nitrile band at  $2243\text{ cm}^{-1}$  in the negative direction. However, the small positive direction of the nitrile band suggests that PC2 does not describe nitrile hydrolysis. Instead, bands in the H, I, and J regions are tentatively attributed to OH stretching from inter- and intra-molecular bonds of alcohols, acids and water. These bands likely correspond to positive bands in the P region of PC2 loadings, attributed to alcohol and acid  $\nu\text{C-O}$  and  $\delta\text{O-H}$  modes.<sup>61, 68</sup>

The M region contains three distinct negative bands centered at 1739, 1672, and 1595  $\text{cm}^{-1}$ . The highest frequency band is likely associated with the BA-ester carbonyl.<sup>52</sup> Its opposing direction relative to bands in the OH stretching region suggests that PC2 partially describes acid and alcohol formation from BA hydrolysis at the carbonyl functionality, similar to PC1. This is further supported by the negative directionality of the N and O bands, which can be attributed to BA pendant alkyl bending, and ester C-O stretching modes, respectively.<sup>52</sup> The broad M features centered at 1672 and 1595  $\text{cm}^{-1}$  can be attributed to amide I ( $\nu\text{C=O}$ ) or amidine ( $\nu\text{C=N}$ ) modes and amide II or amidine ( $\delta\text{N-H}$ ) modes, respectively.<sup>62, 64, 66–68</sup> The negative direction of the M bands, coupled with the positive direction of bands in the OH stretching regions, suggests further hydrolysis of amide and amidine groups into acids, as proposed by Litmanovich et al. (**Figure 2.5d, e**). Conjugated amidine sequences may continue reacting to form additional acid functionality.<sup>66</sup> Some C-O-H bending modes from acid and alcohol moieties may be obscured by overlapping bands from C-H vibrational modes in the polymer. Small molecule amide hydrolysis products, such as ammonia, may have continued to react<sup>70</sup> or left the system via diffusion.

The hydrolysis mechanisms for pendant nitrile groups are strongly regulated by the local chemical environment within the solid polymer matrix. Factors such as polymer chain mobility, degree of crystallinity, local polarity, and the presence and accessibility of water play a key role in determining both the probability and kinetics of hydrolysis, which can differ substantially from solution-phase chemistry.<sup>71</sup> In solid-state matrices, the chemical environment is inherently dynamic and heterogeneous, evolving over time as degradation proceeds.

Amorphous regions, characterized by greater chain mobility and free volume, facilitate the diffusion of water molecules and allow functional groups to reorient and interact, enabling

hydrolysis of accessible nitrile groups. In contrast, crystalline domains, where nitrile functionalities are tightly packed and often buried within ordered regions, tend to exclude water, until the surrounding amorphous matrix is sufficiently degraded to disrupt the crystal lattice and permit water ingress.<sup>72</sup> Conversion of nitriles to amides increases local hydrophilicity, attracting more water and promoting subsequent hydrolysis events. Formation of cyclic amidine structures in adjacent AN groups can locally elevate the pH within the polymer matrix, even when the bulk environment remains neutral<sup>73</sup> further facilitating nitrile hydrolysis. As amidines hydrolyze to acids and secondary amides, the matrix becomes increasingly heterogeneous, with acidic and basic microdomains that seed hydrolysis events. This spatially and temporally evolving chemical environment results in multi-year progression of AN hydrolysis, gradually shifting the matrix toward a more hydrophilic state with macroscopic consequences for mechanical and dielectric properties that unfold over years of service.

While PC1 primarily describes hydrolysis of BA-AN pendant groups, PC2 appears to capture secondary hydrolysis of amide and amidine functionalities. Similar to PC1, PC2 likely represents additional secondary reactions beyond successive hydrolysis. For example, the K band in PC2 loadings, centered at  $2891\text{ cm}^{-1}$ , is associated with methyl  $\text{CH}_3$  stretching modes.<sup>52</sup> The positive direction of this band, coupled with the negative direction of methylene stretching modes captured in the L region, may indicate polymer backbone fragmentation. Additionally, the band in the J region, centered at  $3060\text{ cm}^{-1}$ , can be attributed to alkene  $\text{C}=\text{C}-\text{H}$  stretching modes.<sup>74, 75</sup> Alkene  $\text{C}=\text{C}$  stretching and  $\text{C}=\text{C}-\text{H}$  bending modes (typically found between  $1660\text{--}1630\text{ cm}^{-1}$  and  $800\text{--}1000\text{ cm}^{-1}$ , respectively<sup>75</sup>) may be obscured by overlapping bands associated with amide/amidine  $\text{N}-\text{H}$  bending and alkyl bending modes.

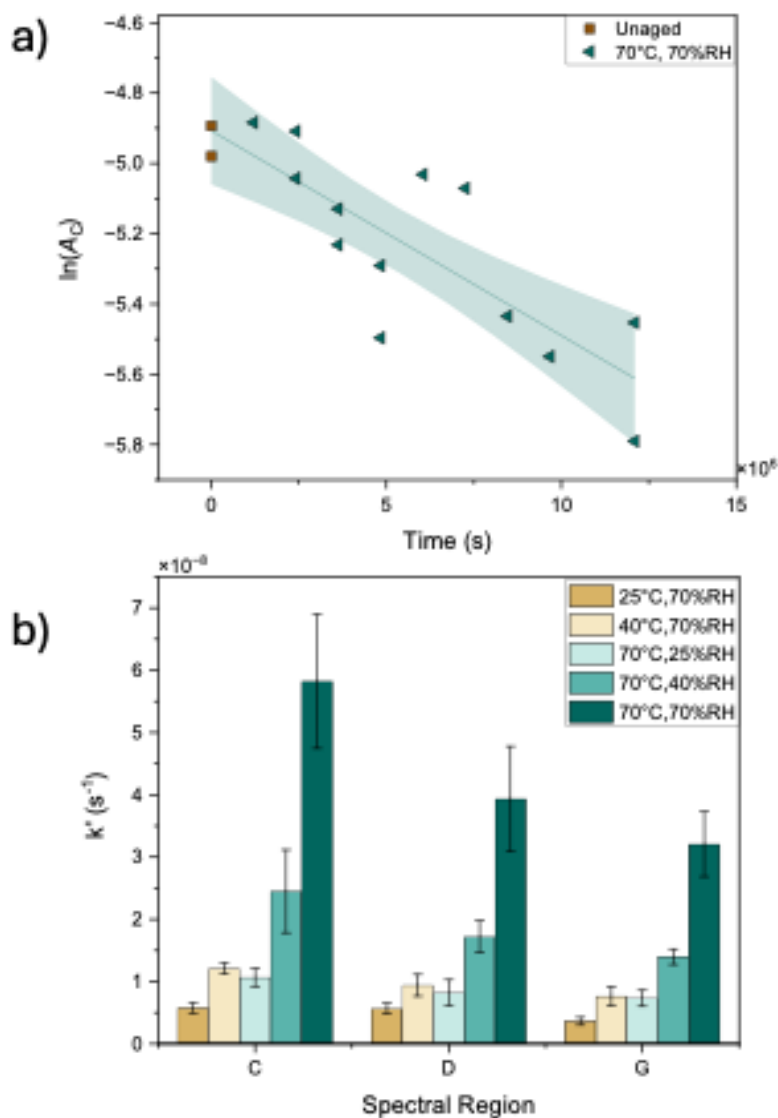
The origins of alkene functionality in aged BA-AN is unclear from spectral analysis alone. Many of these reactions likely promote additional crosslinking, which can significantly impact the adhesive's mechanical and dielectric properties. Ambiguities in our findings emphasize the need for additional methods to understand the range of possible hydrolysis reactions and subsequent reactions associated with flat-flex cable adhesive degradation.

#### 2.4.4 Time-dependence of Adhesive Degradation

As described in Section 2.4.2, principal component 1 (PC1) scores and its corresponding spectral regions exhibit a clear trend with aging duration. To quantify these relationships, two complementary approaches were employed. First, for bands corresponding to primary hydrolyzable groups, specifically, ester (regions D and G) and nitrile (region C) functionalities identified in Section 2.4.3, pseudo-first order reaction rate constants were extracted from the time-dependent integrated absorbance of these regions. It is acknowledged that the spectral regions selected for COOC (regions D and G) may include contributions from vibrational modes of other functional groups present in the adhesive; however, based on spectral assignments and comparative analysis, the majority of the absorbance in these bands is most appropriately attributed to the ester (COOC) functionality. Second, for all other bands, normalized accumulation and decay rates were determined by linear regression of integrated spectral areas as a function of time under each condition. All kinetic and regression analyses were performed using Origin(Pro) Version 2023b.

The hydrolysis mechanisms for ester and nitriles (see **Figure 2.5a, b**) follow second-order kinetics with respect to the hydrolyzable group (COOC or CN) and water. Under conditions of excess water, the reactions were modeled as pseudo-first order, with the rate law  $rate = -k'A$ , where  $k' = k[H_2O]$  and  $A$  is the integrated absorbance for COOC (regions D or

G) or CN (region C). The linearized form,  $\ln A = \ln A(0) - k't$ , was used to extract  $k'$  values by fitting the weighted data (see **Figure 2.6a**, with 95% confidence intervals indicated). All calculated  $k'$  values were statistically significant ( $p < 0.05$ , based on t-test) and are summarized in **Table 2.5**. Rate constants for regions D and G were statistically equivalent across all aging conditions, supporting the assignment of these bands to ester hydrolysis, which results in the simultaneous loss of C=O and C-O-C stretching and bending modes. The rate constant for region C was consistently higher, indicating that nitrile hydrolysis proceeds more rapidly than ester hydrolysis under all tested conditions.

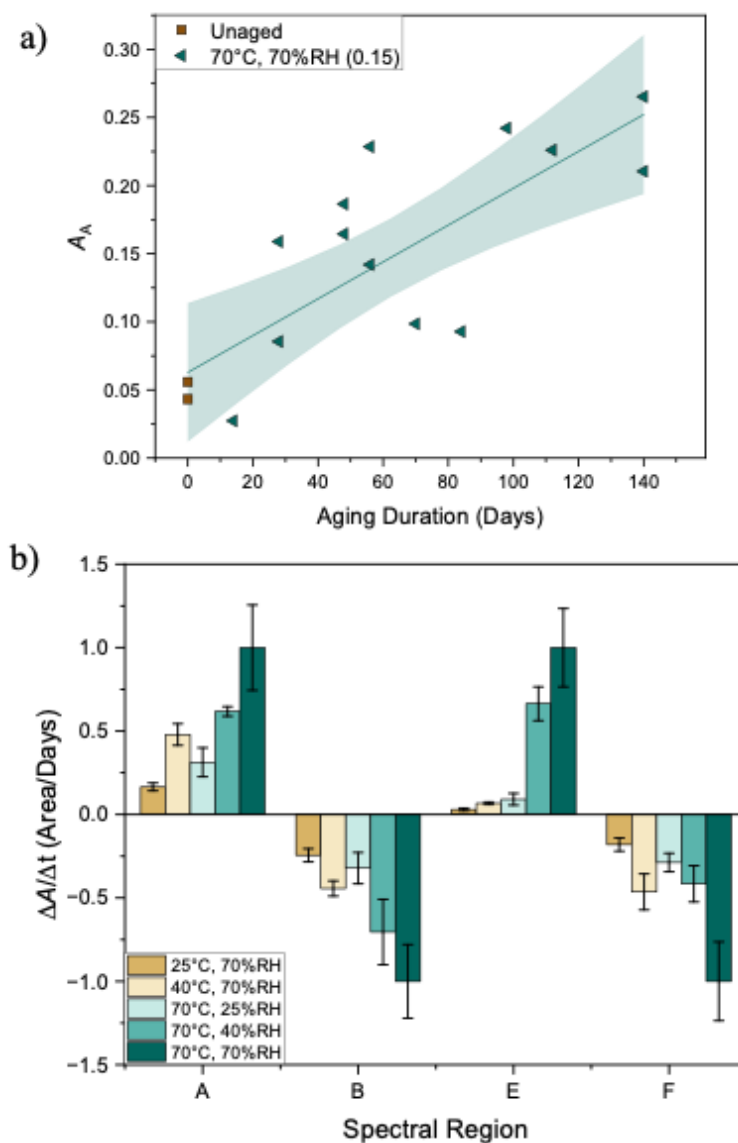


**Figure 2.6.** (a) Plot of log of the integrated ATR-FTIR absorbance areas for region C ( $A_C$ ) over aging time (s) for cables that were unaged and aged at 70°C and 70%RH. The solid line represents the linear fit ( $-k'$ ) while the shaded bands represent the 95% CI of the fit. b) Bar plot showing the calculated  $k'$  values for CN (region C) and COOC (region D and G) hydrolysis color-coded by aging condition as specified. Error bars represent the propagated errors in the regression fit.

**Table 2.5.** Summary of  $k'$  values for regions C, D and G for each condition. The uncertainty is the standard error of calculated values.

| Condition   | $k'_C (\times 10^9 s^{-1})$ | $k'_D (\times 10^9 s^{-1})$ | $k'_G (\times 10^9 s^{-1})$ |
|-------------|-----------------------------|-----------------------------|-----------------------------|
| 25°C, 70%RH | $5.8 \pm 0.8$               | $5.6 \pm 0.8$               | $3.6 \pm 0.6$               |
| 40°C, 70%RH | $12 \pm 2$                  | $9 \pm 2$                   | $8 \pm 2$                   |
| 70°C, 25%RH | $11 \pm 1$                  | $8 \pm 2$                   | $7 \pm 1$                   |
| 70°C, 40%RH | $24 \pm 7$                  | $17 \pm 3$                  | $14 \pm 1$                  |
| 70°C, 70%RH | $60 \pm 10$                 | $39 \pm 8$                  | $32 \pm 5$                  |

For regions A and E, which contain overlapping vibration modes, and for bands B and F, which are associated with C-H stretching and bending but are not directly linked to specific hydrolysis reactions, time-dependent changes were analyzed by linear regression. **Figure 2.7a** shows an example linear fit for integrated region A at 70 °C/70% RH, with the slope  $\Delta A_A/\Delta t$  quantifying the rate of change in OH and NH functionalities over 140 days. All rates were statistically significant ( $p < 0.05$ ). To facilitate comparison, rates for each band were normalized to the rate at 70 °C and 70% RH (**Figure 2.7b**), with error bars representing the standard error of the calculated values. Detailed statistics are provided **Table S2.4**.



**Figure 2.7.** (a) Plot of the integrated ATR-FTIR absorbance areas corresponding to region A as a function of exposure duration from cables that were unaged and aged at 70 °C/70% RH. The solid line represents the linear fit ( $\Delta A_A/\Delta t$ ), while the shaded band indicates the standard error of the slope. (b) Bar plot showing rates of change in integrated areas ( $\Delta A/\Delta t$ ) for regions A, B, E, and F as a function of aging duration, color-coded by aging condition as specified. Error bars represent the standard error of the values. PC1 loadings plot is included for reference.

Loss of absorbance in region B and F, attributed to C-H stretching and bending, respectively, increased with aging “severity.” The similar loss rates for these bands suggest that C-H containing species, such as butanol generated during ester hydrolysis, were lost from the adhesive matrix, likely via diffusion or further reaction. Accumulation rates for bands A and E were similar at 70 °C, 40 and 70% RH conditions; however, under other conditions, the rate for region E was significantly lower than for region A. This indicates an increase contribution of amide, amidine, and acid (from amide hydrolysis) N-H and O-H stretching in region A under high humidity and elevated temperatures.

#### 2.4.5 Water Vapor Diffusion with PMDA-ODA and BA-AN

Understanding the kinetics of adhesive degradation requires not only characterization of the chemical transformations but also a quantitative assessment of water transport within the cable structure. Because hydrolysis rates are inherently dependent on local water concentration, it is essential to evaluate how water vapor diffuses through and equilibrates within the polyimide (PMDA-ODA) and adhesive (BA-AN) layers under relevant environmental conditions. Water vapor diffusion through the polyimide and adhesive layers of flat-flex cables was characterized by combining dynamic vapor sorption (DVS) experiments on cured BA-AN adhesive with literature-based DVS data for Kapton® H (PMDA-ODA) from Foley, et al.<sup>29</sup> Kapton® H and HN are chemically identical polyimides, with HN containing a calcium phosphate dibasic ( $\text{CaHPO}_4$ ) processing aid.<sup>78</sup> Although HN absorbs more water than H, this additional uptake is attributed to strong chemisorption on  $\text{CaHPO}_4$  particles.<sup>79</sup> The effect of  $\text{CaHPO}_4$  particles on vapor dynamics is most pronounced at high humidity levels (e.g. 80–90% RH) and is significantly reduced at lower humidities,<sup>79</sup> which is the focus of this study. Furthermore,  $\text{CaHPO}_4$  particles are dispersed on the HN surface<sup>78</sup> such that water transport through the HN

bulk is effectively described by water sorption through H. Therefore, only the mobile water content in Kapton® H was considered for modeling diffusion through the cable materials.

Best-fit parameters for the dual-mode sorption model (see Section 2.2.8) are summarized in **Table 2.6**. **Figure 2.8** presents experimental and model fits for water uptake and effective diffusion coefficients in BA-AN as a function of relative humidity. Notably, at 70 °C, a pronounced hysteresis was observed between sorption and desorption isotherms, with desorption showing higher water uptake. This effect, most prominent at elevated temperatures (see **Figure S2.9** for time-resolved uptake curves), suggests water is not readily removed from the adhesive, likely due to concurrent hydrolysis reactions. Increased noise in the effective diffusion at higher temperatures is also consistent with hydrolysis-induced changes in the polymer matrix.

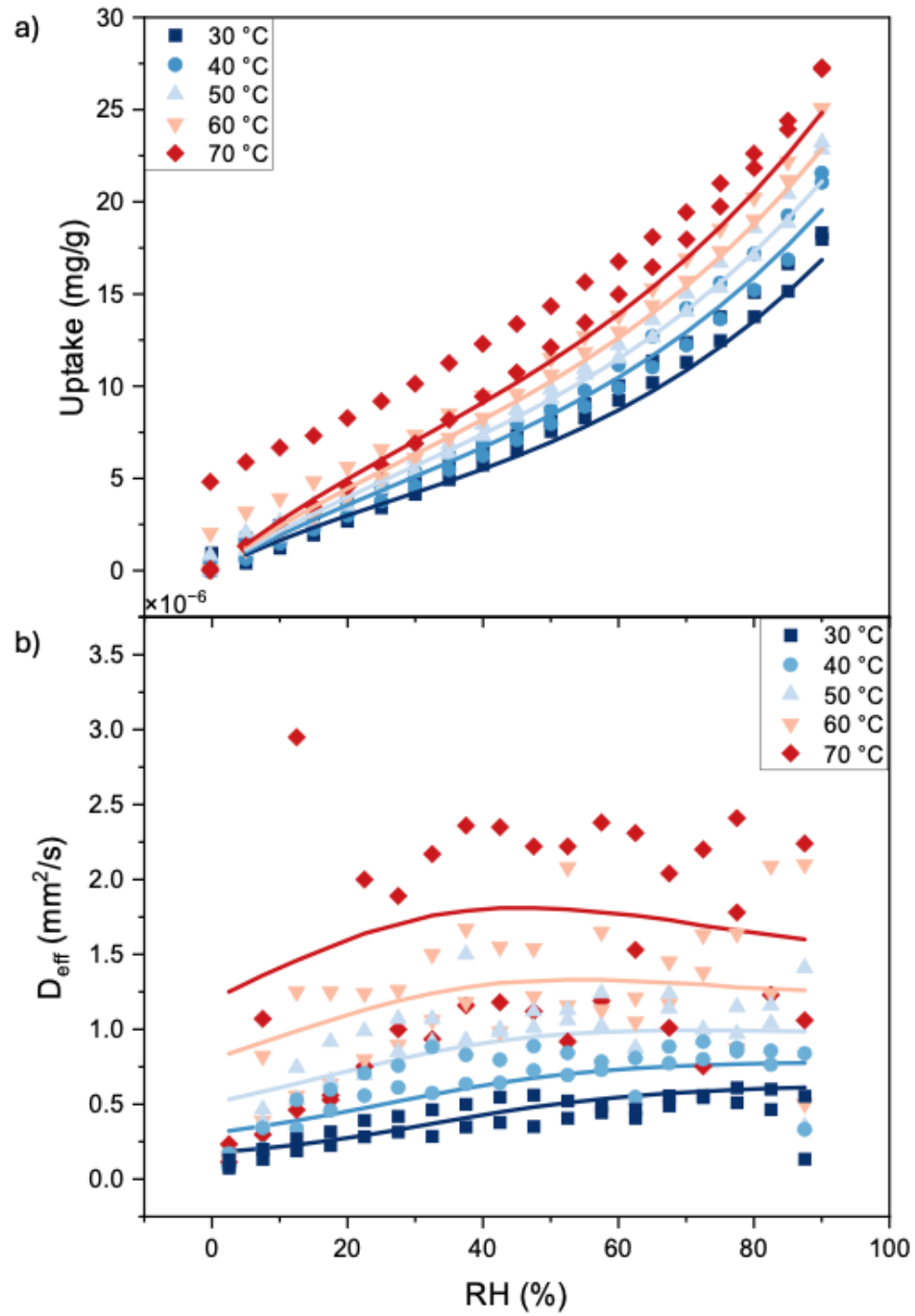
Effective diffusion coefficients ( $D_{\text{eff}}$ ) for both PMDA-ODA and BA-AN under relevant aging conditions are summarized in **Table 2.7**. The results show that water diffuses through BA-AN approximately 2.5 to 4 times faster than through PMDA-ODA. This indicates that the polyimide layers serve as the primary barrier to water vapor transport in the cable structure. To estimate the overall rate of water transport through the entire cable, the modeled  $D_{\text{eff}}$  values and thicknesses of each layer ( $L$ ; see **Figure 2.1**) were used to calculate the total effective diffusion coefficient ( $D_{\text{eff}_T}$ ) according to  $D_{\text{eff}_T} \approx \frac{L_T}{\sum L_i/D_{\text{eff}}}$ . The estimated  $D_{\text{eff}_T}$  values confirm that water transport is limited by the slow diffusion through the PMDA-ODA layers.

The time required to reach steady-state diffusion ( $t_{D_{SS}}$ ) was estimated using  $t_{D_{SS}} \approx \frac{L_T^2}{D_{\text{eff}_T}}$  (see **Table 2.7**), indicating that water vapor rapidly equilibrates throughout the cable layers. To assess whether hydrolysis is limited by water transport or chemical reaction, the global pseudo-first order hydrolysis rate constant ( $k'_H$ ), was determined by summing the  $k'$  values for CN and

COOC hydrolysis (see **Table 2.7**) and compared to the inverse equilibration time ( $t_{D_{SS}}^{-1}$ ). For all conditions,  $t_{D_{SS}}^{-1} \gg k'_H$ , demonstrating that hydrolysis is reaction-limited, not diffusion-limited. As a result, the equilibrium water concentration in each layer is uniform and controlled by the surface concentration at the outer PMDA-ODA layer. This surface concentration was determined using Equation 2.1 and data from Foley et al.,<sup>29</sup> with values provided in **Table 2.7** for each experimental condition.

**Table 2.6.** Summary of best-fit model parameters for mobile (m) and immobile (i) water in PMDA-ODA and cured BA-AN adhesive, and thermodynamic properties at a reference temperature of 20 °C (see Equation 2.1). The van 't Hoff and Arrhenius equations were used to calculate parameters at temperatures > 20 °C. PMDA-ODA parameter fits are from Foley et al.<sup>29</sup>

|          | $H_m$<br>(mg/g)          | $p_m$<br>(mg/g)              | $n_m$                        | D<br>(mm <sup>2</sup> /s)   | $b_l$<br>(mg/g) | $L_l$<br>(mg/g) |
|----------|--------------------------|------------------------------|------------------------------|-----------------------------|-----------------|-----------------|
| PMDA-ODA | 3.59                     | 14.88                        | 1.6                          | $2.64 \times 10^{-7}$       | 3.79            | 6.26            |
| BA-AN    | 1.39                     | 12.05                        | 3.2                          | $3.05 \times 10^{-6}$       | 1.03            | 14.54           |
|          | $\Delta H_m$<br>(kJ/mol) | $\Delta H_{p_m}$<br>(kJ/mol) | $\Delta H_{b_l}$<br>(kJ/mol) | $\Delta E_{aD}$<br>(kJ/mol) |                 |                 |
| PMDA-ODA | -6.63                    | -0.34                        | 0.55                         | 42.53                       |                 |                 |
| BA-AN    | 25.6                     | 3.10                         | 7.65                         | 23.5                        |                 |                 |



**Figure 2.8.** Water (a) uptake and (b) effective diffusion coefficients for transport inside cured BA-AN adhesive at temperatures ranging from 30–70 °C. Symbols denote experimental data points and curves are model fits using the parameters given in **Table 2.6**.

**Table 2.7.** Summary of  $D_{eff}$  values for PMDA-ODA and BA-AN, total effective diffusion, time to reach steady-state diffusion ( $t_{D_{SS}}$ ) and its inverse for all flat-flex cable layers, global pseudo-first order rate constants ( $k'_H$ ), and the concentration of mobile water ( $C_m$ ) at the outer PMDA-ODA layer as a function of aging condition.

| Condition   | $D_{\text{eff}}^{\text{PMDA-ODA}}$<br>( $\times 10^7 \text{ mm}^2/\text{s}$ ) | $D_{\text{eff}}^{\text{BA-AN}}$<br>( $\times 10^7 \text{ mm}^2/\text{s}$ ) | $D_{\text{eff}}^{\text{T}}$<br>( $\times 10^7 \text{ mm}^2/\text{s}$ ) |
|-------------|-------------------------------------------------------------------------------|----------------------------------------------------------------------------|------------------------------------------------------------------------|
| 25°C, 70%RH | 2.13                                                                          | 8.87                                                                       | 2.86                                                                   |
| 40°C, 70%RH | 4.81                                                                          | 15.9                                                                       | 6.26                                                                   |
| 70°C, 25%RH | 13.4                                                                          | 33.7                                                                       | 16.8                                                                   |
| 70°C, 40%RH | 16.3                                                                          | 39.3                                                                       | 20.2                                                                   |
| 70°C, 70%RH | 19.7                                                                          | 47.4                                                                       | 24.5                                                                   |

| Condition   | $t_{\text{D}_{\text{SS}}}$<br>(hr) | $t_{\text{D}_{\text{SS}}}^{-1}$<br>( $\times 10^{-7} \text{ s}^{-1}$ ) | $k_H'$<br>( $\times 10^7 \text{ s}^{-1}$ ) | $C_{\text{m}}$<br>(mg/g) |
|-------------|------------------------------------|------------------------------------------------------------------------|--------------------------------------------|--------------------------|
| 25°C, 70%RH | 35                                 | 78                                                                     | 0.13                                       | 10.91                    |
| 40°C, 70%RH | 16                                 | 170                                                                    | 0.21                                       | 10.88                    |
| 70°C, 25%RH | 6                                  | 460                                                                    | 0.19                                       | 2.51                     |
| 70°C, 40%RH | 5                                  | 560                                                                    | 0.42                                       | 4.85                     |
| 70°C, 70%RH | 4                                  | 670                                                                    | 0.98                                       | 10.84                    |

While techniques such as dynamic mechanical analysis and dielectric spectroscopy could provide valuable independent validation of the state of water (distinguishing mobile from immobile populations) during hydration and aging, these methods were not employed in the present study. Instead, we relied on triple-mode sorption modeling (Henry's, Langmuir, and pooling modes), which has demonstrated strong agreement with experimental data for water sorption and outgassing in polymers and ceramics (e.g., from Sharma et al.<sup>80, 81</sup> and Foley et al.<sup>29</sup>). However, in the absence of direct in-situ validation, our analysis inherently assumes that the ratio of bound to unbound water remains consistent throughout aging and hydration, which is

unlikely to strictly hold as the polymer matrix degrades. Future work should incorporate spectroscopic or mechanical relaxation techniques to directly monitor changes in water state and polymer dynamics during hygrothermal aging.

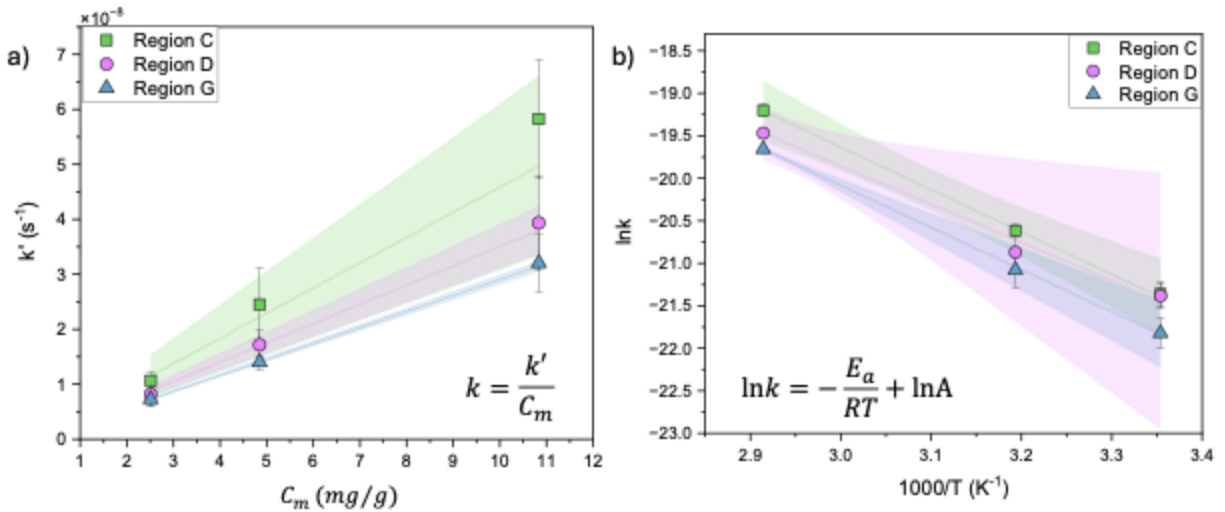
This approach provides a robust framework for quantifying water transport, despite the inherent limitations discussed above. The  $D_{\text{eff}}$  values for PMDA-ODA agree with previous reports, such as  $D_{30^\circ\text{C}} = 2 \times 10^{-7} \text{ mm}^2/\text{s}$  and  $E_{a_D} = 42 \text{ kJ/mol}$  for PMDA-ODA.<sup>82</sup> The diffusion coefficients for BA-AN are within the range reported for polymers with similar pendant groups, such poly(ethyl methacrylate) ( $D_{25^\circ\text{C}} = 1 \times 10^{-5} \text{ mm}^2/\text{s}$ )<sup>82</sup> and polyacrylonitrile ( $D_{30^\circ\text{C}} = 2.5 - 4 \times 10^{-8} \text{ mm}^2/\text{s}$  and  $D_{35^\circ\text{C}} = 2.5 \times 10^{-7} \text{ mm}^2/\text{s}$ )<sup>83, 84</sup>. To our knowledge, this is the first report of DVS-derived diffusion data for BA-AN.

#### 2.4.6 Activation Energies for CN and COOC Hydrolysis

Quantifying water vapor diffusion and equilibrium concentrations within the cable layers provides the essential context for interpreting the observed hydrolysis kinetics. With reliable estimates of mobile water concentrations now established, it is possible to decouple the effects of water transport from intrinsic chemical reactivity. Second order rate constants for hydrolysis of nitrile (region C) and ester (regions D and G) functionalities were determined using the pseudo-first order rate constants ( $k'$ , see **Table 2.5**) and the steady-state mobile water concentrations ( $C_m$ , see **Table 2.7**) within flat-flex cables. For 25 and 40 °C, the second order rate constant was calculated as  $k = k'/C_m$ , where  $k'$  is the observed pseudo-first order rate constant ( $\text{s}^{-1}$ ) and  $C_m$  is the equilibrium mobile water concentration (mg/g). A 70 °C,  $k$  values for CN and COOC hydrolysis were obtained from the slope of a weighted linear regression of  $k'$  versus  $C_m$

(Figure 2.9a), with error bands representing the standard error for each  $k'$  value and shaded bands indicating 95% CI of the fits.

Activation energies ( $E_a$ ) were extracted by fitting the Arrhenius equation,  $k = A \exp(-E_a/RT)$ , to the rate constants determined at 25, 40 and 70 °C (Figure 2.9b). Here,  $A$  is the pre-exponential factor,  $R$  is the universal gas constant, and  $T$  is the absolute temperature. All weighted regression analyses were performed using Origin(Pro) Version 2023b, and uncertainties in the  $E_a$  values correspond to the standard error of the calculated values. The calculated second order rate constants and activation energies are summarized in Table 2.8.



**Figure 2.9.** a) Observed  $k'$  values for spectral regions corresponding to CN (region C) and COOC (regions D and G) absorbances at 70 °C and 25, 40 and 70% RH plotted against the concentration of mobile water within the flat-flex cable. (b) An Arrhenius plot of the log of second order rate constants as a function of inverse temperature. Solid lines represent linear fits to the data, error bars represent the standard error, and colored bands represent the 95% CI in the fits.

**Table 2.8.** Summary of calculated second order rate constants ( $k$ ) at each aging temperature and activation energies ( $E_a$ ) for CN and COOC hydrolysis determined from Arrhenius relationships to the decay of absorbances in regions C (CN), D and G (COOC). The uncertainty is reported as the standard error in the calculated values.

| Temperature    | $k(\times 10^{10} \text{ gm}^{-1} \text{ s}^{-1})$ |             |            |
|----------------|----------------------------------------------------|-------------|------------|
| (°C)           | Region C                                           | Region D    | Region G   |
| 25 °C          | $5 \pm 2$                                          | $5 \pm 2$   | $3 \pm 1$  |
| 40 °C          | $11 \pm 2$                                         | $9 \pm 4$   | $7 \pm 4$  |
| 70 °C          | $50 \pm 20$                                        | $35 \pm 4$  | $29 \pm 8$ |
| $E_a$ (kJ/mol) | $40 \pm 10$                                        | $40 \pm 30$ | $40 \pm 7$ |

It is important to note that the activation energies reported here are effective activation energies rather than intrinsic activation barriers for bond hydrolysis. These effective values reflect the combined influence of chemical reactivity and the physical microenvironment within the polymer matrix, including local water concentration, molecular mobility, and reactant orientation. The relatively lower glass transition temperature ( $T_g \approx 37$  °C; from this work) compared to polycarbonate ( $T_g \approx 147$  °C)<sup>89</sup> results in increased free volume and higher segmental motion, which enhances water permeability and increases the frequency of molecular motions, thus increasing the apparent rate constant without necessarily lowering the intrinsic energy barrier for the reaction.

The observed activation energies for both CN and COOC hydrolysis are nominally 40 kJ/mol, which is substantially lower than literature values for analogous hydrolyzable bonds in other polymers. For example, activation energies for ester hydrolysis in polycarbonate under humid conditions are reported in the range of 77–87 kJ/mol.<sup>85–88</sup> Similarly, activation energies

for nitrile hydrolysis in solution are much higher than those observed in this work. For instance, Krämer et al. reported an  $E_a$  of 128 kJ/mol for acrylonitrile hydrolysis at 23 MPa,<sup>90</sup> and Rabinovitch et al. found  $E_a = 107$  kJ/mol for propionitrile hydrolysis in 1M hydrochloric acid.<sup>91</sup> These literature values were obtained under solution-phase conditions, often with strong acid catalysts and elevated pressures. In contrast, the solid-state polymer environment is more complex, and localized catalytic effects from acidic hydrolysis products may reduce the apparent activation. Additional factors such as polymer morphology, free volume, and water clustering likely play a significant role in the observed kinetics.

## 2.5 Relationship Between Macro- and Microscale Test Results

The relationship between macroscopic properties (relative peel strength,  $P$ , and breakdown voltage,  $V$ ) and microscale adhesive aging signatures was quantitatively described using a mechanistic model that links observed pseudo-first order rate constants ( $k'$ ) for nitrile and ester hydrolysis to the decay in  $P$  and  $V$  as functions of time  $t$ , temperature  $T$ , and water activity  $a$ :

$$\Phi(t, T, a) = \Phi_0 - \alpha A_{\text{COOC}_0} (1 - e^{-k'_{\text{COOC}} t}) - \beta A_{\text{CN}_0} (1 - e^{-k'_{\text{CN}} t})$$

$$k'(T, a) = C_m(a)k(T) = C_m(a)Ae^{-E_a/RT} \quad (2)$$

$$k(T) = Ae^{-E_a/RT}$$

Here,  $\Phi$  represents the modeled macroscopic property (peel strength or breakdown voltage), and  $\Phi_0$  is the initial property value.  $A_{\text{COOC}_0}$  and  $A_{\text{CN}_0}$  are the initial integrated absorbances for ester and nitrile groups, respectively, while  $\alpha$  and  $\beta$  are sensitivity parameters quantifying the contribution of each hydrolysis pathway.  $C_m(a)$  is the equilibrium concentration of mobile water (see Equation 2.1), and  $k(T)$  is the second-order rate constant for hydrolysis, with  $A$  and  $E_a$

denoting the Arrhenius pre-exponential factor and activation energy. The equations for  $k'(T, a)$  and  $k(T)$  illustrate the dependence of  $k'$  on temperature and humidity, though these relationships are not explicitly included in the mechanistic model. The  $k'$  values used in the model were determined from the time-dependent ATR-FTIR absorbance measurements, as described in Section 2.4.4.

To rigorously quantify parameter uncertainty and propagate it to model predictions, a Monte Carlo simulation ( $N = 1000$  iterations) was performed as described in Section 2.2.9. Parity plots (**Figure 2.10**) visualize model predictive accuracy and associated uncertainties. The best-fit  $\alpha$  parameters for both models were approximately zero, indicating that ester hydrolysis (COOC loss) does not measurably influence either adhesion or dielectric strength under the tested conditions. In contrast, the best-fit  $\beta$  values were  $130 \pm 10$  for peel strength and  $32 \pm 3$  for breakdown voltage, indicating that nitrile hydrolysis (CN loss) is strongly coupled to macroscopic property decay, with a greater effect on adhesion than on dielectric performance. The mechanistic model and best-fit sensitivity parameters ( $\alpha, \beta$ ) clarify the relative impact of each hydrolysis pathway on macroscopic property decay. While the model directly incorporates only the loss of ester (COOC) and nitrile (CN) functionalities, the underlying chemistry of the BA-AN adhesive suggests a more nuanced hierarchy of degradation effects. Literature on poly(acrylonitrile) hydrolysis demonstrates that the intrinsic rate order for hydrolysis is amidine > amide > nitrile.<sup>70</sup> Furthermore, ammonia generated during amide hydrolysis can catalyze additional nitrile hydrolysis, amplifying the overall rate of AN degradation.<sup>70</sup>

In the context of BA-AN adhesives, this sequence has important implications for macroscopic properties. Hydrolysis of nitrile groups, especially when accelerated by the formation and subsequent consumption of amidine and amide intermediates, leads to a

progressive increase in polar, hydrogen-bonding groups (e.g., acid). This disrupts any AN-driven crystallinity, increases water uptake, and facilitates plasticization, all of which strongly compromise BA-AN mechanical properties, particularly peel strength. In addition to their impact on bulk properties, the hydrolysis products of AN groups, specifically amidine and amide functionalities, fundamentally alter the hydrogen-bonding network and chemical interactions with the PMDA-ODA layer and facilitating interactions with copper surfaces that may accelerate oxidation or form metal-organic complexes that weaken the adhesive-copper interface.<sup>92</sup> However, peel test results indicate BA-AN failure is cohesive, rather than interfacial (i.e., adhesive failure), suggesting that bulk mechanical weakening, rather than interfacial degradation, is the primary driver of peel strength decay under the conditions studied.

The rapid consumption of amidine and amide intermediates, relative to nitrile groups, means that even modest initial conversion of AN pendant groups can trigger a cascade of secondary reactions that dominate long-term property decay. In contrast, ester hydrolysis in the BA segments primarily results in small molecule formation (e.g., butanol) and modest changes in local polarity but does not significantly affect mechanical properties governed by the AN domains. Accordingly, the model's finding that  $\alpha \approx 0$  and  $\beta > 0$  is consistent with the mechanistic expectation that nitrile hydrolysis and its downstream products (amidine, amide and acid) are the primary drivers of both peel strength and, to a lesser extent, dielectric strength. The stronger correlation between BA-AN aging signatures and peel strength, compared to breakdown voltage, is consistent with the adhesive's mechanical role in the cable structure.

The root mean square error (RMSE) for voltage breakdown and peel strength predictions were 3% and 16%, respectively. The higher RMSE for peel strength may reflect greater experimental noise or the influence of additional degradation mechanisms (e.g., continued

hydrolysis—as suggest by PC2; see Section 4.3—crosslinking, etc.) not explicitly captured by the model.

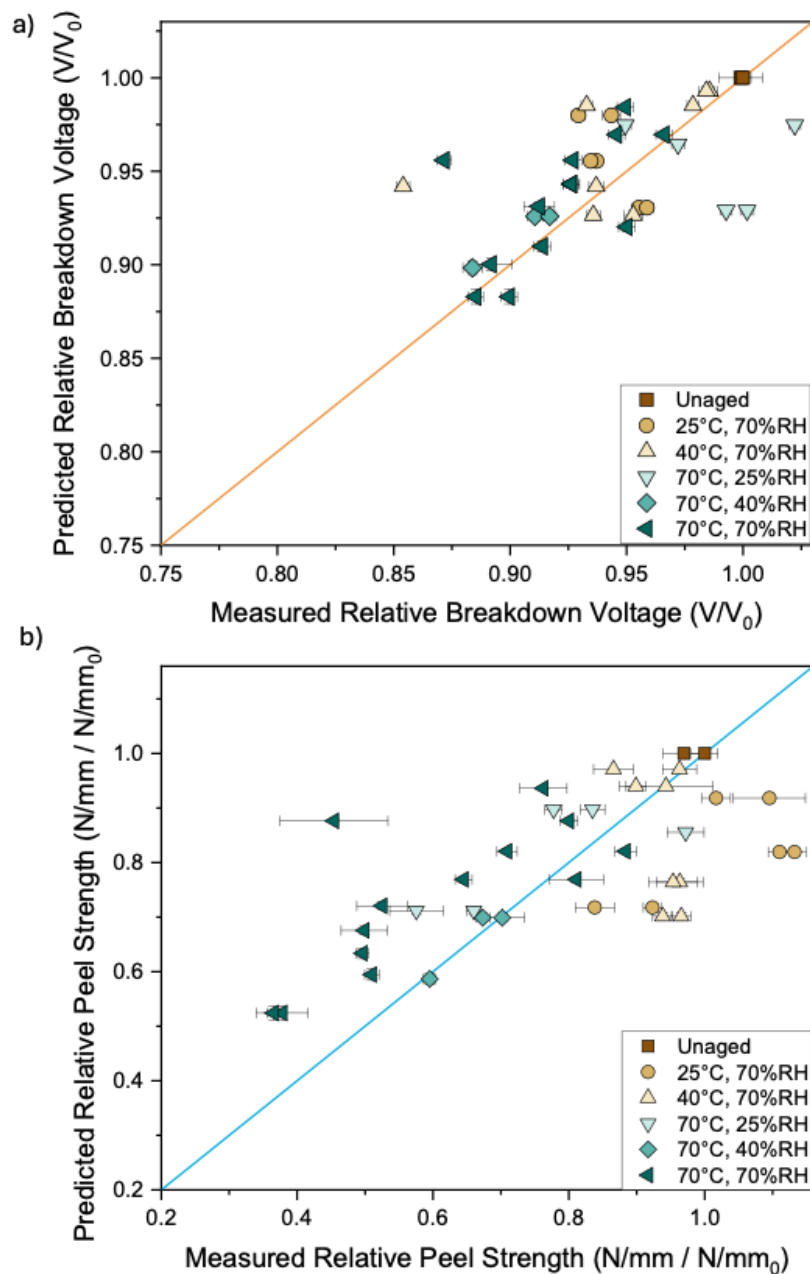
By coupling the mechanistic model with water vapor diffusion data in PMDA-ODA, macroscopic property decay can be predicted across a range of environmental conditions.

**Figure 2.11** plots model long-time predictions for breakdown voltage and peel strength at 25 °C and 70% RH. At this condition, the model predicts a 50% loss in peel strength within 5 years, but only a 14% reduction in dielectric strength. Over 50 years, dielectric strength is predicted to decrease by 23%, while peel strength is nearly exhausted due to BA-AN nitrile hydrolysis. However, in the absence of mechanical loading, the loss of peel strength may have minimal functional impact. The model also predicts that both properties plateau at long times, reflecting consumption of the most accessible hydrolyzable groups and the dominant contribution of PMDA-ODA to dielectric stability.

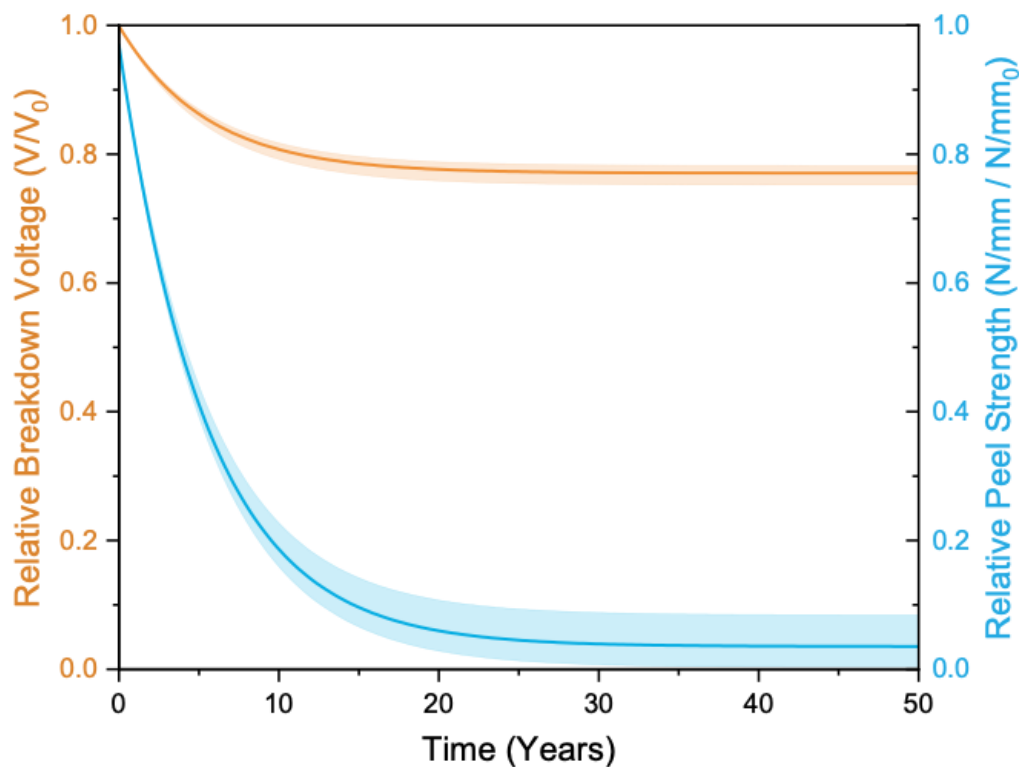
Accelerated aging experiments at elevated temperatures provide valuable insight into the chemical degradation kinetics of cable adhesives, however we acknowledge the inherent limitations in extrapolating these results to predict long-term performance under ambient conditions. The underlying assumption is that the dominant aging mechanisms remain unchanged across the accelerated temperature range (up to 70 °C) and at lower, service-relevant temperatures. However, during extended aging near room temperature, additional slow processes, including physical aging (e.g., polymer chain relaxation and densification),<sup>93</sup> interface creep and stress relaxation,<sup>94</sup> and potential microbial erosion,<sup>95, 96</sup> may become significant. These mechanisms are often masked or inadequately captured under accelerated aging protocols, which primarily emphasize chemical hydrolysis and related reactions. As a result, predictions based solely on accelerated aging data may underestimate or overlook the contributions of these slower

processes, leading to incomplete assessment of long-term material reliability. Therefore, while accelerated aging is a powerful tool for elucidating chemical degradation pathways and kinetics, it does not fully represent all relevant mechanisms that may govern adhesive and cable performance at lower temperatures and longer timescales. Future work should incorporate complementary long-term ambient aging studies and mechanistic analyses to address these additional factors.

While uncertainty in model predictions was rigorously quantified and propagated using Monte Carlo simulation, the resulting confidence intervals do not widen substantially over extended timescales. This suggests that the simulation primarily reflects uncertainty in the fitted kinetic parameters and does not fully capture the additional uncertainty associated with possible changes in degradation mechanisms or the emergence of slow processes during long-term aging. Therefore, while accelerated aging provides valuable mechanistic insight into adhesive chemical degradation, it may not fully represent all relevant failure modes and environmental interactions at lower temperatures and longer timescales. Future work should incorporate complementary long-term ambient aging studies and mechanistic analyses to address these additional factors.



**Figure 2.10.** MM parity plots fits for (a) breakdown voltage and (b) relative peel strength values of aged flat-flex cables derived from spectroscopically observed reaction kinetics. Orange and blue lines are included to indicate ideal parity. Horizontal error bars represent experimental uncertainty of the measured values and represent the propagated uncertainty in the model prediction.



**Figure 2.11.** Mechanistic model fits as a function of time in days for relative breakdown voltage (orange) and peel strength (blue). Solid lines represent the mean fits and shaded bands represent 95% confidence intervals.

## 2.6 Conclusion

Accelerated aging experiments on flat-flex cable assemblies, comprising copper conductors, PMDA-ODA dielectric and BA-AN adhesive layers, reveal the critical mechanisms underlying long-term cable degradation in humid environments. The integration of mechanical and dielectric testing, and ATR-FTIR spectroscopy provided a comprehensive view of the relationship between molecular-scale chemical changes and macroscopic performance loss. The key findings of this study are summarized as follows:

1. **Environmental Sensitivity:** Both peel strength and breakdown voltage decrease with aging, with humidity exerting a particularly strong influence on adhesion loss.
2. **Chemical and Dielectric Stability of PMDA-ODA:** The PMDA-ODA dielectric remains chemically stable under all tested conditions, confirming its suitability as a long-term insulator.
3. **Characterization of the Adhesive, Degradation Products and Mechanisms:** The flat-flex cable adhesive is identified as a BA-AN copolymer through ATR-FTIR spectroscopy and BA-AN adhesive undergoes hydrolysis at both ester and nitrile sites, as evidenced by clear ATR-FTIR spectral changes and the formation of amide, acid, and alcohol functionalities.
4. **Water Sorption and Transport:** Water rapidly equilibrates throughout the cable structure, with the BA-AN adhesive exhibiting the highest diffusion rates. Equilibrium water content is governed by the outer PMDA-ODA layer.
5. **Mechanistic Insights into Performance Loss:** Mechanistic modeling directly links the hydrolysis of nitrile moieties--located on the polymer acrylonitrile pendants--to pronounced losses in both peel and dielectric breakdown voltage. In contrast, ester hydrolysis is found to be inconsequential to macroscopic cable performance.
6. **Unexpected Role of Nitrile Hydrolysis:** The strong impact of nitrile hydrolysis on adhesion and dielectric properties is notable, especially given the pendant location of nitrile group. This suggests that initial hydrolysis may trigger subsequent reactions or structural changes in the polymer matrix, amplifying its effect on cable performance.
7. **Performance Plateau and Long-Term Predictions:** While adhesive degradation leads to rapid initial declines in peel strength, dielectric strength loss is more moderate

and plateaus over time, consistent with the dominant role of the PMDA-ODA dielectric.

This work demonstrates that nitrile hydrolysis in BA-AN adhesives is the primary driver of flat-flex cable degradation. The mechanistic model employed in this study aimed to facilitate the interpretation of complex chemical processes, however overlapping bands in the complex ATR-FTIR spectra of aged BA-AN likely masked the presence of a various degradation products generated from the hydrolysis at BA-AN pendant groups and reactions at the polymer backbone. Although clear evidence of ester hydrolysis was observed in the adhesive, this process does not measurably contribute to the observed losses in peel strength or dielectric performance. These findings highlight the need for future studies to probe the fate of the pendant nitrile groups post-hydrolysis and to elucidate any subsequent degradation or crosslinking mechanisms. Further, the role of copper migration and its interaction with polymer degradation remains an open question. Quantifying copper transport and its chemical influence will be essential for developing lifetime predictions and more robust cable assemblies.

The mechanistic models for flat-flex cable dielectric breakdown and peel strength loss developed here provide a quantitative framework linking molecular-level adhesive degradation to macroscopic cable performance. This enables prediction of cable reliability under diverse environmental conditions, which can inform decisions on long-term storage and deployment. We anticipate that the experimentally informed modeling framework developed here can be applied to predict cable reliability in future systems that adopt next-generation adhesives and insulating materials for demanding environments.

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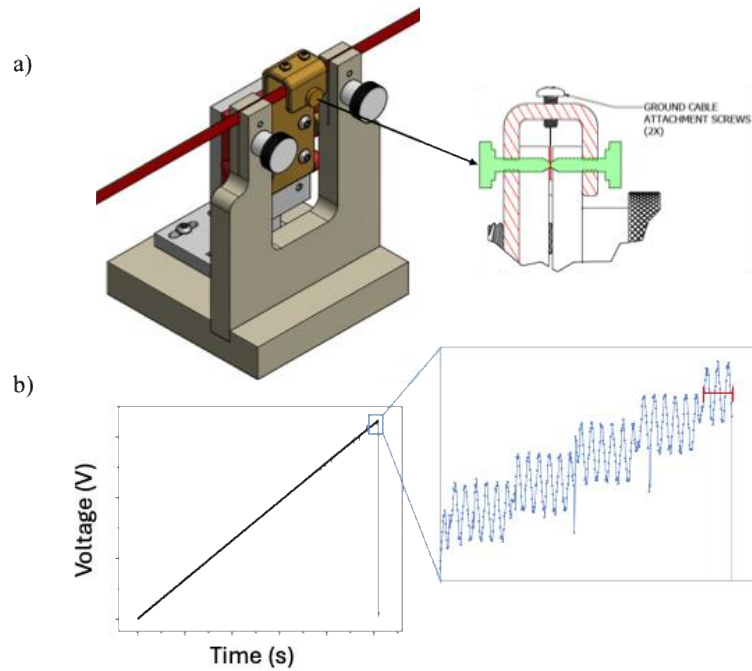
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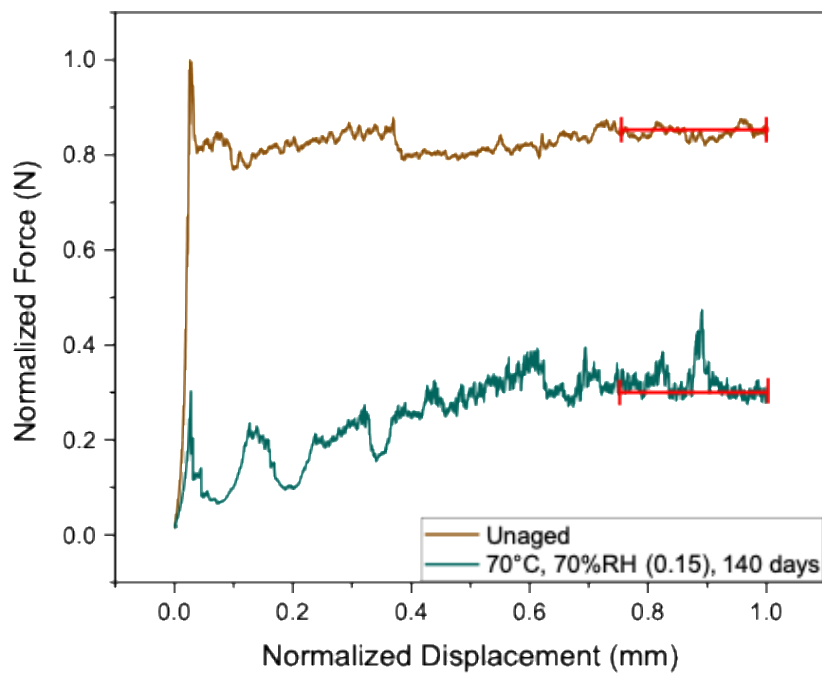
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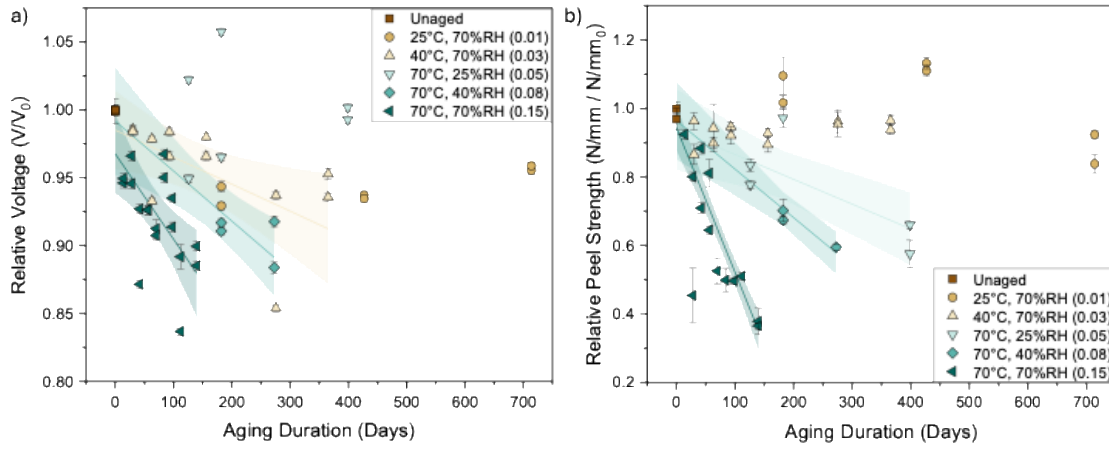
## 2.7 Supplementary Data



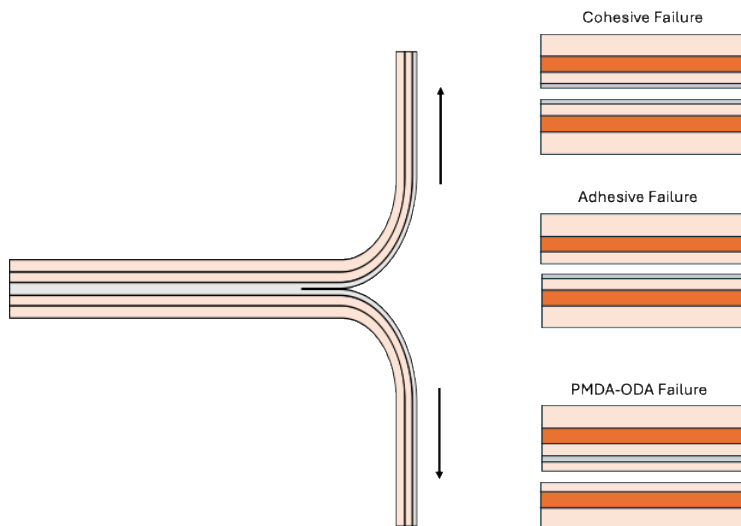
**Figure S2.1.** (a) Three-dimensional schematic of the custom high potential dielectric tester designed to evaluate the localized dielectric breakdown voltage of flat-flex cables. Brass grounding pins are indicated, along with an illustration showing the pins in contact with a cable during testing. (b) Representative voltage versus time curve from dielectric breakdown testing, illustrating the linear voltage followed by a sudden voltage drop, characteristic of dielectric breakdown. A magnified view near the peak voltage prior to breakdown reveals oscillations during the ramp and discrete voltage steps caused by the analog voltage controller. The red line marks the maximum voltage range from the final discrete step, which was used to calculate the average breakdown voltage and associated error, which was defined as one standard deviation of the average value. Pin size is 1.3 mm diameter.



**Figure S2.2.** Representative normalized force (N) versus displacement (mm) curves from T-peel testing, comparing an unaged cable (brown) and a cable aged for 140 days at 70 °C/70% RH (dark teal). The curves illustrate increase noise in the force-displacement data and a reduction in the length of the flat region with age. Red lines mark the force range within the flat portion of the curve, which was used to calculate the average peel strength. The associated error was defined as one standard deviation of the calculated average peel strength.



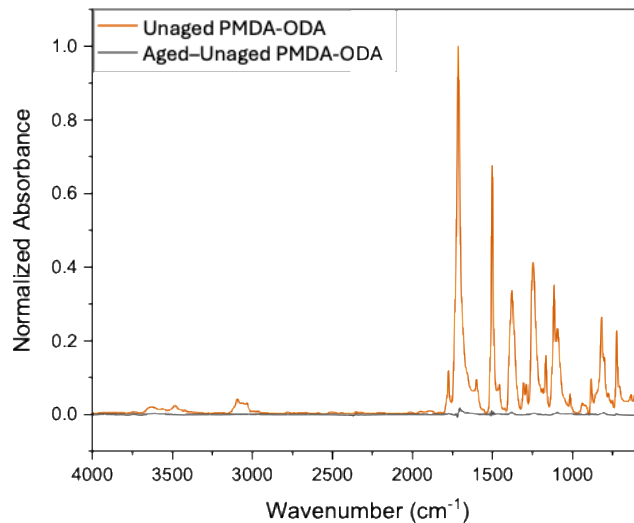
**Figure S2.3.** Breakdown voltage (a) and peel strength (b) data, normalized to the values for unaged cables, plotted as a function of aging duration under various environmental conditions: unaged (brown squares), 25 °C/70% RH (tan circles) 40 °C/70% RH (beige upward triangles), 70 °C /25% RH (light teal downward triangles), 70 °C /40 %RH (teal diamonds), and 70 °C/70% RH (dark teal leftward triangles). Specific humidity values for each condition are provided in the parenthesis. Error bars indicate one standard deviation of the measured data. For statistically significant trends, solid lines represent linear fits to the data, while shaded bands (color-coded to match each aging condition) denote the 95% confidence interval (CI) for the linear slopes.



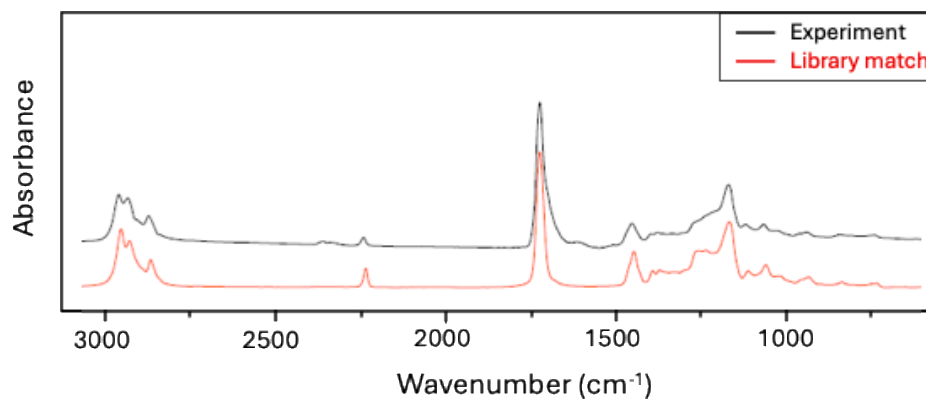
**Figure S2.4.** Illustration of a T-peel test performed on a flat flex cable (left) and the corresponding potential failure modes (right). The PMDA-ODA layers are depicted in light orange, the BA-AN adhesive layers in gray, and copper strips in dark orange. Failure modes include: (1) cohesive failure, characterized by crack propagation within the adhesive layer; (2) adhesive failure, involving delamination between the adhesive and PMDA-ODA layers, and (3) PMDA-ODA failure, resulting from crack propagation within a PMDA-ODA layer. In this study, 85% of cables failed cohesively, while 15% exhibited PMDA-ODA failure.

**Table S2.1.** Summary of relative peel force measurements for cables exhibiting either cohesive or PMDA-ODA failure, aged under identical conditions and durations. Corresponding relative breakdown voltage measurements for the cables are also provided. Reported errors represent one standard deviation from average measured values.

| Aging Condition | Aging Duration (days) | Failure Material | Relative Peel Strength (N/mm / N/mm <sub>0</sub> ) | Relative Breakdown Voltage (V/V <sub>0</sub> ) |
|-----------------|-----------------------|------------------|----------------------------------------------------|------------------------------------------------|
| 70°C, 70%RH     | 14                    | PMDA-ODA         | 0.76 ± 0.03                                        | 0.946 ± 0.004                                  |
|                 | 14                    | Adhesive         | 0.92 ± 0.01                                        | 0.949 ± 0.004                                  |
|                 | 70                    | PMDA-ODA         | 0.42 ± 0.05                                        | 0.908 ± 0.004                                  |
|                 | 70                    | Adhesive         | 0.53 ± 0.04                                        | 0.912 ± 0.007                                  |
|                 | 84                    | PMDA-ODA         | 0.43 ± 0.03                                        | 0.950 ± 0.004                                  |
|                 | 84                    | Adhesive         | 0.50 ± 0.03                                        | 0.967 ± 0.004                                  |
|                 | 98                    | PMDA-ODA         | 0.45 ± 0.06                                        | 0.934 ± 0.003                                  |
|                 | 98                    | Adhesive         | 0.496 ± 0.009                                      | 0.914 ± 0.004                                  |
|                 | 112                   | PMDA-ODA         | 0.35 ± 0.05                                        | 0.892 ± 0.009                                  |
|                 | 112                   | Adhesive         | 0.51 ± 0.01                                        | 0.834 ± 0.003                                  |
| 70°C, 40%RH     | 273                   | PMDA-ODA         | 0.33 ± 0.01                                        | 0.884 ± 0.004                                  |
|                 | 273                   | Adhesive         | 0.595 ± 0.009                                      | 0.918 ± 0.004                                  |
| 70°C, 25%RH     | 182                   | PMDA-ODA         | 0.83 ± 0.02                                        | 0.965 ± 0.003                                  |
|                 | 182                   | Adhesive         | 0.97 ± 0.03                                        | 1.060 ± 0.003                                  |

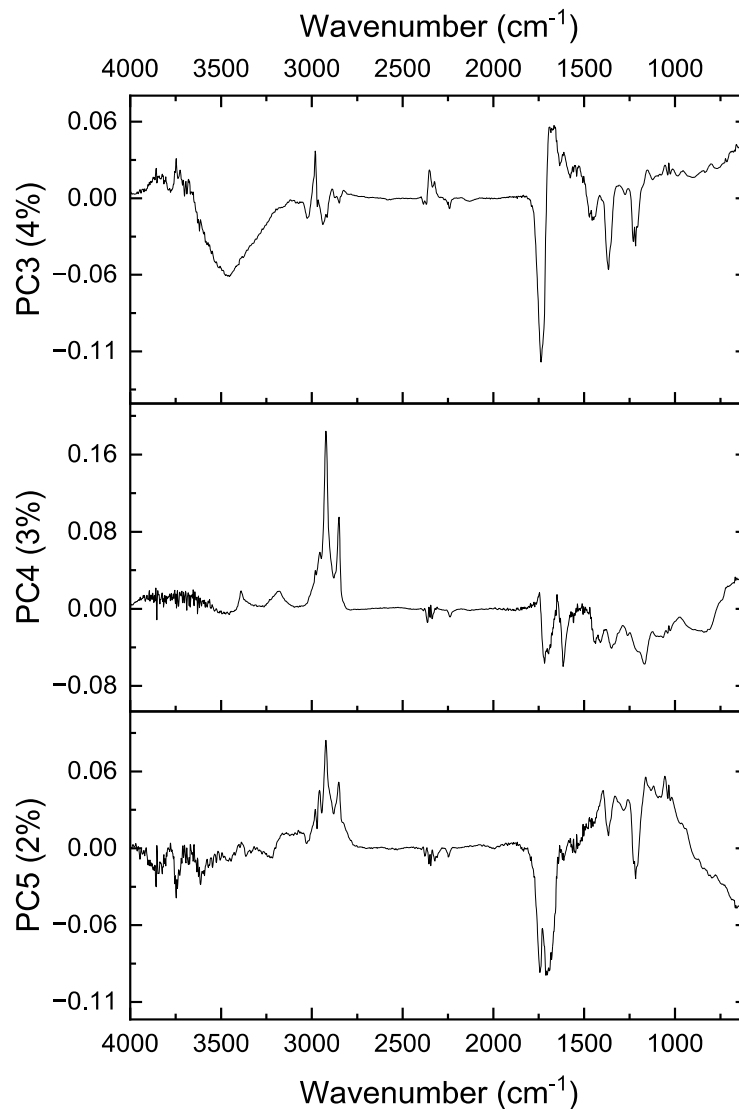


**Figure S2.5.** Representative ATR-FTIR spectra of PMDA-ODA from an unaged cable (orange) and the difference spectrum (gray) obtained by subtracting the normalized spectrum of an unaged cable from that of a cable aged for 140 days at 70 °C and 70% RH. Absorbances for both aged and unaged PMDA-ODA were normalized to 1 prior to subtraction. The resulting difference spectrum confirms the absence of detectable aging signatures in PMDA-ODA from aged cables.



**Figure S2.6.** Representative ATR-FTIR spectra of flat-flex cable adhesive from an unaged cable (black) compared to the reference spectrum of 1:1 wt.% BA-AN (red) obtained from the Bio-Rad

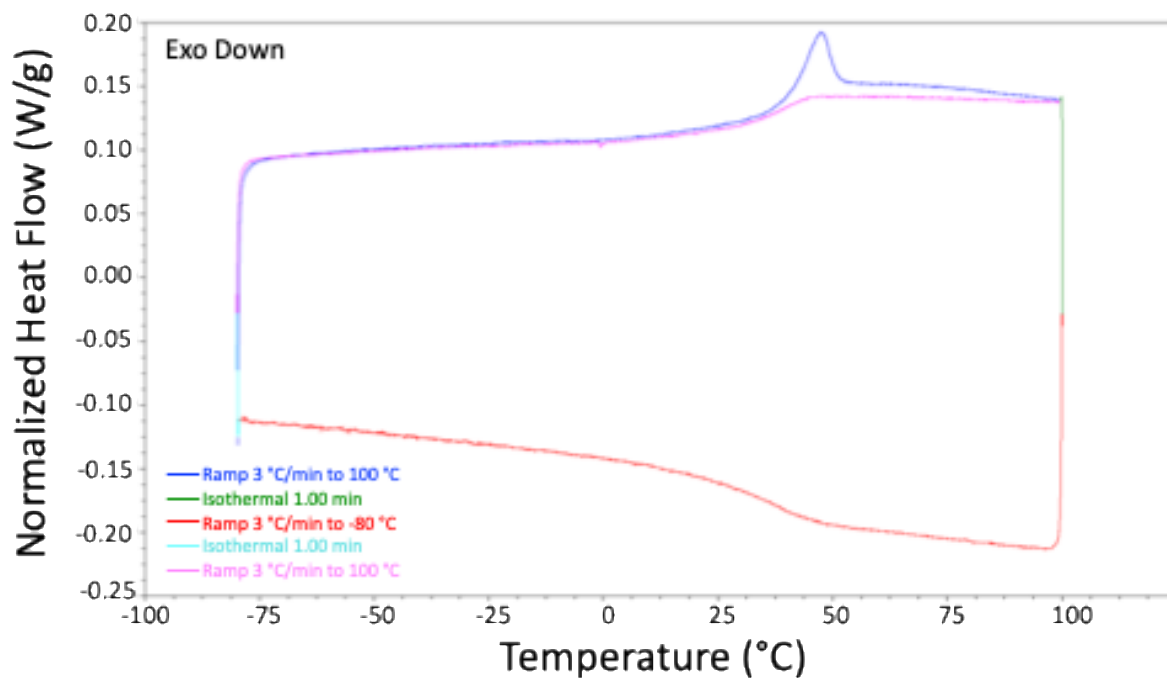
Laboratories Database [55]. The spectral comparison yielded a 95% Hit Quality Index match, indicating a strong match between the experimental adhesive and database reference material.



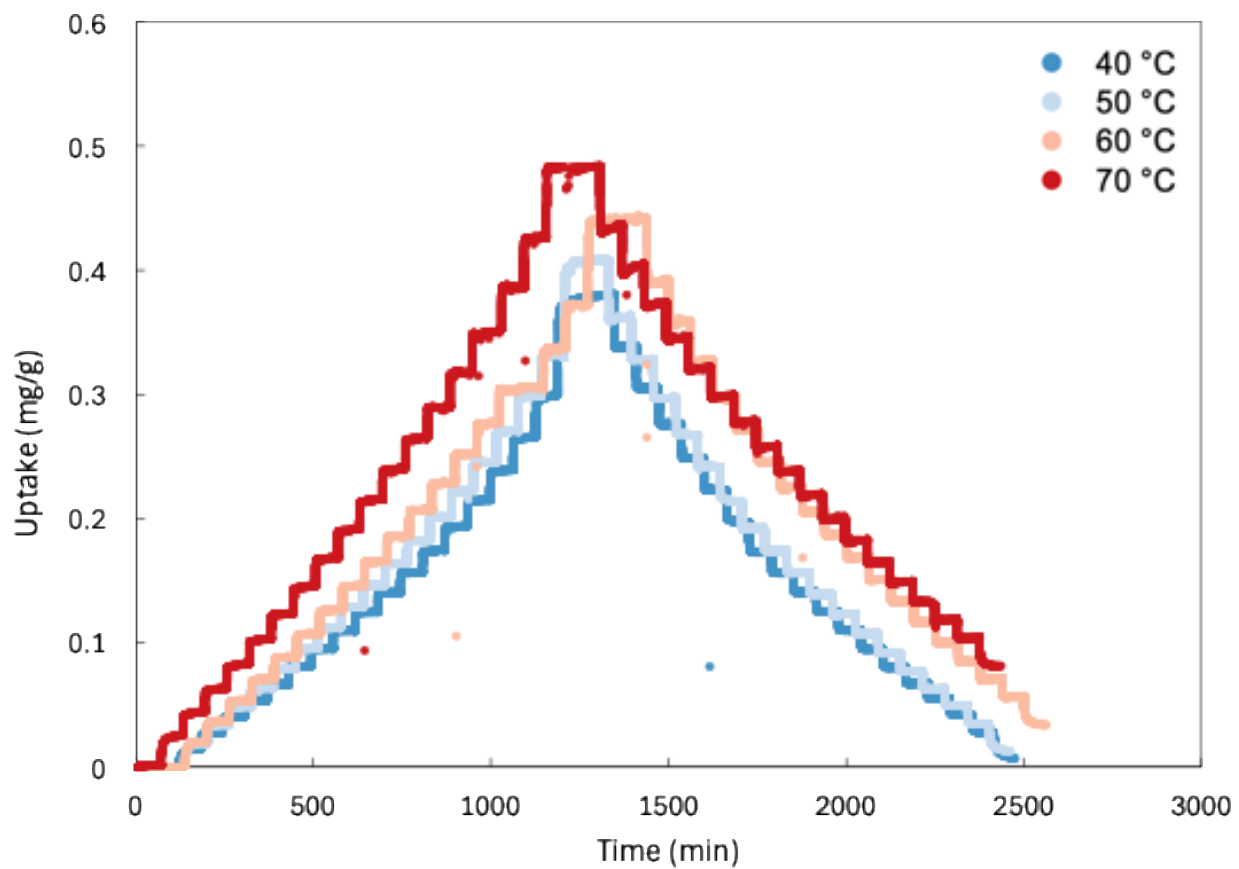
**Figure S2.7.** Loadings for principal components (PCs) 3 to 5 as a function of wavenumber (cm<sup>-1</sup>), derived from PCA of flat-flex cable adhesive spectra across all aging conditions. The percentage contribution of each PC to the total spectral variance is provided in parenthesis.

**Table S2.2.** Summary of fit statistics from linear regressions analyzing relationships between aging durations (in days; specific to aging conditions), and principal component (PC) scores 1 to 5. The percentage indicated for each PC corresponds to its contribution to the total variance. Statistics are reported as Pearson's correlation coefficient (R), degrees of freedom, and statistical significance (p-value). Linear trends with statistical significance ( $p < 0.05$ ) are highlighted in blue.

| Principal Component | Aging Condition           |                          |                          |                          |                            |
|---------------------|---------------------------|--------------------------|--------------------------|--------------------------|----------------------------|
|                     | 25 °C,<br>70% RH          | 40 °C,<br>70% RH         | 70 °C,<br>25% RH         | 70 °C,<br>40% RH         | 70 °C,<br>70% RH           |
| PC 1 (65%)          | R(6) = .96,<br>p = 0.0002 | R(8) = .84,<br>p = 0.003 | R(5) = .87,<br>p = 0.01  | R(3) = .97,<br>p = 0.002 | R(13) = .68,<br>p = 0.0002 |
| PC 2 (21%)          | R(6) = .91,<br>p = 0.002  | R(8) = .82,<br>p = 0.004 | R(5) = .66,<br>p = 0.1   | R(3) = -.81,<br>p = 0.09 | R(13) = -.41,<br>p = 0.1   |
| PC 3 (4%)           | R(6) = -.18,<br>p = 0.7   | R(8) = .66,<br>p = 0.1   | R(5) = -.68,<br>p = 0.09 | R(3) = -.56,<br>p = 0.3  | R(13) = .27,<br>p = 0.3    |
| PC 4 (3%)           | R(6) = -.54,<br>p = 0.2   | R(8) = .42,<br>p = 0.2   | R(5) = -.22,<br>p = 0.6  | R(3) = -.42,<br>p = 0.5  | R(13) = .34,<br>p = 0.2    |
| PC 5 (2%)           | R(6) = -.18,<br>p = 0.7   | R(8) = -.31,<br>p = 0.2  | R(5) = .75,<br>p = 0.05  | R(3) = -.77,<br>p = 0.2  | R(13) = -.34,<br>p = 0.2   |



**Figure S2.8.** Representative DSC thermogram for unaged, cured BA-AN adhesive with heating and cooling cycles from -80 to 100 °C and ramp rate of 3 °C/min. An endothermic crystalline melt peak is observed at 47 °C, with an inflection characteristic of a glass transition at 37 °C.



**Figure S2.9.** Time-resolved water vapor uptake in BA-AN from 40 to 70 °C and 0 to 90% RH with 5% RH steps. The uptake after desorption (end of experiment) is greater than the initial uptake (start of experiment).

## Chapter 3

### 3 Influence of Local Sequence Architecture on the Hydrolysis Pathways and Dielectric Property Evolution of Butyl Acrylate-co-Acrylonitrile Adhesives

*My contribution to this work included executing all computational simulations and writing.*

C.A. Fox, J.A. Scher, M.P. Kroonblawd, R.H. Gee, R. Faller

#### Abstract

This work identifies the sequence-specific 5:12 butyl acrylate-co-acrylonitrile (BA-AN) architecture as the life-limiting structural and electronic feature of acrylate-nitrile adhesives. By integrating ensemble steered molecular dynamics (SMD) with multivariate spectral deconvolution, we show that dense acrylonitrile blocks enforce an orthogonal arrangement of nitrile dipoles that quench inter-dipole coupling within the polymer and kinetically favor the formation of cyclic amidine species over terminal hydrolysis products. Multivariate optimization of aged ATR-FTIR spectra indicates a total hydrolysis level of 45.3%, with the degraded matrix dominated by nitrogen-containing intermediates. Electronic structure analysis further shows that the 5:12 architecture is intrinsically less dielectrically stable than a 1:1 alternating system, with a band gap  $E_g$ , nearly 1.0 eV lower. However, the principal driver of dielectric decay is the transition from this initially quenched state to a more dissipative aged state. Aging narrows the band gap modestly, from 6.77 to 6.74 eV, while the intensity-derived transition dipole moment (TDM) increases by 17.7%, from 3.34 to 3.93. We further identify a near-linear correlation

between the experimentally observed 15.5% reduction in breakdown strength and the calculated electronic quality factor,  $\chi = E_g/\text{TDM}$ . These results suggest that less constrained nitrogenous dipoles promote failure through increased dipolar dielectric loss and localized energy dissipation. Although the global chemical state is substantially altered, the degree of hydrolysis lies between the observed 15.5% dielectric decay and a 62% loss in mechanical cohesion, supporting the conclusion that the 5:12 sequence distribution as the primary driver of hierarchical adhesive failure.

### 3.1 Introduction

Butyl acrylate-co-acrylonitrile (BA-AN) is an acrylate adhesive used in high-performance flat-flex cable assemblies for applications in aerospace, defense, and high-performance computing.<sup>1-4</sup> In these systems, BA-AN often appears in multiple layers within high-voltage material stack-ups, where it serves to bond polyimide layers to each another and conductive copper layers. The environmental stability of BA-AN is therefore a critical determinant of cable lifetime. However, degradation in crosslinked polymeric adhesives integrated into multilayer assemblies is particularly challenging to characterize because the materials are chemically intractable and only partially accessible. These limitations preclude conventional liquid-state characterization methods such as nuclear magnetic resonance (NMR) spectroscopy and gel-permeation chromatography (GPC).

In our previous work (see Chapter 2), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to monitor BA-AN hydrolysis in peeled flat-flex cable assemblies following accelerated aging under controlled temperature and relative humidity.<sup>1</sup> Those measurements showed significant age-induced chemical evolution in the adhesive, which was attributed to hydrolysis at both the acrylonitrile nitrile site and butyl

acrylate ester site.<sup>1</sup> Peel testing and high potential breakdown measurements performed on unaged and aged cables revealed concurrent degradation in mechanical cohesion and dielectric performance. A kinetic model based on spectroscopically derived pseudo-first-order rate constants for nitrile and ester hydrolysis linked ATR-FTIR aging signatures to macroscopic property loss and further indicated that nitrile hydrolysis was the dominant contributor to both peel and dielectric decay, whereas ester hydrolysis was comparatively inconsequential to cable performance.<sup>1</sup>

Although FTIR is a powerful tool for tracking chemical transformation and degradation kinetics, its utility is often limited by spectral band overlap and the inherent complexity of polymer mixtures. Our previous study identified several plausible hydrolysis pathways and eight candidate products, designated E1, E2, and N1 through N6 (**Figure 3.1**).<sup>1</sup> However, strong spectral overlap, particularly among amide (N1) and cyclic amidine species (N4 and N5), prevents confident assignment of product speciation and therefore limited mechanistic interpretation. In such systems, quantum chemical calculations based on Density Functional Theory (DFT)<sup>5–8</sup> have become essential for assigning overlapping vibrational signatures and providing molecular-level structural context.

Here, we introduce a multiscale computational framework to resolve the hydrolytic stability and property decay of this complex polymeric adhesive. The approach follows a hierarchical workflow consisting of: (1) density functional tight binding (DFTB)<sup>9–11</sup> screening to identify accessible hydrolysis reactions at specific BA-AN sites; (2) conformational analysis to determine low-energy structures of product species; and (3) DFT-based vibrational analysis to generate theoretical FTIR spectra for direct comparison with experiment. This strategy is

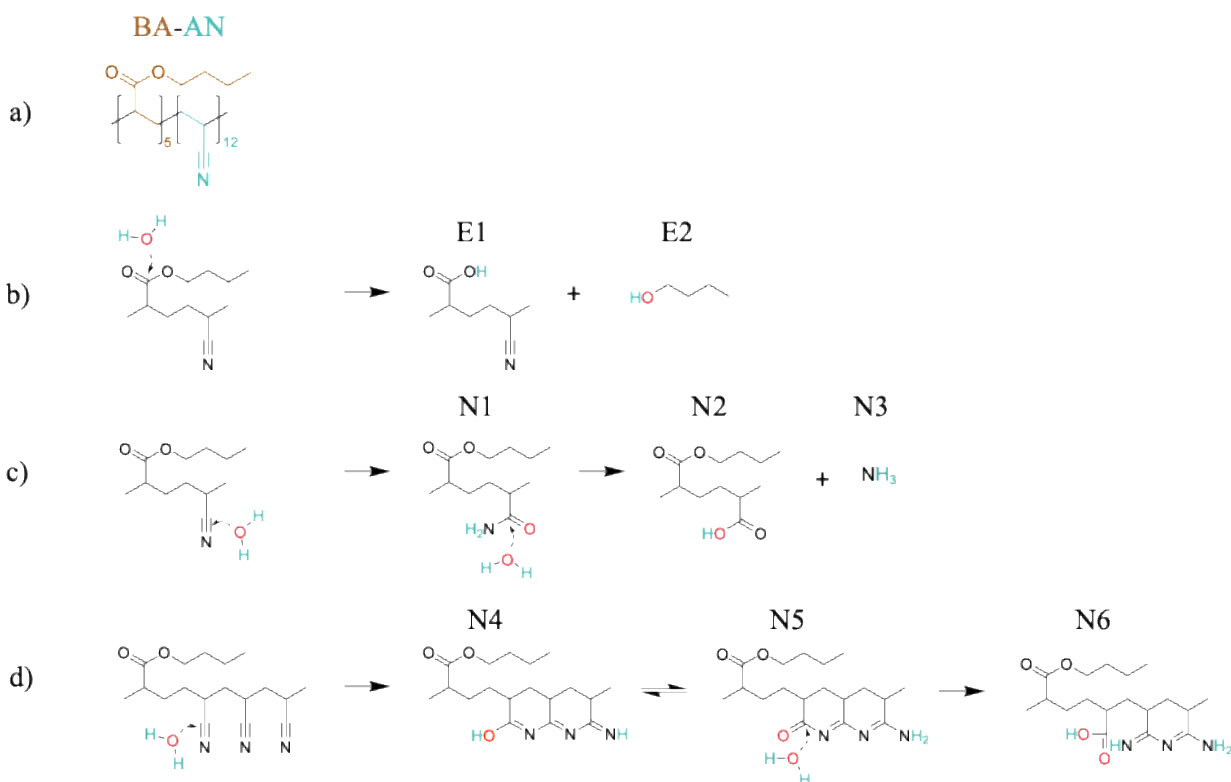
particularly valuable for polymer systems that are experimentally inaccessible because of crosslinking, interfacial confinement, or material intractability.

Because full DFT treatment is prohibitively expensive for large-scale reaction screening, self-consistent charge DFTB (SCC-DFTB)<sup>8</sup> provides an efficient intermediate method for sampling broad degradation landscapes.<sup>10–13</sup> Recent studies have successfully applied SCC-DFTB to polymer oxidation and hydrolysis problems, including degradation of polyethylene across different morphologies and hydrolysis of ester-like motifs using specialized parameter sets with near-DFT accuracy.<sup>14, 15</sup> To account for the high conformational flexibility of polymer fragments and degradation products, we coupled this screening strategy with conformer-rotamer ensemble sampling tool (CREST) and the extended tight-binding (xTB) engine.<sup>16–18</sup> CREST employs iterative metadynamics and genetic crossing to avoid repeat trapping in local minima, making it well suited for flexible oligomeric systems in which multiple rotamers produce nearly degenerate structures and heavily overlapping IR features.<sup>17–20</sup> This level of conformational sampling is necessary to reproduce the broadening and shoulder structures observed experimentally in ATR-FTIR spectra.

The primary objectives of this study are to: (1) determine the unknown copolymer stoichiometry through multivariate deconvolution of the hydrocarbon backbone, necessitated by the material's intractability to GPC and liquid-state NMR; (2) identify plausible hydrolysis products and quantify their contributions to the overall degradation process; (3) characterize the molecular drivers of dielectric decay by evaluating electronic band gaps and transition dipole moments (TDM) as descriptors for insulation stability and energy dissipation; and (4) assess the impact of site-specific hydrolysis on macroscopic properties such as peel strength and dielectric

breakdown, thereby clarifying why nitrile hydrolysis is substantially more damaging to macroscopic properties than ester hydrolysis.

By integrating non-equilibrium steered molecular dynamics (SMD) work functions with Boltzmann-weighted ensemble IR simulations, we show that failure of the BA-AN adhesive is not governed solely by pendant-group chemistry. Instead, it is fundamentally dictated by local sequence architecture. Specifically, we provide evidence that the 1:1 weight-percent formulation, corresponding to a 5:12 molar ratio, creates a crowded nitrile-rich environment that steers degradation toward localized amidine clusters. These specific species emerge as dielectric sinks because they combine reduced electronic band gaps with enhanced transition dipole moments, thereby coupling molecular-scale hydrolysis to macroscopic adhesive failure.



**Figure 3.1.** Structural representations of (a) BA-AN with a 5:12 BA:AN molar ratio and proposed hydrolysis reactions at the (b) BA ester site, (c) AN nitrile site without adjacent AN units, and (d) AN nitrile site with adjacent AN units. Hydrolysis products are numbered sequentially and labeled with an “E” or “N” prefix according to ester- or nitrile-derived origin.

## 3.2 Methods

### 3.2.1 Model BA-AN Oligomers

Two BA-AN oligomer models were constructed using Avogadro (v1.2.1)<sup>21, 22</sup> to investigate the influence of chain length and sequence distribution on hydrolysis behavior. A 1:1 molar ratio was used as a reductionist model system to establish baseline hydrolysis dynamics and identify primary reaction products. A 2:3 molar ratio oligomer was also considered to more closely match the experimentally determined ratio, which requires a larger atom count, but allows for exploring post-hydrolysis secondary reactions, particularly formation of amidine rings. The 2:3 oligomer was designed with a nitrogen-rich distribution of BA-AN-AN-AN-BA.

Condensed-phase configurations were generated using Packmol<sup>23</sup> at a target density of 0.97 g/cm<sup>3</sup>. To initiate hydrolysis, one water molecule was inserted into each periodic simulation cell. The 1:1 system contained seven oligomers in a cubic cell with side length 13 Å, whereas the 2:3 system contained four oligomers in a cubic cell with side length 14.2 Å.

### 3.2.2 Steered Molecular Dynamics (SMD)

High-throughput structural optimizations and reactivity screening of BA-AN oligomers were carried out using SCC-DFTB<sup>9–11, 15</sup> as implemented in DFTB+.<sup>24</sup> DFTB is derived from an expansion of the Kohn-Sham total energy around a reference density, typically represented as a superposition of non-interacting atomic densities.<sup>8</sup> The total energy is expressed as

$$\text{DFTB} = E_{\text{BS}} + E_{\text{Coul}} + E_{\text{Rep}} + E_{\text{Disp}} \quad (3.2.1)$$

where  $E_{\text{BS}}$  denotes the electronic band-structure energy,  $E_{\text{Coul}}$  accounts for second-order charge fluctuations, and  $E_{\text{Rep}}$  and  $E_{\text{Disp}}$  represent empirical repulsive and dispersion contributions, respectively. We used the third-order 3ob-3-1 parameter set, which is optimized for CHON-containing organic systems and polymers.<sup>12</sup> Long-range dispersion interactions were treated using the Grimme-D3 correction with Becke-Johnson damping.<sup>25</sup> All SMD calculations were performed using a three-dimensional periodic simulation cell. Electronic structure was evaluated at the  $\Gamma$ -point without spin polarization. Fermi–Dirac thermal smearing<sup>26</sup> was applied at 300 K to facilitate convergence, and the SCC accuracy convergence threshold was set to  $10^{-6}$  eV.

All systems were equilibrated in the canonical NVT ensemble for 10 ps using a 0.2 fs timestep. Temperature was controlled at 300 K with a Nosé-Hoover thermostat.<sup>27</sup> Stability during equilibration was verified by monitoring convergence of the total potential energy and expected distribution of temperature fluctuations (**Figure S3.1**). To ensure robust statistical sampling of the reaction landscape, an ensemble of 100 independent simulations was generated for each molecular configuration using randomized initial velocity seeds.

Hydrolysis mechanisms were then probed using steered molecular dynamics (SMD) in PLUMED v2.9.4.<sup>28, 29</sup> A moving harmonic bias potential,  $V_{\text{bias}}$ , was applied along a reaction coordinate,  $R(t)$ , defined specifically for each reaction site. The harmonic force constant was set to  $239 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$ , and the equilibrium position,  $R_0(t)$ , was translated at constant nominal velocity of  $0.08 \text{ \AA/ps}$ . Although this pulling rate lies within a non-equilibrium regime imposed by the computational cost, equilibrium free energies can be estimated using the Jarzynski equality.

Each SMD simulation was propagated for 30 ps. The harmonic bias was applied during the first 15 ps to drive the water molecule toward the targeted reactive site. Final configurations were then geometry-optimized using a conjugate-gradient algorithm with a force convergence threshold of  $2 \times 10^{-2}$  eV Å<sup>-1</sup>. The Helmholtz free energy change,  $\Delta F$ , was extracted from the work distribution ( $W$ ) using the Jarzynski equality:<sup>30, 31</sup>

$$e^{-\beta\Delta F} = \langle e^{-\beta W} \rangle \quad (3.2.2)$$

where  $\beta = 1/k_B T$ . This enabled decomposition of the total work into the equilibrium free energy,  $\Delta F_{\text{total}}$ , and the dissipated work,  $W_{\text{diss}} = \langle W \rangle - \Delta F_{\text{total}}$ . Because the total work includes the moving restraint contribution ( $\Delta F_{\text{restraint}}$ ),<sup>32</sup> the equilibrium free energy was defined as

$$\Delta F_{\text{system}} = \Delta F_{\text{total}} - \Delta F_{\text{restraint}} \quad (3.2.3)$$

To quantify the precision of the calculated  $\Delta F$ , we used bootstrap<sup>33</sup> resampling of the work distribution with replacement over 1000 iterations. Uncertainty in the dissipated work ( $W_{\text{diss}}$ ) was estimated as the standard error of the mean,  $\text{SE} = \text{SD}/\sqrt{n}$ , where SD is the standard deviation of the work distribution and  $n$  is the number of trajectories.

It is important to distinguish the physical meaning of these quantities in the present non-equilibrium SMD framework. The quantity  $\Delta F_{\text{system}}$  does not represent an intrinsic bond dissociation energy or an elementary activation barrier. Rather, it reflects the apparent free-energy cost associated with driving the selected transformation along the imposed reaction coordinate after removals of the restraint contribution. Its magnitude therefore contains contributions from chemical bond rearrangement, steric deformation, constrained water approach, and local segmental reorganization within the condensed polymer environment. Since

these transformations are enforced under a stiff moving bias and over a finite simulation timescale, the resulting  $\Delta F_{\text{system}}$  values are best interpreted as protocol-dependent apparent free energy costs, or upper bound estimates within the present force-coordinate framework, rather than intrinsic reaction energetics. By contrast, the dissipated work,  $W_{\text{diss}}$ , quantifies the excess non-equilibrium work required to drive the system faster than local structural relaxation can occur, and is therefore used here as a descriptor of kinetic resistance associated with matrix reorganization.

### 3.2.3 Product Identification and Structure Analysis

Due to the large number of trajectories generated in the SMD ensemble, reaction products were identified automatically using graph-based analysis of covalent connectivity following the protocol of Kroonblawd et al.<sup>34</sup> Covalent bonds were assigned using fixed bond-length cutoffs, and unique connected components in the post-optimized configurations were identified with the NetworkX Python package.<sup>35</sup> These products were then cross-referenced against a library of known chemical structures to determine final molecular compositions and verify reaction pathways. Unique chemical species identified in this manner were subsequently subjected to conformational sampling to capture flexibility relevant to the polymer-state spectroscopy.

### 3.2.4 Conformational Ensemble Generation, CREST/xTB

Conformational landscapes of identified hydrolysis products were explored with CREST<sup>16, 17</sup> driven by the semi-empirical GFN2-xTB method.<sup>36, 37</sup> This approach provides an efficient balance between speed and qualitative accuracy for flexible molecular systems. To approximate a water-saturated copolymer environment representative of humid aging conditions, we utilized the Analytical Linearized Poisson-Boltzmann (ALPB)<sup>38, 38</sup> implicit solvation model with ethanol as a surrogate solvent (dielectric constant,  $\epsilon \approx 24.3$ ). This moderate dielectric was

chosen instead of water ( $\epsilon \approx 78.5$ ) to avoid excessive polarization while still capturing relevant electrostatic screening.

The resulting ensembles, which contained thousands of candidate structures, were processed with the conformer-rotamer ensemble generator (CREGEN) tool.<sup>17</sup> Redundant geometries were clustered using K-means-based filtering according to energy and Cartesian root-mean-squared deviation (RMSD). Only unique conformers within 3 kcal/mol of the global minimum were retained and exported for higher-level DFT refinement and final property analysis.

### 3.2.5 Electronic Structure and Vibrational Frequency Analysis

Representative conformers from the CREST/xTB workflow were refined using DFT<sup>5-8</sup> in Gaussian 16.<sup>39</sup> Geometry optimizations and frequency calculations were performed at the B3LYP/6-31G(d) level of theory.<sup>40-44</sup> To represent the polymer matrix after removal from high-humidity aging conditions, we used a self-consistent reaction field (SCRF)<sup>45</sup> with the SMD solvation model.<sup>46</sup> Instead of a standard solvent, we defined a custom ether-like aprotic medium intended to approximate the density and polarizability of a solid polymer environment. The static dielectric constant was set to 4.5 and the optical dielectric constant to 2.2, corresponding to a refractive index range of approximately 1.45 to 1.6, consistent with typical solid polymers.<sup>47</sup> Hydrogen-bond acidity was set to 0.05 and hydrogen-bond basicity to 0.3 to reflect the modest donor and acceptor capacity of the adhesive matrix. Surface tension was set to 35.0 cal mol<sup>-1</sup> Å<sup>2</sup> to provide appropriate stabilization of dispersion and van der Waals interactions in the condensed phase.

For each species, the electronic band gap was calculated as the Boltzmann-weighted average HOMO-LUMO energy difference across the conformer ensemble. To estimate relative dielectric response, an intensity-derived dipole-coupling descriptor was constructed from the calculated IR intensities using the proportionality  $I \propto \left| \frac{\partial \mu}{\partial Q} \right|^2$ , such that the relevant dipole-coupling amplitude scales with the square root of intensity.<sup>48, 49</sup> In the discussion below, this quantity is denoted TDM and used as a spectrally averaged comparative measure molecular coupling to an external oscillating field. It is therefore interpreted as an operational descriptor for relative comparisons across the hydrolysis product landscape, rather than as a rigorously extracted absolute transition dipole moment.

### 3.2.6 Spectral Processing and Multivariate Deconvolution

A multistep post-processing workflow was applied to better connect the predicted vibrational normal modes and IR intensities with experimental ATR-FTIR measurements of the adhesive at finite temperature. These steps include:

1. Combined spectra were generated as Boltzmann-weighted conformer ensembles using Gibbs free energies at 298.15 K. To mimic inhomogeneous broadening within the polymer matrix, each vibrational transition was broadened with a pseudo-Voigt profile having a full width at half maximum of 25 cm<sup>-1</sup>.<sup>50</sup>
2. A Dual-frequency scaling scheme was applied to account for basis-set incompleteness, anharmonicity, and the difference between the implicit-solvent DFT model and the bulk polymer environment. Frequencies above 2000 cm<sup>-1</sup>, dominated primarily by C≡N, C–H, N–H, and O–H stretching modes, were scaled by 0.950.

Frequencies below 2000 cm<sup>-1</sup> were scaled by 0.958 to improve agreement in the fingerprint region.<sup>51</sup>

3. Representative conformers from the Boltzmann-weighted ensembles were inspected manually to map specific molecular orientations onto key spectral features. This step was especially important in the carbonyl region, where broadening and splitting were linked with sequence-induced conformational inequivalence.
4. The experimental ATR-FTIR spectrum of aged BA-AN was modeled as a weighted linear combination of the pristine copolymer and its hydrolysis products. The global spectral profile ( $S$ ) was defined as:

$$S = (1 - h)S_{\text{pristine}} + (h \cdot S_{\text{degraded}}) \quad (3.2.4)$$

where  $h$  is the global hydrolysis fraction and  $S_{\text{degraded}}$  is the weighted sum of the identified product basis spectra. Spectral optimization was performed using a constrained limited-memory Broyden-Fletcher-Goldfarb-Shanno algorithm with bounds (L-BFGS-B)<sup>52, 53</sup> to minimize the mean squared error between experimental and modeled area-normalized intensities. Area normalization was used to emphasize spectral shape rather than absolute absorbance.

To best match the experimental monomer ratio, the optimization was constrained using bounds derived from 5:12 BA:AN stoichiometry and the branching behavior observed in the SMD ensembles. The carboxylic acid (E1) and terminal amide (N1) were assigned minimum thresholds consistent with their roles as primary intermediates. Butanol and ammonia were constrained to remain below 0.1 in relative weight to account for probable diffusion of small-molecule byproducts out of the bulk matrix. The global hydrolysis level was bounded at 0.60, consistent with the theoretical fraction of accessible hydrolyzable groups in the 5:12 architecture.

These chemically informed constraints allowed product weights to vary independently while preserving consistency with the sequence architecture and hydrolysis mechanisms observed in simulation.

To evaluate the effect of the experimentally relevant 5:12 molar composition, a synthetic 5:12 spectrum was estimated by linear extrapolation from the computed 1:1 and 2:3 ensemble-averaged spectra:

$$\text{Abs}_{5:12} = a(\text{Abs}_{1:1}) + b(\text{Abs}_{2:3}) \quad (3.2.5)$$

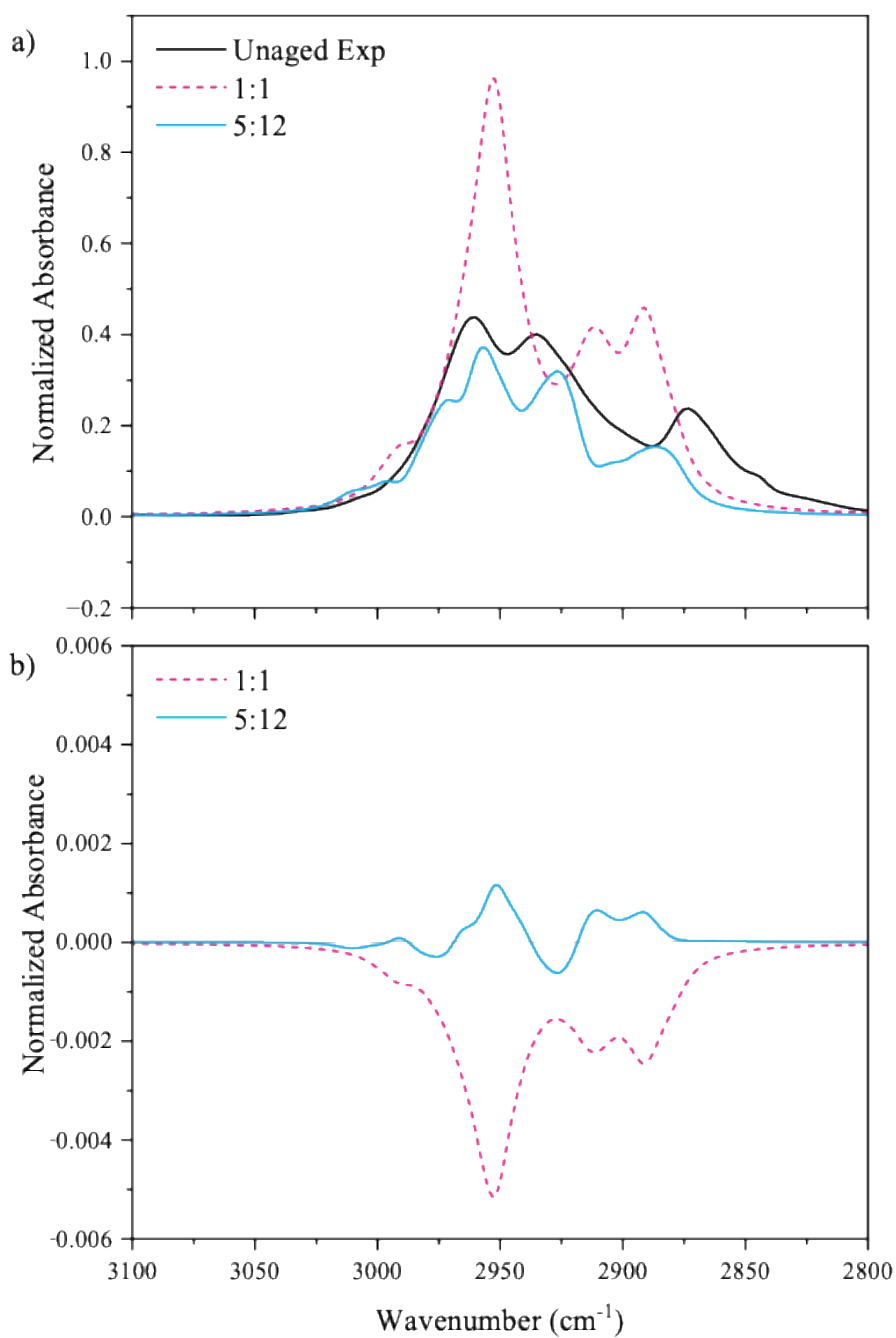
where  $a = -1.06$  and  $b = 2.06$ . These coefficients were obtained by matching the target 5:12 carbonyl fraction,  $5/17 = 0.294$ , and nitrile fraction  $12/17 = 0.706$ , from the explicitly modeled 1:1 and 2:3 systems (Equation S3.1). Because the target AN fraction lies outside the range spanned by the two modeled compositions, these coefficients should be treated as linear extrapolation coefficients rather than physical mixture weights. The extrapolated 5:12 spectrum provided a better match to the hydrocarbon backbone region than the 1:1 model alone. However, the 1:1 basis set was retained for multivariate deconvolution in the carbonyl region to avoid numerical artifacts introduced by extrapolation and preserve stable product-specific fitting.

### 3.3 Results and Discussion

#### 3.3.1 Stoichiometric Validation and Sequence-Dependent Microstructure

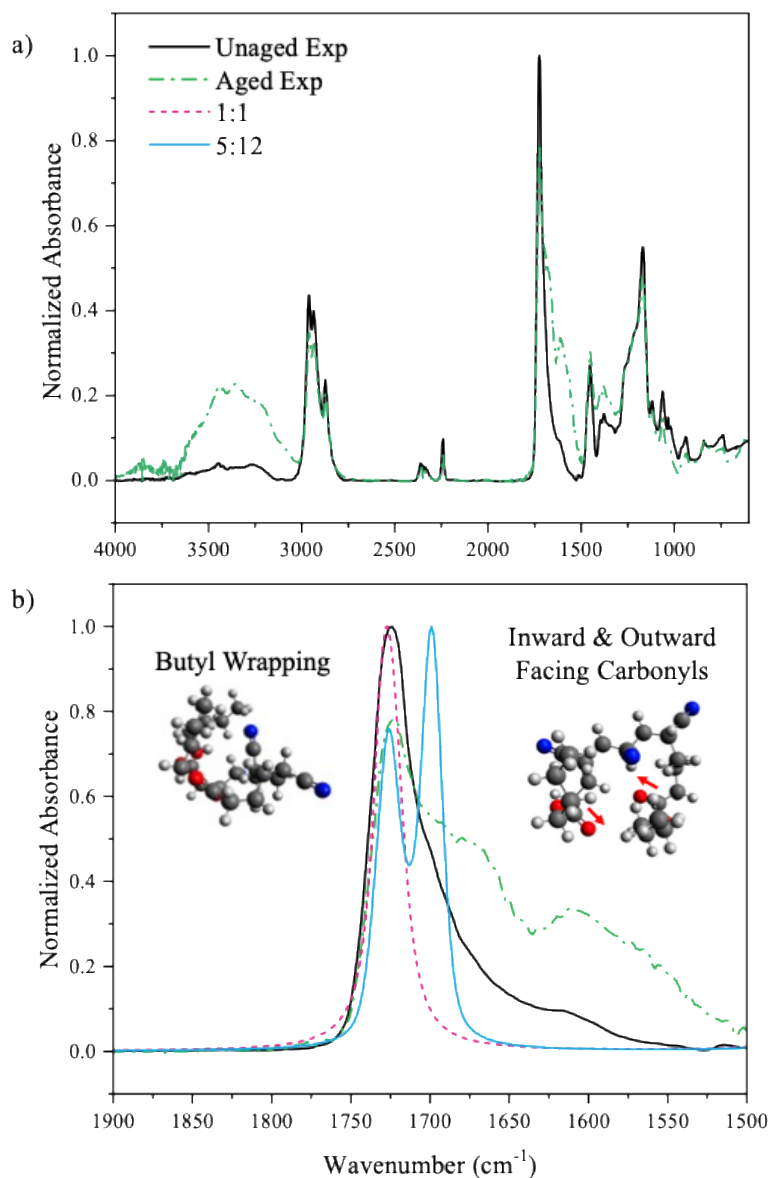
Analysis of the C–H stretching region for the 1:1 and 2:3 copolymer models, together with the extrapolated 5:12 system, shows that the 5:12 architecture provides the best quantitative match to the experimental unaged spectrum (**Figure 3.2**). The root mean squared error decreases from 0.1554 for the 1:1 model to 0.0989 for the 5:12 model, corresponding to a 36.4% improvement. This result indicates that the 5:12 architecture more accurately captures the

average hydrocarbon density and vibrational environment of the polymer backbone. Because the target 5:12 composition lies outside the range spanned by the explicitly modeled 1:1 and 2:3 systems, the corresponding 5:12 spectral descriptors should be interpreted as extrapolated estimates rather than direct predictions from an explicitly simulated 5:12 oligomer ensemble. The improved agreement is therefore most appropriately viewed as support for the proposed sequence architecture and its associated local environments, rather than as a literal reconstruction of the full 5:12 spectral landscape.



**Figure 3.2.** Comparison of computed and experimental spectra used for stoichiometric validation. (a) C–H stretching region of the extrapolated 5:12 BA:AN spectrum, the computed 1:1 model spectrum, and the experimental unaged BA-AN adhesive ATR-FTIR spectrum. (b) Residuals between modeled and experimental spectra across the same region.

Inspection of the carbonyl stretching region reveals the structural origin of the observed band splitting. Visual analysis of the Boltzmann-weighted 2:3 conformer ensemble identifies two distinct carbonyl environments: one inward-facing carbonyl oriented toward the AN-rich block, and one outward-facing carbonyl directed toward the surrounding matrix (**Figure 3.3**). The inward facing carbonyl is red shifted, indicating a weakened C=O force constant arising from the strong local electrostatic field and steric confinement imposed by adjacent acrylonitrile units together with hydrophobic butyl-chain wrapping. Although the mathematical extrapolation used to generate the 5:12 spectrum introduces minor sharpening artifacts, the underlying peak positions remain governed by the sequence-specific models and provide a more realistic representation of the BA-AN local chemical environment than isolated monomer analogs. The alignment of the 5:12 molar ratio with a practical 1:1 weight ratio formulation further supports the physical relevance of this structural model for industrially used adhesives.



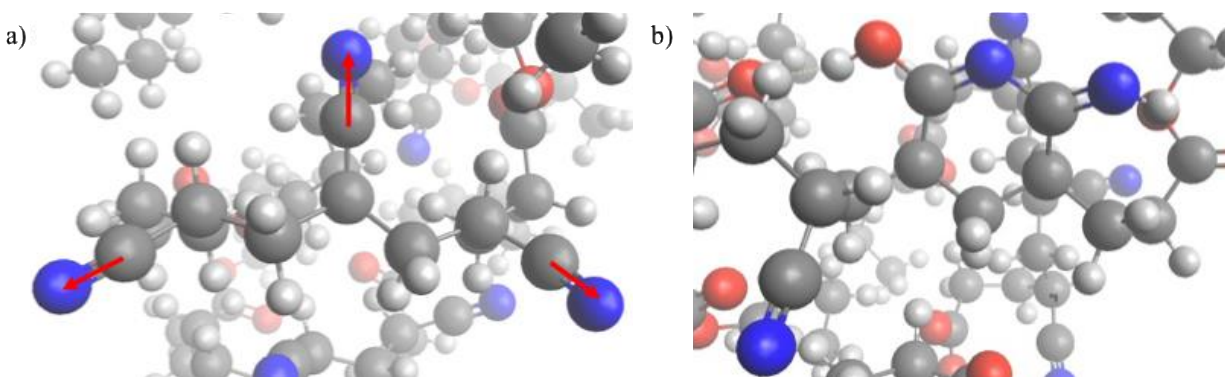
**Figure 3.3.** Sequence-dependent spectral features in BA-AN. (a) Experimental ATR-FTIR spectra, 600–4000  $\text{cm}^{-1}$ , for unaged and aged BA-AN adhesive. (b) Carbonyl stretching region of the extrapolated 5:12 system, the computed 1:1 model, and the experimental unaged and aged BA-AN adhesive spectra, together with representative 2:3 conformer snapshots showing butyl wrapping and conformational inequivalence of the two BA carbonyls that give rise to band splitting.

Beyond peak position, relative band areas also provide insight into the chemical state of the pristine copolymer. The theoretical response factor,  $\epsilon_{\text{C=O}}/\epsilon_{\text{C}\equiv\text{N}}$ , was derived from the integrated molar absorptivity of the individual functional groups within the 5:12 ensemble. Using the proportionality between absorbance and the square of the transitional dipole moment ( $A \propto |\mu|^2$ ), we estimated the average intensity contribution of a single acrylate carbonyl and single acrylonitrile group. For the pristine 5:12 BA:AN system, this yielded an intrinsic response factor of 6.67, indicating that a carbonyl group is nearly seven times more intense than a nitrile group. Based on the 5:12 stoichiometry, the theoretical band-area ratio  $A_{\text{C}\equiv\text{N}}/A_{\text{C=O}}$  was predicted to be 0.359.

Experimentally, however, integration of the pristine ester window (1680–1752  $\text{cm}^{-1}$ ) in the unaged spectrum gave a substantially smaller ratio of 0.042. This deficit is partially consistent with pre-existing hydrolysis, as suggested by the visible N–H and O–H activity between 3100–2600  $\text{cm}^{-1}$  (**Figure 3.3**). More importantly, it also suggests significant dipole dampening within dense 5:12 AN blocks. Examination of the equilibrated 2:3 ensemble reveals an orthogonal arrangement of neighboring nitrile dipoles, in which adjacent groups align approximately along the +x, +y, and +z directions (**Figure 3.4**). This non-parallel configuration minimizes inter-dipole repulsion while strongly quenching the net transition dipole moment, thereby reducing the nitrile stretching intensity and providing a physical explanation for the low experimental area ratio relative (0.042) to the theoretical prediction. This same arrangement also imposes a structural barrier to cyclization, because the system must expend mechanical work to rotate these orthogonal dipoles into the more parallel geometry required for amidine formation.

After aging in humid thermal conditions, specifically at 70 °C and 70% relative humidity for 140 days, the pristine ester area decreases by 31.9%, from 0.127 to 0.086, whereas the nitrile

signal decreases by 56.7%, from 0.007 to 0.004. The resulting band-area ratio decreases further to 0.0275. This preferential depletion of nitrile character relative to ester character indicates that the 5:12 sequence architecture selectively promotes nitrile-branch activation. Together, the 36.4% improvement in the C–H region agreement and the accurate prediction of the primary ester frequency shift establish the 5:12 architecture as the most physically representative model for the adhesive backbone. Although the carbonyl shoulder indicates a chemically heterogeneous population, the underlying vibrational environment is most consistent with the AN-rich 5:12 sequence distribution rather than a simple 1:1 mixture.



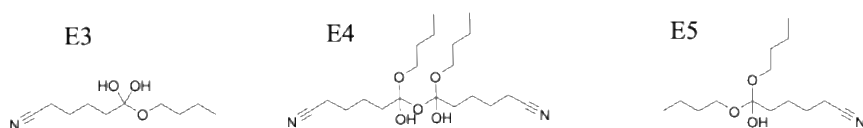
**Figure 3.4.** Representative snapshots of the BA-AN 2:3 sequence environment. (a) Orthogonal arrangement of the nitrile triad, in which electrostatic minimization quenches the net transition dipole moment. (b) Structural distortion required for cyclization, highlighting the significant backbone rotation needed to bring neighboring nitrogen atoms into the geometry required for amidine formation.

### 3.3.2 Mechanistic Insights into BA-AN Hydrolysis, Intermediates, and Energetics

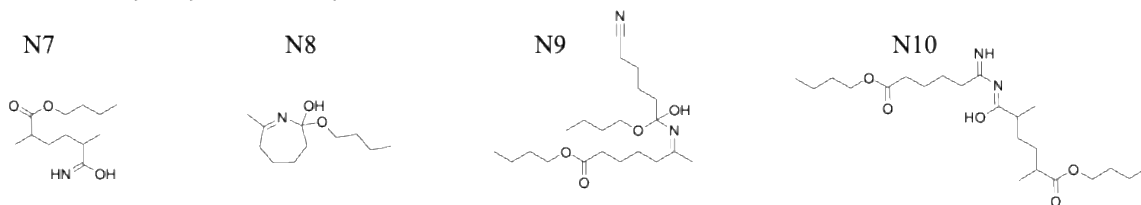
Steered molecular dynamics (SMD) simulations were performed to identify products arising from hydrolysis at both ester and nitrile sites. These simulations confirmed the primary products anticipated from the initial mechanism framework, namely N1–N6, and E1–E2 (see

**Figure 1**), and also revealed a subset of transient, but locally stable intermediates (**Figure 3.5**). For ester-site hydrolysis, the initial nucleophilic attack frequently produced a geminal alcohol intermediate (E3). Although E3 corresponds to a local minimum on the potential energy surface, its relatively high frequency of occurrence ( $n = 30$ ), together with its thermodynamic profile, suggests that it functions primarily as a transient intermediate rather than a stable terminal product. The reverse dehydration reaction back to a carbonyl is expected to proceed rapidly,<sup>54, 55</sup> likely competing effectively with forward progression to the carboxylic acid and butanol products (E1 and E2). This suggests that a significant fraction of ester-branch activity remains kinetically stalled near the geminal alcohol state, thereby delaying irreversible acrylate degradation.

#### Additional Ester Hydrolysis Chemistry



#### Additional Nitrile Hydrolysis Chemistry



**Figure 3.5.** Expanded library of BA-AN hydrolysis products and transient intermediates identified by ensemble SMD simulations. Species shown include both primary products and metastable intermediates considered in the spectral deconvolution workflow.

Ensemble-averaged SMD results for the initial ester- and nitrile-site hydrolysis pathways are summarized in **Table 3.1**. The absolute magnitudes of the calculated  $\Delta F_{\text{system}}$  values are

substantially larger than the typical gas-phase bond dissociation energies and should not be interpreted that way. In the present simulations, these values represent the apparent free energy costs for forced transformations in a dense polymer environment under a stiff external bias. As such, they include not only the local chemistry of bond breaking and bond formation, but also contributions from steric confinement, segmental deformation, constrained approach of water to the reactive site, and the free energy penalty associated with driving the system along a prescribed, non-native coordinate. The resulting values are therefore best viewed as protocol-dependent, upper-bound apparent free energy costs associated within this SMD framework, rather than intrinsic reaction barriers of the underlying elementary chemistry. Within that context, the relative trends remain informative. In the 1:1 system, ester hydrolysis to E1 and E2 is thermodynamically more favorable than the primary nitrile pathway, with

$\Delta F_{\text{system}} = 304 \pm 4$  kcal/mol versus  $\Delta F_{\text{system}} = 335 \pm 8$  kcal/mol for N7 formation. However, the primary ester pathway is observed in only 34 of 100 trajectories, whereas the primary nitrile pathway occurs in 94 out of 100 trajectories. This contrast indicates that ester hydrolysis is thermodynamically favored, but nitrile hydrolysis is more kinetically accessible. The ester branch also shows a substantial population of transient geminal alcohol intermediates (E3), together with 31 no-reaction trajectories, consistent with kinetic stalling near the initial hydration state.

In the 2:3 nitrile-rich system, the number of no-reaction trajectories rises sharply to 46, and the primary N7 pathway is observed in only 36 trajectories. Alternative nitrile speciation remains rare in both systems, although N10 appears somewhat more frequently in the 2:3 rich environment than the 1:1 system, consistent with increased accessibility of sequence-dependent rearrangements under nitrile-rich conditions.

**Table 3.1.** Ensemble-averaged SMD results for initial ester- and nitrile-site hydrolysis pathways in 1:1 and 2:3 BA-AN copolymer models. Frequency,  $n$ , denotes the number of successful reaction events out of 100 independent simulations. Reported uncertainties for  $\Delta F_{\text{system}}$  were obtained by bootstrap resampling, and uncertainties for  $W_{\text{diss}}$  correspond to the standard error of the mean. A dash indicates that uncertainty was not reported because only a single event was observed.

| Ester-Branch Ensemble Pathways (1:1 System)   |                                                    |                                           |                                   |                        |
|-----------------------------------------------|----------------------------------------------------|-------------------------------------------|-----------------------------------|------------------------|
| Reaction Scenario                             | $\Delta F_{\text{system}}^{\dagger}$<br>(kcal/mol) | $W_{\text{diss}}$<br>(kcal/mol)           | Frequency <sup>‡</sup><br>( $n$ ) | Interpretation         |
| E1 + E2                                       | $304 \pm 4$                                        | $45 \pm 4$                                | 34                                | Primary Ester Path     |
| E3                                            | $313 \pm 5$                                        | $50 \pm 5$                                | 30                                | Transient Intermediate |
| No Reaction                                   | $322 \pm 5$                                        | $38 \pm 3$                                | 31                                | Kinetic Failure        |
| E4                                            | $320 \pm 10$                                       | $23 \pm 9$                                | 4                                 | Alternative Speciation |
| E5 + E2                                       | 318                                                | —                                         | 1                                 | Alternative Speciation |
| Nitrile-Branch Ensemble Pathways (1:1 System) |                                                    |                                           |                                   |                        |
| Reaction Scenario                             | $\Delta F_{\text{system}}$<br>(kcal/mol)           | $W_{\text{diss}}^{\dagger}$<br>(kcal/mol) | Frequency<br>( $n$ )              | Interpretation         |
| N7                                            | $335 \pm 8$                                        | $41 \pm 1$                                | 94                                | Primary Nitrile Path   |
| N8                                            | 345                                                | —                                         | 1                                 | Alternative Speciation |
| N9                                            | $364 \pm 4$                                        | $4 \pm 3$                                 | 2                                 | Alternative Speciation |
| N10                                           | $376 \pm 6$                                        | $6 \pm 4$                                 | 2                                 | Alternative Speciation |
| No Reaction                                   | 401                                                | —                                         | 1                                 | Kinetic Failure        |
| Nitrile-Branch Ensemble Pathways (2:3 System) |                                                    |                                           |                                   |                        |
| Reaction Scenario                             | $\Delta F_{\text{system}}$<br>(kcal/mol)           | $W_{\text{diss}}$<br>(kcal/mol)           | Frequency<br>( $n$ )              | Interpretation         |
| No Reaction                                   | $374 \pm 2$                                        | $26 \pm 2$                                | 46                                | Kinetic Failure        |
| N7                                            | $344 \pm 8$                                        | $43 \pm 3$                                | 36                                | Primary Nitrile Path   |
| N9                                            | $381 \pm 2$                                        | $9 \pm 3$                                 | 7                                 | Alternative Speciation |
| N10                                           | $359 \pm 7$                                        | $30 \pm 5$                                | 11                                | Alternative Speciation |

<sup>†</sup>Reported free energy values represent apparent free energy costs for forced coordinate driven transformations and should not be interpreted as bond dissociation energies or elementary activation barriers.

<sup>‡</sup>Dissipated work for sample size  $n = 1$  cannot be determined.

The subsequent branching behavior of the primary nitrile pathway in the 2:3 system is summarized in **Table 3.2**. Formation of the imidic acid intermediate N7 requires

$\Delta F_{\text{system}} = 344 \pm 8$  kcal/mol and  $W_{\text{diss}} = 47 \pm 2$  kcal/mol, establishing it as the principal entry point for nitrile hydrolysis. Once formed, N7 can evolve either to the amide N1 or to the amidine N4. These two pathways have nearly identical free-energy minima,  $239 \pm 1$  and

$238 \pm 3$  kcal/mol, respectively, but differ strongly in dissipated work. Conversion to the amide requires only  $20 \pm 1$  kcal/mol, whereas amidine formation requires  $47 \pm 2$  kcal/mol, more than double the non-equilibrium structural work. Despite this higher mechanical cost, amidine formation is sampled much more frequently, 85 versus 35 events, indicating that the nitrile-rich sequence architecture strongly biases the system toward cyclization once the initial intermediate is formed.

**Table 3.2.** Ensemble-averaged SMD results for primary nitrile-path branching and sequential hydrolysis pathways in the 2:3 system. Frequency,  $n$ , denotes the number of successful reaction events out of 100 independent simulations.

| Primary Nitrile Path Branching (2:3 System) |                                                   |                                                    |                                 |                      |
|---------------------------------------------|---------------------------------------------------|----------------------------------------------------|---------------------------------|----------------------|
| Reaction Scenario                           | Description                                       | $\Delta F_{\text{system}}^{\dagger}$<br>(kcal/mol) | $W_{\text{diss}}$<br>(kcal/mol) | Frequency<br>( $n$ ) |
| BA-AN + H <sub>2</sub> O → N7               | BA-AN → Imidic Acid                               | 344 ± 8                                            | 43 ± 3                          | 36                   |
| N7 → N1                                     | Imidic Acid → Amide                               | 239 ± 1                                            | 20 ± 1                          | 35                   |
| N7 → N4                                     | Imidic Acid → Amidine                             | 238 ± 3                                            | 47 ± 2                          | 85                   |
| Sequential Hydrolysis Pathways (2:3 System) |                                                   |                                                    |                                 |                      |
| Reaction Scenario                           | Description                                       | $\Delta F_{\text{system}}^{\dagger}$<br>(kcal/mol) | $W_{\text{diss}}$<br>(kcal/mol) | Frequency<br>( $n$ ) |
| N1 + H <sub>2</sub> O → N2 + N3             | Amide + H <sub>2</sub> O → Acid + NH <sub>3</sub> | 262 ± 5                                            | 22 ± 5                          | 11                   |
| N5 + H <sub>2</sub> O → N6                  | Amidine + H <sub>2</sub> O → Acid                 | 293 ± 5                                            | 33 ± 7                          | 5                    |

<sup>†</sup>Reported free energy values represent apparent free energy costs for forced coordinate driven transformations and should not be interpreted as bond dissociation energies or elementary activation barriers.

We interpret the dissipated work,  $W_{\text{diss}}$ , as a computational descriptor of the kinetic resistance in the constrained polymer environment. Whereas  $\Delta F_{\text{system}}$  characterizes the apparent free energy cost of the forced transformation,  $W_{\text{diss}}$  isolates the excess non-equilibrium work associated with driving the system faster than local structural relaxation can occur. This distinction is important because the experimental activation energy derived from solid-state ATR-FTIR kinetics reflects an effective barrier for the observed process, not merely an intrinsic molecular activation energy. In addition to local bond rearrangement, it necessarily includes the energetic costs of segmental motion, steric accommodation, and matrix reorganization required to reach a reactive configuration in the solid state. The encouraging agreement between the calculated dissipated work for the cyclization step,  $W_{\text{diss}} = 47 \pm 2$  kcal/mol, and the experimentally measured effective activation energy,  $E_a = 40 \pm 10$  kcal/mol,<sup>1</sup> therefore

supports the interpretation that hydrolysis at the BA-AN matrix is limited primarily by configurational reorganization of the local polymer environment, rather than by bond rearrangement alone. Accordingly,  $W_{\text{diss}}$  is the more physically relevant quantity for qualitative comparison with experiment in this system.

This structural reorganization also provides a plausible explanation for the experimentally observed loss of mechanical integrity. Formation of cyclic amidines requires the polymer backbone to adopt a more constrained and locally distorted geometry, which is expected to reduce segmental mobility and increase local chain rigidity within the adhesive matrix. In polymeric adhesives, cohesive peel strength depends strongly on the ability of the network to undergo local viscoelastic deformation, chain reorientation, and energy dissipation during debonding.<sup>56–59</sup> Chemical transformations that increase backbone stiffness or introduce conformational restraints can therefore suppress these dissipative mechanisms and promote more brittle cohesive failure.<sup>60–62</sup> In the degraded BA-AN system, amidine formation is expected to act in exactly this manner: cyclization locks nearby chain segments into a more rigid configuration, reduces their ability to relax under stress, and alters the rheological response of the adhesive toward a less compliant and less energy-dissipative state. Under peel loading, this reduction in local mobility would be expected to decrease the adhesive's capacity for plastic deformation and stress redistribution, thereby lowering cohesive peel strength. In this interpretation, amidines serve not only as chemical markers of nitrile hydrolysis, but also mechanically consequential structural defects that locally stiffen the matrix and accelerated cohesive failure within the cable assembly. In the AN-dense 5:12 environment, the local availability of neighboring nitrile groups, together with the conformational constraints of the sequence, directs the chemistry toward the amidine pathway. Finally, the energetic profile suggests that these amidine clusters are

kinetically persistent intermediates as subsequent conversion to the terminal acid state remains energetically disfavored under this framework.

### 3.3.3 Multivariate Deconvolution of the Degraded Polymer

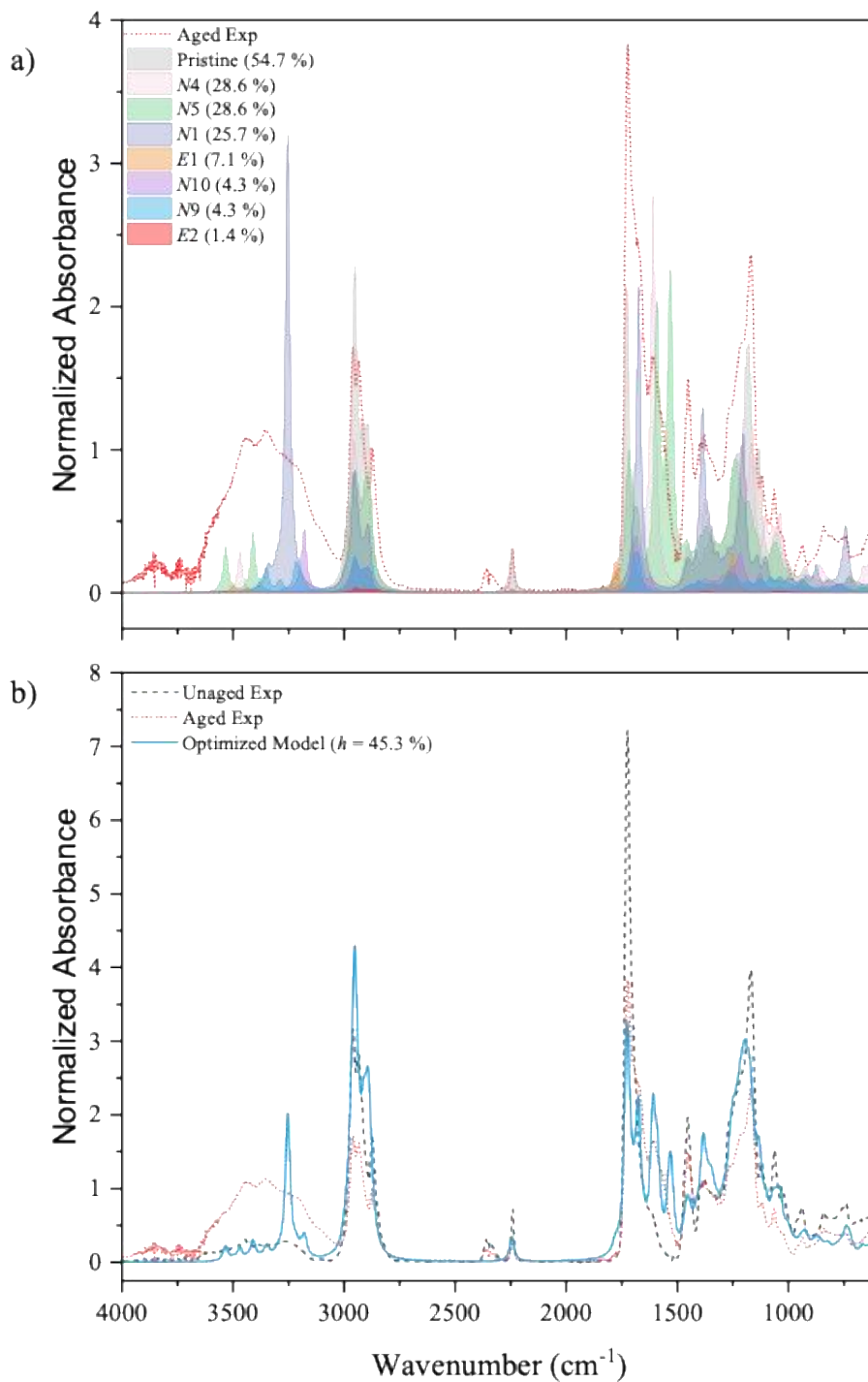
Although the 2:3 model was used to examine the effect of steric crowding on hydrolysis energetics, the vibrational basis sets employed in the multivariate deconvolution were derived from DFT analysis of the 1:1 product analogs. Because the key chemical connectivities are conserved across both oligomer lengths, the 1:1 models provide high-resolution spectral signatures of nitrile and ester chemistry without the added computational cost and spectral complexity of the longer backbone.

To reconstruct the experimental aged ATR-FTIR spectrum, the optimization routine included both the primary hydrolysis products, N1 through N6 and E1 through E2, and the transient intermediates identified in the SMD screen (**Figure 3.5**). Inclusion of these intermediates was necessary because the primary product basis alone was insufficient to reproduce the intensity and broadening of the carbonyl shoulder. The resulting dependence on amidine-like species, particularly N4, N5 and N10, supports the interpretation that the 5:12 environment promotes complex product distribution that cannot be captured adequately by simplified monomeric or purely alternating models.

### **Stoichiometric Constraints and Optimization Performance**

Relative band-area analysis provided target molar weights for the optimization. Based on the experimentally observed preferential consumption of nitrile groups, 56.7%, relative to esters, 31.9%, together with the 5:12 stoichiometry, the target hydrolysis product distribution was set to 81% nitrile-derived products and 19% ester-derived products hydrolysis products.

The robustness of this 5:12 scaffold was tested by comparing bounded and unbounded optimizations. The bounded L-BFGS-B optimization<sup>52, 53</sup> converged to a 91.5:8.5 (AN:BA) product ratio with a relative error of 10.86% and overall hydrolysis level of 45.3%. Removing the physical bounds improved the fit by only 0.8%, indicating that the 5:12-derived constraints do not artificially force the solution, but instead provide a chemically meaningful framework that remains consistent with the experimental spectral features. **Figure 3.6** shows the optimized hydrolysis product distribution and overall optimized fit.



**Figure 3.6.** Optimized spectral deconvolution of aged BA-AN adhesive. (a) Individual species contributions and their fitted relative weights overlaid with the experimental aged spectrum. (b) Overall optimized fit compared with the experimental aged and unaged ATR-FTIR spectra.

## Product Speciation and Mass Loss

Comparison of target and optimized product weights further supports the amidine-dominated speciation model (**Table 3.3**). The nitrile-branch products show close agreement between the target (Equation S3.2) and fitted values, with amidine contributions of 57.4% versus 57.2% and amide contributions of 23.6% versus 25.7%. By contrast, the ester-branch products are substantially underrepresented in the optimized fit relative to their target values. The carboxylic acid E1 decreases from a target weight of 19.0% to a fitted value of 7.1%, whereas butanol E2 decreases from 19.0% to only 1.4%. These deviations correspond to percent deviations from target of 0.3%, 8.9%, 62.6%, and 92.6% for amidine, amide, carboxylic acid, and butanol, respectively.

**Table 3.3.** Comparison of target and optimized weights for major nitrile- and ester- branch hydrolysis products classes obtained from multivariate deconvolution of the aged ATR-FTIR spectrum. Percent deviation from target is defined as  $100 \times |\text{Target} - \text{Predicted}|/\text{Target}$ .

| Product Category | Branch  | Ensemble Frequency ( <i>n</i> ) | Target Weight (%) | Predicted Weight (%) | Percent Deviation from Target (%) |
|------------------|---------|---------------------------------|-------------------|----------------------|-----------------------------------|
| Amidine (N4, N5) | Nitrile | 85                              | 57.4              | 57.2                 | 0.4                               |
| Amide (N1)       | Nitrile | 35                              | 23.6              | 25.7                 | 8.9                               |
| Acid (E1)        | Ester   | 34                              | 19.0              | 7.1                  | 62.6                              |
| Butanol (E2)     | Ester   | 34                              | 19.0              | 1.4                  | 92.6                              |

The severe deficit in butanol is consistent with diffusion of small volatile products out of the adhesive matrix, whereas the underrepresentation of E1 is more consistent with secondary interactions, such as hydrogen bonding and inhomogeneous broadening, that shift its spectral signature away from the isolated basis-state representation. In the crowded, 5:12 environment, carboxylic acid groups are likely to participate in stable hydrogen-bonding interactions with amidines, amides, and unreacted nitriles, and any residual water. These interactions broaden and shift the C=O stretching response away from the idealized 1:1 basis signature. Accordingly, the observed discrepancy likely reflects incorporation of acid groups into a broader hydrogen-bonded network rather than failure of acid formation.

Similarly, the apparent overuse of N10 and N1 species in the fitted spectrum likely reflects the use of 1:1-derived basis spectra to model the more heterogeneous broadening and sequence-induced frequency shifts apparent in the 2:3 simulations. The fitting routine therefore appears to use these species as high-resolution spectral proxies for a broader family of hydrolyzed local environments.

It is also informative to compare the predicted hydrolysis level, 45.3%, with the degradation level estimated from mechanical testing. Using the measured decline in peel strength as a proxy for interfacial and cohesive integrity yields a substantially higher effective degradation of 62.2% (**Table S3.1**). This disparity underscores the disproportionate effect of hydrolysis on the mechanical network relative to the global chemical conversion. Whereas the spectroscopic fit captures average functional group transformation, the larger decline in peel strength likely reflects additional structural damage associated with byproduct diffusion. As butanol and ammonia leave the matrix, a process consistent with the depressed C–H and the absence of ammonia in the optimized spectrum, they are expected to create microvoids and

disrupt local entanglement. Under this interpretation, amidine formation serves not merely as a marker for chemical hydrolysis, but as a signature of a broader structural collapse that outpaces the average extent of functional-group conversion.

Most notably, the absence of detectable nitrile-derived carboxylic acid product N6 in the optimized fit highlights the persistence of trapped amidine intermediates. These species prevent the system from progressing to a terminal fully acidic state and therefore have direct consequences for the evolving electronic behavior of the aged adhesive.

### 3.3.4 Electronic Structure and Dielectric Decay

To connect the observed chemical speciation with the experimentally measured decline in dielectric strength, we evaluated the electronic properties of the BA-AN hydrolysis products identified through the SMD simulations. Two primary descriptors were used to characterize dielectric stability in these polymer matrices: the electronic band gap,  $E_g$ , which sets the threshold for electronic excitation and charge leakage; and the transition dipole moment (TDM), which reflects the strength of molecular coupling to an oscillating electric field.

Electronic properties for the 1:1 and 2:3 baseline systems, together with each unique conformer of products N1 through N10 and E1 through E5, were extracted from the DFT frequency calculations. Because direct calculation of the pristine 5:12 was not computationally practical, its properties were estimated by linear extrapolation of the 1:1 and 2:3 conformer-ensembles averages using the same coefficient framework employed for the synthetic 5:12 spectrum:  $(\text{Value}_{5:12} = -1.06(\text{Value}_{1:1}) + 2.06(\text{Value}_{2:3}))$ . Because these pristine 5:12 electronic descriptors were obtained by extrapolation from the 1:1 and 2:3 model systems, they should be interpreted as composition-guided estimates rather than direct predictions for an

explicitly simulated 5:12 ensemble. Accordingly, the absolute values are best viewed as approximate, while the relative trends, particularly the lower projected band gap of the nitrile-rich architecture and the increase in TDM upon aging, provide the more robust basis for mechanistic interpretation

The electronic descriptors summarized in **Table 3.4** clarify why nitrile hydrolysis is disproportionately damaging to dielectric performance. Relative to the 1:1 oligomer, the pristine 5:12 architecture already exhibits a lower band gap, 6.77 versus 7.67 eV, creating an intrinsically more vulnerable electronic structure. At the same time, its average TDM is lower, 3.34 versus 3.61, consistent with dipole quenching in the nitrile-rich sequence environment. Among the hydrolysis products, the amidine species are particularly destabilizing (**Figure 3.7**). N4 and N5 exhibit band gaps of 6.30 and 5.83 eV, respectively, together with elevated TDM values of 4.42 and 4.70. By contrast, ester-derived products such as E1 and E2 retain wider bands gaps, 7.79 and 9.31 eV, and comparatively moderate TDM values.

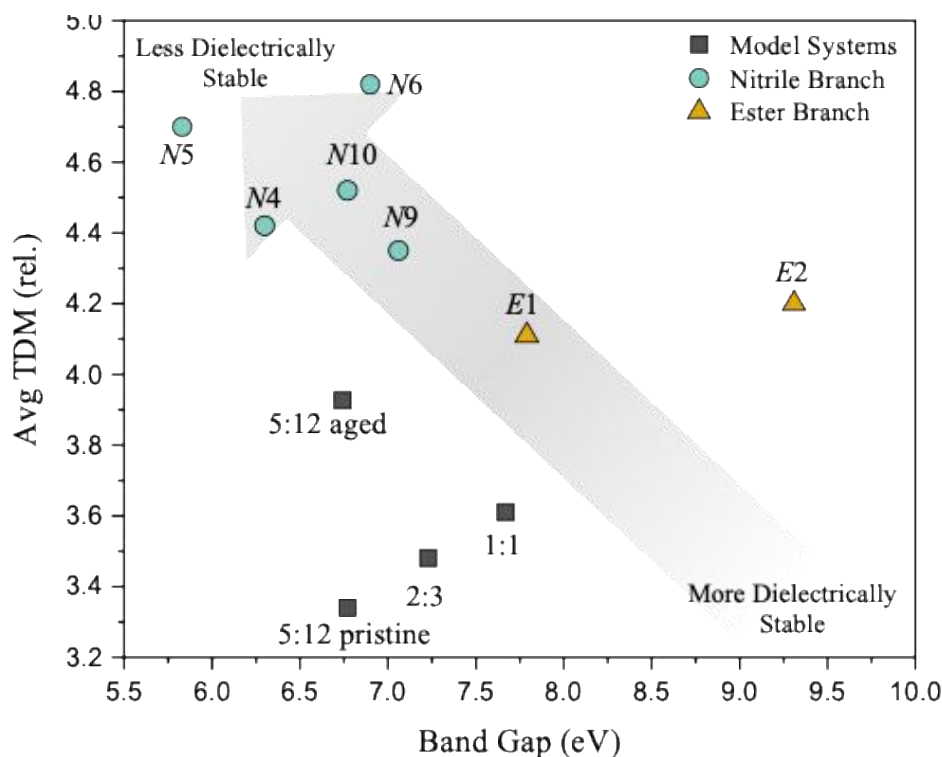
**Table 3.4.** Conformer ensemble-averaged electronic properties of BA-AN oligomers and hydrolysis products, including band gap ( $E_g$ ) and average transition dipole moment (TDM) obtained from DFT calculations.

| Hydrolysis Products  | Band Gap (eV) | Average TDM (rel.) |
|----------------------|---------------|--------------------|
| N1 (amide)           | 6.90          | 4.82               |
| N2 (carboxylic acid) | 7.72          | 4.33               |
| N3 (ammonia)         | 9.49          | 4.26               |
| N4 (amidine)         | 6.30          | 4.42               |
| N5 (amidine)         | 5.83          | 4.70               |
| N8                   | 7.08          | 4.92               |
| N9                   | 7.06          | 4.35               |
| N10                  | 6.77          | 4.52               |
| E1 (carboxylic acid) | 7.79          | 4.11               |
| E2 (butanol)         | 9.31          | 4.20               |
| E4                   | 7.75          | 3.80               |
| E5                   | 8.21          | 3.93               |
| Oligomers (BA:AN)    | Band Gap (eV) | Average TDM (rel.) |
| 1:1                  | 7.67          | 3.61               |
| 2:3                  | 7.23          | 3.48               |
| 5:12 (pristine)      | 6.77          | 3.34               |
| 5:12 (aged)          | 6.74          | 3.93               |

Aging therefore introduces products with substantially different electronic character. The reduced band gaps lower the energetic threshold for charge hopping under high electric field, thereby increasing the likelihood of dielectric breakdown. Simultaneously, elevated TDM values create localized regions of enhanced polarizability, which increase dipolar dielectric loss and promote field-driven conversion of electrical energy into heat. The coupled changes provide a molecular explanation for why nitrile hydrolysis, rather than ester hydrolysis, dominates the observed dielectric decay in BA-AN-based cable assemblies.

The onset of hydrolysis therefore destabilizes the dielectric state of the 5:12 architecture in a highly specific way. Although complete conversion of nitrile sites to carboxylic acids might be expected to occur thermodynamically, the combined SMD energetics, multivariate deconvolution, and electronic-structure analysis indicate that the pathway is kinetically trapped at the amidine stage. If hydrolysis were to proceed fully to acid species, which generally exhibit larger band gaps and lower average TDM values, then partial recovery of the dielectric properties with further reaction progression might be expected. Instead, the pathway arrests at a more electronically dissipative intermediate state.

To estimate the dielectric properties of the aged 5:12 system, the pristine 5:12 baseline and the weighted average properties of the optimized product ensemble were combined using the fitted hydrolysis,  $h = 45.3\%$ :  $\text{Value}_{5:12,\text{aged}} = (1 - h)\text{Value}_{5:12,\text{pristine}} + h(\sum_{i=1}^n w_i \text{Value}_i)$ , where  $w_i$  is the optimized contribution of species  $i$ . The calculated band gap of the aged system decreases only slightly from 6.77 to 6.74 eV, a reduction of 0.44%. In contrast, the average TDM increases from 3.34 to 3.93, corresponding to a 17.67% increase. The resulting combination of a reduced transport barrier and enhanced field coupling generates a more dissipative dielectric environment.



**Figure 3.7.** Electronic descriptors of pristine and aged BA-AN model systems. Conformer ensemble-averaged band gap and transition dipole moment values are shown for the 1:1, 2:3, pristine 5:12 and aged 5:12 systems, together with the representative hydrolysis products derived from the optimized spectral fit.

To connect these molecular descriptors with the observed breakdown voltage decay, we define a system-specific electronic quality factor,  $\chi = E_g/\text{TDM}$ . This quantity is introduced here as a heuristic composite descriptor that balances two physically relevant trends: larger band gaps generally correspond to greater resistance to electronic excitation and charge transport in insulating materials, whereas larger dipole-coupling amplitudes indicate stronger interaction with an external oscillating field, and therefore, greater susceptibility to polarization-mediated energy dissipation.<sup>63–66</sup> Although  $\chi$  is not intended as a universal dielectric figure of merit, it provides a physically motivated internal metric for comparing dielectric vulnerability across the chemically

evolving BA-AN landscape. The relative decline in this quality factor,  $1 - \chi_{\text{aged}}/\chi_{\text{pristine}}$ , predicts a 16.4% reduction in dielectric strength. This value closely matches the experimentally measured 15.4% decline in breakdown strength (**Table S3.1**). This correspondence supports the interpretation that amplification of the transition dipole moment, rather than band gap narrowing alone, is the dominant molecular contributor to dielectric decay in the aged adhesive.

The contrast between the 45.3% spectroscopic hydrolysis level and the 16.4% decline in the electronic quality factor also clarifies the hierarchical nature of degradation in this material. Mechanical performance is more severely affected than dielectric performance, consistent with experimental observations showing approximately 62% loss in cohesion, but only 15.4% loss in breakdown strength. These differences indicate that hydrolysis has a broader impact on the mechanical network than on the average dielectric state, whereas dielectric failure is governed more specifically by the emergence of localized electronically active intermediates. Within this framework, the 5:12 architecture acts as a dual bottleneck, promoting both mechanical collapse through structural reorganization and dielectric decay through high-TDM amidine clusters.

### 3.4 Conclusion

This study supports the conclusion that the sequence-specific 5:12 BA-AN architecture plays an important role in governing chemical speciation and macroscopic failure in acrylate-nitrile adhesives. By combining ensemble SMD simulations with multivariate spectral deconvolution, we find that the nitrile-rich local environment is consistent with orthogonal nitrile dipole arrangements and favors formation of cyclic amidine-like products over terminal hydrolysis products. The resulting aged state is associated with substantial chemical transformation, with the extent of hydrolysis falling between the experimentally observed decay in dielectric strength and the larger loss in mechanical adhesion. This hierarchy indicates that

chemical aging is expressed unevenly across properties, with mechanical cohesion showing greater sensitivity to network-level disruption than dielectric breakdown.

The dielectric results provide especially strong support for the proposed mechanistic picture. Although the pristine 5:12 architecture is already less dielectrically stable than the 1:1 alternating baseline, aging produces only a modest additional decrease in band gap while substantially increasing the intensity-derived transition dipole moment. The close agreement between the decline in the calculated electronic quality factor,  $\chi = E_g/\text{TDM}$ , and the experimentally observed reduction in breakdown strength indicates that amplification of dipolar coupling in the aged matrix is a key contributor to dielectric decay. Within this framework, kinetically persistent amidine-rich states emerge as the most consequential degradation products because they combine sequence-selective formation with electronically dissipative character.

A limitation of the present analysis is that the key spectral and electronic descriptors for the 5:12 BA-AN architecture were obtained by extrapolation from smaller explicitly modeled systems, rather than from direct calculations on an explicit 5:12 oligomer ensemble. Accordingly, the quantitative values associated with the 5:12 state should be interpreted as model-based estimates, while the mechanistic trends inferred from them, specifically the importance of sequence architecture, nitrile-rich local environments, and kinetically persistent amidine-rich states, remain the more robust conclusion. Overall, these results provide a self-consistent framework linking local polymer architecture to chemical aging, dielectric evolution, and mechanical degradation in BA-AN adhesive systems.

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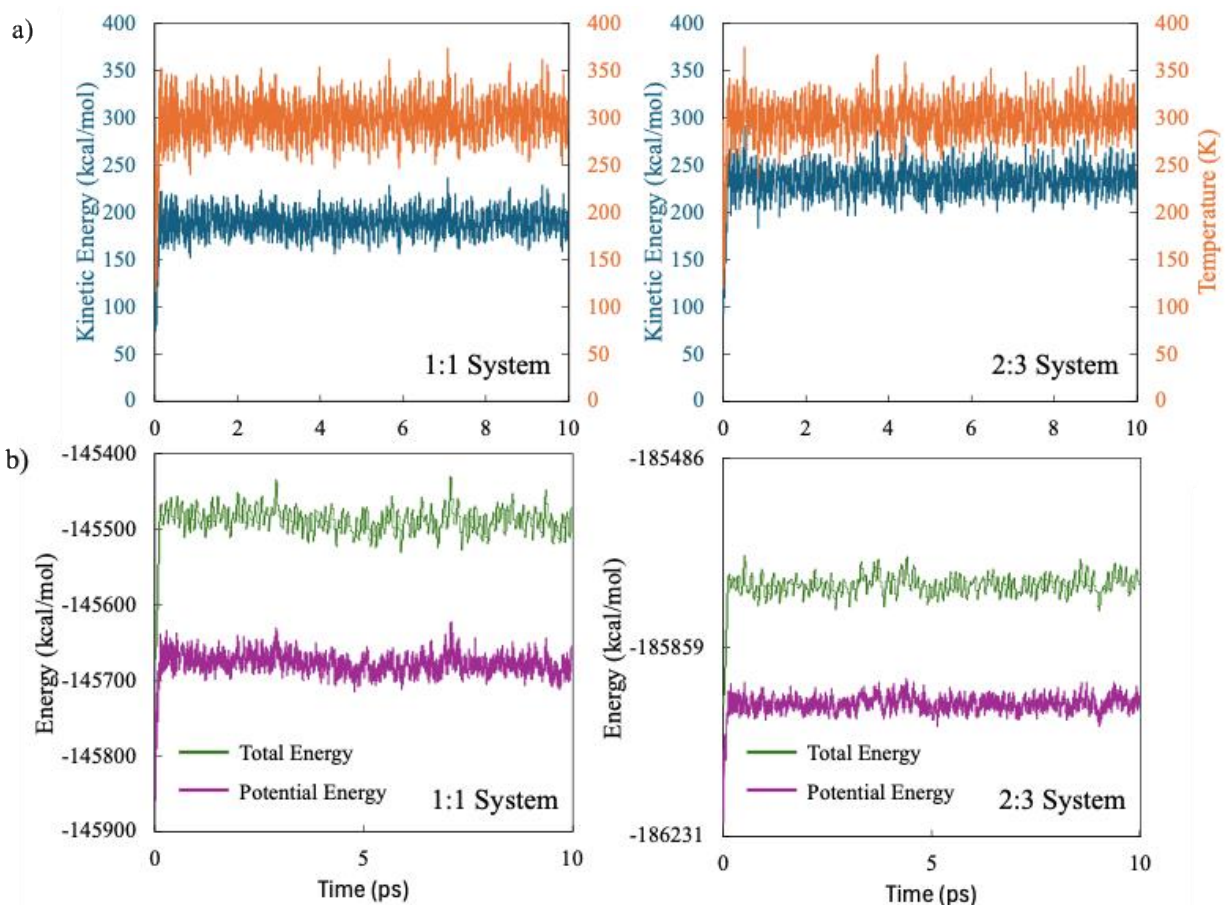
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### 3.5 Supplementary Data



**Figure S3.1.** Time evolution of (a) kinetic energy and temperature and (b) total and potential energy for the 1:1 system (left) and 2:3 system (right) during NVT equilibration. Both systems were equilibrated for 10 ps at 300 K. The stabilization in potential energy profiles indicates that the system reached stable equilibrium state over the simulation interval.

To estimate spectral and electronic properties for the 5:12 BA:AN architecture, linear extrapolation coefficients were derived from the explicitly modeled 1:1 and 2:3 systems using their respective nitrile and ester carbonyl fractions. The target 5:12 system contains a nitrile fraction of  $12/17 = 0.706$  and an ester carbonyl fraction of  $5/17 = 0.294$ . The modeled 1:1 system contains equal nitrile and carbonyl fractions of 0.5 and 0.5, whereas the 2:3 system contains nitrile and carbonyl fractions of 0.6 and 0.4, respectively. The extrapolation coefficients,  $a$  and  $b$ , were obtained by solving

$$0.5a + 0.6b = 0.706$$

$$0.5a + 0.4b = 0.294$$

which yields

$$a = -1.06, \quad b = 2.06.$$

The resulting extrapolated property is therefore given by

$$\text{Abs}_{5:12} = a(\text{Abs}_{1:1}) + b(\text{Abs}_{2:3}).$$

Because the target 5:12 composition lies outside the range spanned by the explicitly modeled systems, these coefficients represent extrapolation coefficients rather than physical mixture weights.

**Equation S3.1.** Derivation of the coefficients used for linear extrapolation of spectral and electronic properties of the 5:12 system from the computed ensemble-averaged values of the 1:1 and 2:3 systems.

The relative contribution of amidine and amide species to the overall hydrolysis profile were estimated by combining the experimentally derived nitrile-associated degradation fraction with the SMD ensemble branching frequencies for nitrile-path conversion. Experimental analysis assigned 81.01% of the total degradation to nitrile-derived products and 18.99% to ester-derived products. Within the nitrile branch, the SMD ensemble yielded 85 amidine-forming events and 35 amide-forming events, giving a total of 120 nitrile-branch conversion events. The corresponding branching fractions are

$$f_{\text{amidine}} = \frac{85}{120} = 0.7083$$

$$f_{\text{amide}} = \frac{35}{120} = 0.2917$$

Applying these branching fractions to the experimentally derived nitrile contribution gives

$$\% \text{ amidine} = 0.708 \times 81.01\% = 57.38\%$$

$$\% \text{ amide} = 0.2917 \times 81.01\% = 23.63\%$$

**Equation S3.2.** Estimation of amidine and amide contributions to the overall hydrolysis profile based on the experimentally derived nitrile-associated degradation fraction and the SMD ensemble branching frequencies for nitrile-path conversion.

**Table S3.1.** Experimental relative peel and dielectric breakdown values for unaged and aged flat-flex cables. The accelerated aging environment was 70 °C and 70% relative humidity for 140 days.

| Condition                | Unaged            | Aged              | Percent Decrease (%) |
|--------------------------|-------------------|-------------------|----------------------|
| Peel Strength (rel.)     | $1.00 \pm 0.01$   | $0.38 \pm 0.03$   | $62 \pm 3$           |
| Breakdown Voltage (rel.) | $1.000 \pm 0.002$ | $0.845 \pm 0.003$ | $15.5 \pm 0.3$       |

## Chapter 4

### 4 Development of a ReaxFF Reactive Force Field for Thiol-Ene Systems: Identifying the Steric Origins of Low Crosslink Density

*My contribution to this work included ReaxFF force field development, implementation, and writing.*

#### Abstract

Volumetric additive manufacturing (VAM) enables rapid, single-step fabrication but requires photoresins with tunable mechanical performance. In thiol-ene systems, the link between molecular architecture and network formation remains unclear, particularly for the triethylene glycol diallyl ether (TEGDAE) and tris[2(3-mercaptopropionyloxy)ethyl]isocyanurate (TME-ICN) resin that yields an anomalously soft, highly extensible material. Here, we develop and optimize a C/H/O/N/S ReaxFF reactive force field against DFT reference data, including geometries, partial charges, bond-energy scans, and intrinsic reaction coordinates for propagation and chain-transfer steps. System-level reaction molecular dynamics simulations, combined with radial distribution functions and coordination-number analysis, reveal that dense packing and self-association create a steric, diffusion-limited environment that spatially separates thiol and vinyl functionalities. Despite an energetically accessible chain-transfer step, thiyl radical clustering promotes barrierless radical-radical termination, arresting polymerization and limiting crosslink density. These molecular-scale constraints provide a mechanistic explanation for the experimentally observed low modulus and high failure strain and establish a workflow for using reactive force fields to screen monomer architectures for high-density VAM photoresins.

## 4.1 Introduction

Volumetric additive manufacturing (VAM)<sup>1</sup> has emerged as a transformative 3D fabrication technology, enabling rapid, single-step construction that eliminates the layering artifacts common in traditional point-by-point and layer-by-layer approaches. While VAM has been successfully demonstrated with soft acrylate-based hydrogels,<sup>2-4</sup> these materials often exhibit brittle, glassy behavior. Consequently, there is a critical need for photoresins with tunable mechanical properties to expand the functional utility of VAM-printed parts.

Thiol-ene chemistries are attractive material candidates for VAM due to their rapid kinetics and formation of highly uniform polymer networks. However, the relationship between resin microstructure and macroscopic mechanical performance remains poorly understood.<sup>5, 6</sup> For example, a recent study using triethylene glycol diallyl ether (TEGDAE) and tris[2(3-mercaptopropionyloxy)ethyl] isocyanurate (TME-ICN) produced an unexpectedly soft material (elastic modulus  $E = 0.12$  MPa) with high failure strain (293%) and low glass transition temperature ( $T_g = -56$  °C).<sup>7</sup> These properties suggest a substantially lower effective crosslink density than stoichiometry alone would predict.

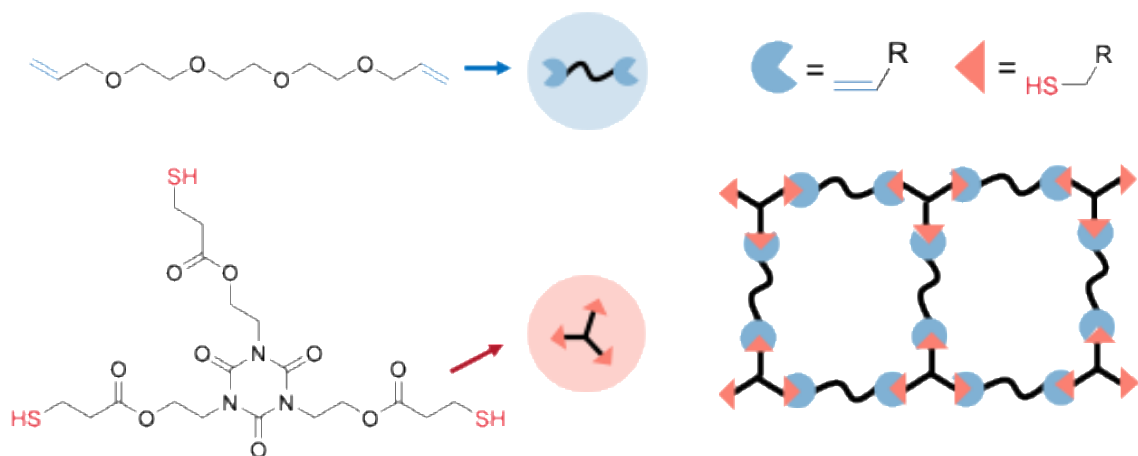
To rationalize the formation of this loose network, we employ reactive molecular dynamics (RMD) using the ReaxFF potential.<sup>8, 9</sup> Unlike classical molecular dynamics, ReaxFF utilizes a dynamic bond-order scheme that permits simulation of bond breaking and formation, making it well suited for studying polymerization kinetics. Here, we aim to identify the molecular-scale bottlenecks, particularly the competition between propagation and chain transfer, that govern the formation of the TEGDAE/TME-ICN network.

## 4.2 Methods

### 4.2.1 Model Systems

The system comprised of a stoichiometric 1:1 molar ratio of triethylene glycol diallyl ether (TEGDAE) and tris[2(3-mercaptopropionyloxy)ethyl] isocyanurate (TME-ICN).

**Figure 4.1** depicts the molecular structures and the idealized network schematic. Condensed-phase simulations were performed in a cubic periodic box ( $L = 4$  nm) containing approximately 6,300 atoms.



**Figure 4.1.** Schematics of monomers with thiol and ene functionality and the corresponding idealized molecular network structure. The thiol tri-functional monomer is tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (TME-ICN) and the ene bi-functional monomer is triethylene glycol diallyl ether (TEGDAE). Adapted from Cook, et al.<sup>7</sup>

### 4.2.2 The ReaxFF Potential

The total ReaxFF energy is expressed as:

$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{angle}} + E_{\text{lone-pair}} + E_{\text{dihedral}} + E_{\text{electrostatic}} + E_{\text{vdW}} \quad (4.2.1)$$

where the right-hand terms represent bond-order dependent contributions (bond energies, atom over- and undercoordination corrections, valence angle energies, lone-pair energies, torsion angle energies) and nonbonding contributions (van der Waals energy and Coulomb interactions).<sup>8, 9</sup>

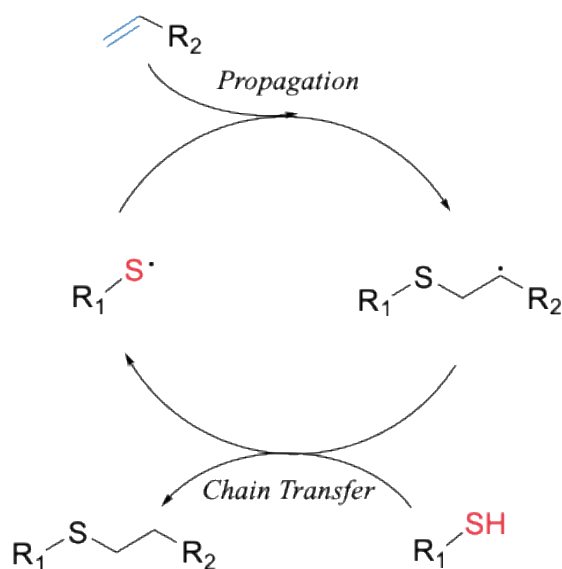
The ReaxFF force field used as a starting point for optimization was the C/H/O/N/S/Si/Na/Al parameterization.<sup>10</sup>

#### 4.2.3 Generating Training Set Data

ReaxFF parameters were fit to a training set comprising quantum mechanical data. Gas-phase structures and energies were obtained from density functional theory (DFT) calculations using Becke, 3-parameter, Lee–Yang–Parr (B3LYP) functional<sup>11, 12</sup> with the 6-311G(d,p) basis set<sup>13, 14</sup> in Gaussian16.<sup>15</sup> Mulliken charge distributions<sup>16</sup> were computed using the 6-31G(d,p) basis set,<sup>17</sup> which also improves consistency with charge equilibrium used in ReaxFF.<sup>8</sup>

Reaction energies were computed for the propagation and chain transfer steps shown in **Figure 4.2**. For each reaction, a transition state was located, and the minimum-energy path was evaluated using intrinsic reaction coordinate (IRC) calculations. Bond energy calculations were performed across multiple spin states (singlet, doublet, triplet or quartet), and the lowest-energy spin state at each point along the coordinate was used for training.

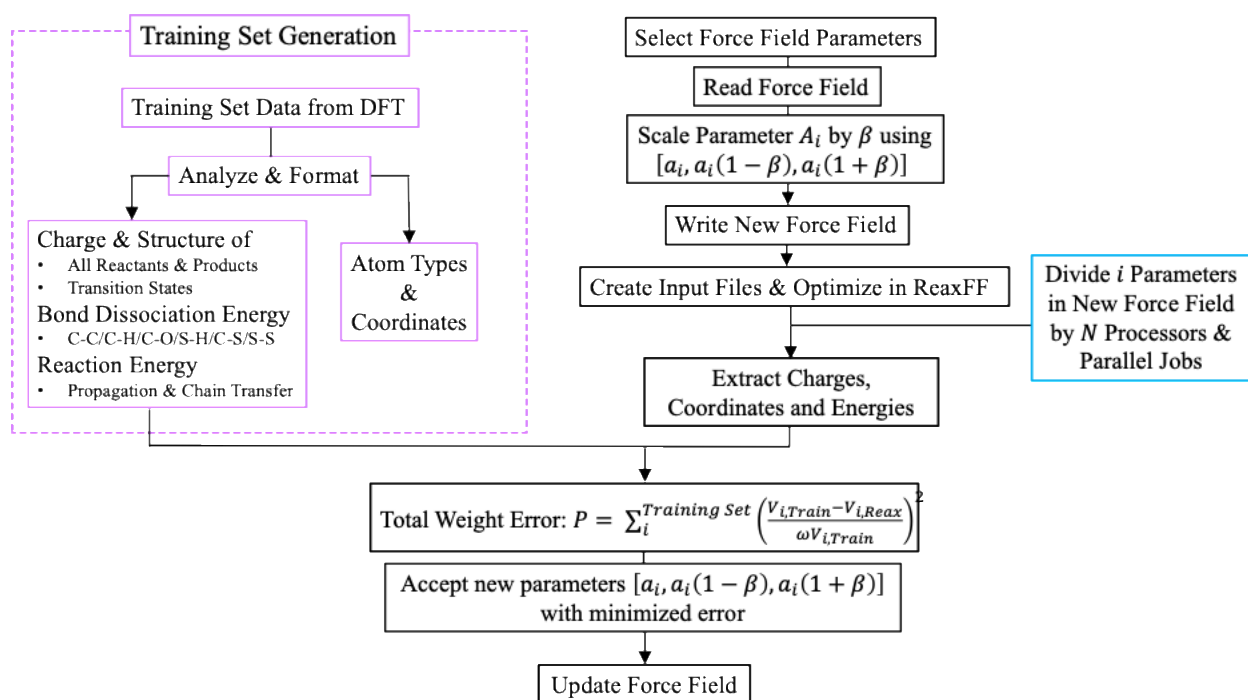
The training set included 338 angles, 268 partial charges, 221 bond lengths, 8 potential energy scans (PES), and 2 IRC scans for a total of 1106 data points.



**Figure 4.2.** General thiol-ene step-growth polymerization mechanism.<sup>18</sup>

#### 4.2.4 Force Field Optimization

Gas phase atomic coordinates from DFT ground-state and transition-state structures were used to generate Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)<sup>19, 20</sup> input files for gas-phase optimization of molecule geometries, partial charges, and energies. The optimization approach of Deetz, et al.<sup>21</sup> was used to train force field parameters toward DFT values. This procedure uses a parallel local search algorithm in which each processor explores a subset of parameters and all parameters are updated at the end of each iteration. **Figure 4.3** summarizes the automated portion of this workflow.



**Figure 4.3.** Flow chart of the automated reactive force field optimization. Each parameter  $a_i$  is scaled by a factor  $\beta$  to generate  $[a_i, a_i(1 - \beta), a_i(1 + \beta)]$ . Parameters are divided across  $N$  processors and evaluated in parallel. Adapted from Huang, et. al.<sup>22</sup>

Each training-set property is assigned a weight that controls its influence during optimization.

Predicted values are compared to DFT targets using a penalty function:

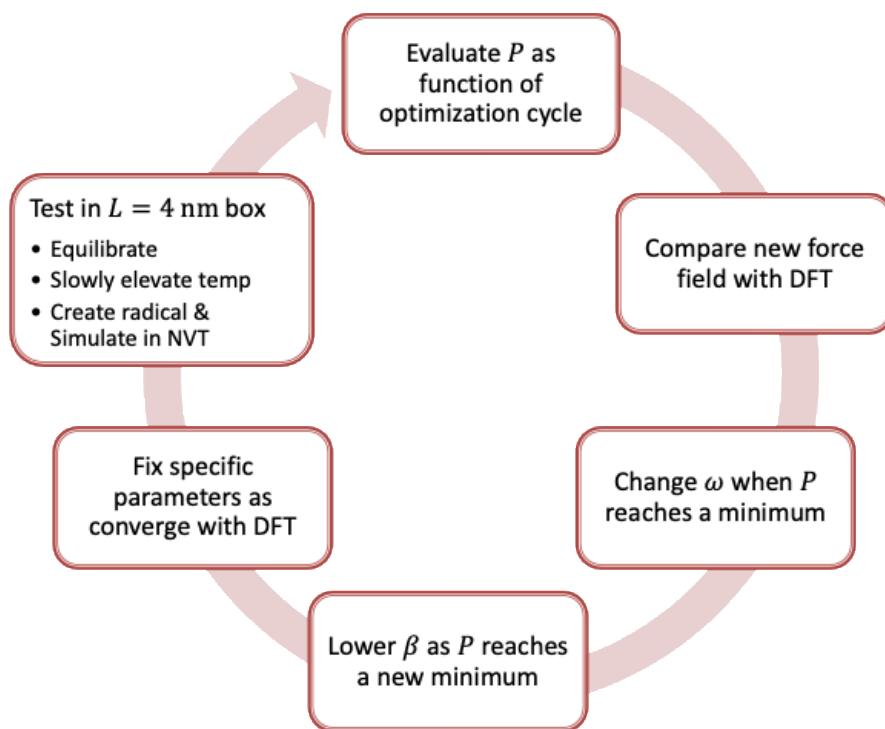
$$P = \sum_i^{training\ set} \left( \frac{V_{i,train} - V_{i,react}}{\omega V_{i,train}} \right)^2 \quad (4.3.1)$$

where  $V_{i,train}$  is a training-set property,  $V_{i,react}$  is the corresponding ReaxFF prediction (for example, bond energies), and  $\omega$  is the inverse weight applied to that property.

Although part of the optimization was automated, the procedure required user monitoring, interpretation, and iterative tuning. Performance was tracked across five property classes: angles, bond lengths, partial charges, bond energies and reaction energies. The penalty

function was evaluated globally and by property class to ensure errors were reduced without overfitting. The inverse weights ( $\omega^{-1}$ ) and scaling factor ( $\beta$ ) were adjusted when errors oscillated around local minima. When the error for a given property was low (typically, below 5%), the parameters associated with that property were often fixed. However, because the energetic terms are interdependent, some properties could drift even with parameters fixed. Once further adjustments no longer improved performance, the force field was tested at the system level.

**Figure 4.4** shows the user-guided component of the workflow.



**Figure 4.4.** Flow chart of the user-guided force field optimization workflow.

The developed C/H/O/N/S ReaxFF force field was optimized from the C/H/O/N/S/Si/Na/Al force field.<sup>10</sup> **Table 1** lists the parameters selected for optimization and the justification for their inclusion.

**Table 1.** Selected ReaxFF parameters optimized in this work and justification for their inclusion.

| Parameter Class | Which Parameters Optimized                                                                                       | Reason for Inclusion                                                          |
|-----------------|------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Atomic          | Covalent bond radii, van der Waals radii, dissociation energy, van der Waals shielding parameters for C, H, O, S | Size and energetics of atoms for bonding prediction & molecular structure     |
| Valence bond    | Bond order, radii, bond dissociation energy parameters for C-C, C-H, C-O, S-H, C-S, S-S                          | Reaction pathways and energetics for bonding prediction & molecular structure |
| Valence Angle   | All parameters for C-C-C, H-C-H, C-C-H, C-C-O, C-O-C, C-S-H, C-C-S, C-S-C, C-S-S                                 | Geometry prediction for molecular structure                                   |
| Van der Waals   | Van der Waals radii, dissociation energy and nucleus screening parameters for all combinations of atom types     | Chemical bonding and phase behavior                                           |
| Off-diagonal    | Van der Waals energy, radii, sigma bond length, pi bond length for all combinations of atoms                     | Chemical bonding and phase behavior                                           |

#### 4.2.5 Simulation Protocol

To reduce unwanted reactions from non-equilibrated initial structures, all systems were first equilibrated using a non-reactive, Optimized Potential for Liquid Simulations/All-Atom (OPLS/AA)<sup>23</sup> force field in the isothermal-isobaric NPT ensemble at 300 K and 1 atm to represent laboratory conditions. A Nosé-Hoover thermostat<sup>24, 25</sup> and barostat<sup>26</sup> was used with coupling parameters respectively set to 100 and 1000 times the timestep, respectively.

Equilibrated systems were then re-equilibrated with the optimized C/H/O/N/S reactive force field prior to production runs. Systems were equilibrated in the canonical NVT ensemble for 50 ps with a 0.1 fs timestep to reach the target temperature, followed by NPT equilibration at 1 atm.

For production runs, thiyl radicals introduced by removing hydrogen atoms, and simulations were run the NVT ensemble at 800 K with a Nosé-Hoover thermostat with a 0.1 fs timestep to observe reactions. LAMMPS<sup>19, 20</sup> was used for all simulations, and snapshots and trajectories were analyzed in Visual Molecular Dynamics (VMD).<sup>27 19</sup>

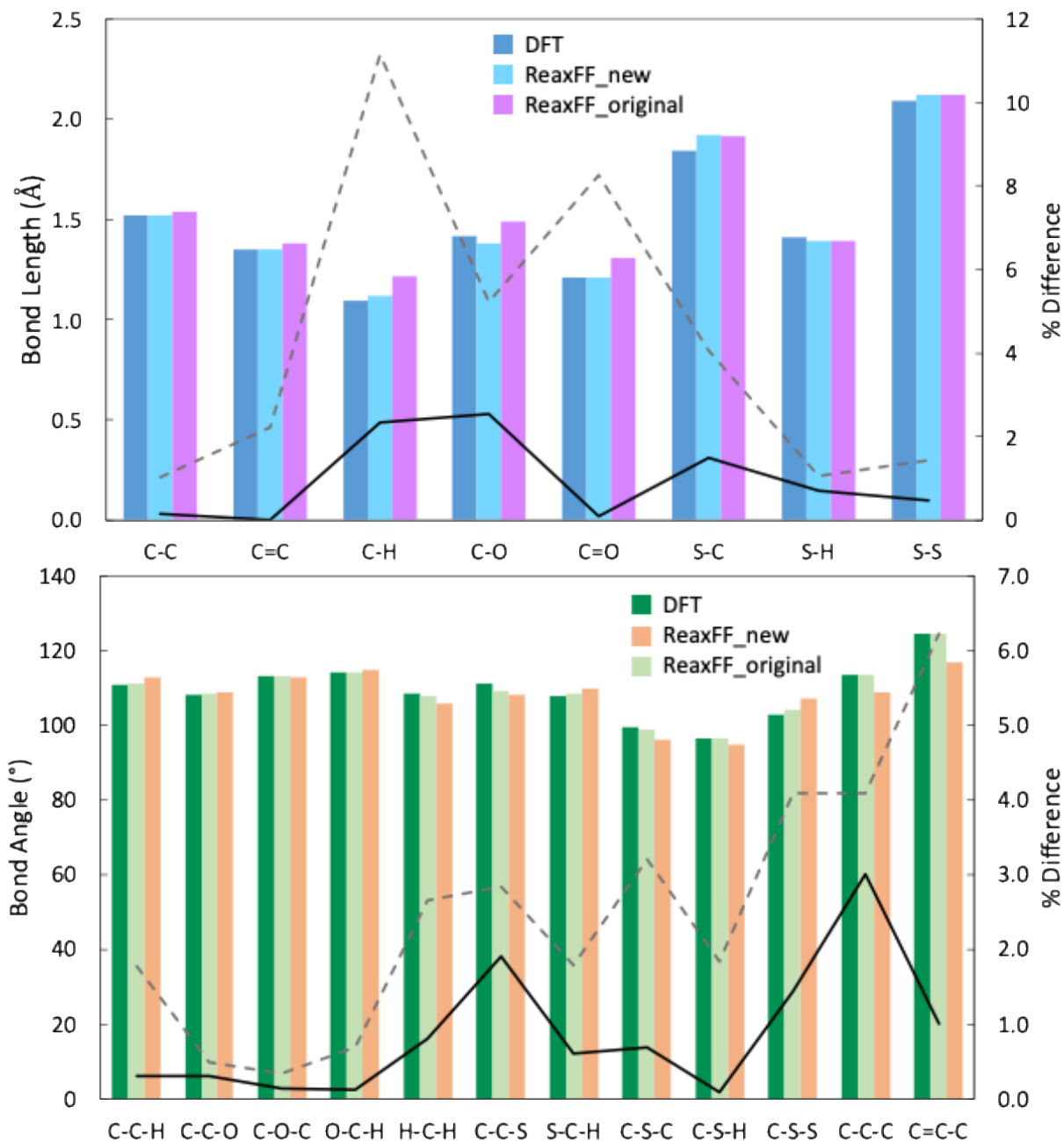
#### 4.2.6 Structural Analysis

To evaluate reactive-site accessibility, radial distribution functions (RDFs;  $g(r)$ ) and cumulative coordination numbers ( $N_c$ ) were calculated for sulfur to vinyl carbon (S–C<sub>vinyl</sub>), carbon to carbon (C–C), vinyl carbon to vinyl carbon (C<sub>vinyl</sub>–C<sub>vinyl</sub>), and sulfur to sulfur (S–S) pairs. Data were time-averaged over frames from production trajectories. Partial RDFs were extracted via weighted subtraction of the total system  $g(r)$  to isolate local environments around reactive centers.

### 4.3 Results and Discussion

#### 4.3.1 Force Field Development

The optimized C/H/O/N/S reactive force field agrees well with DFT for bond lengths and angles. The original C/H/O/N/S/Si/Na/Al force field produced bond angles and lengths that differed from DFT by up to 6% and 11%, respectively. The optimized force field reduced these differences to 3% for bond angles and 2% for bond lengths (**Figure 4.5**), indicating improved reproduction of molecular geometries and charges for TEGDAE, TME-ICN, associated radicals, and transition-state molecules.



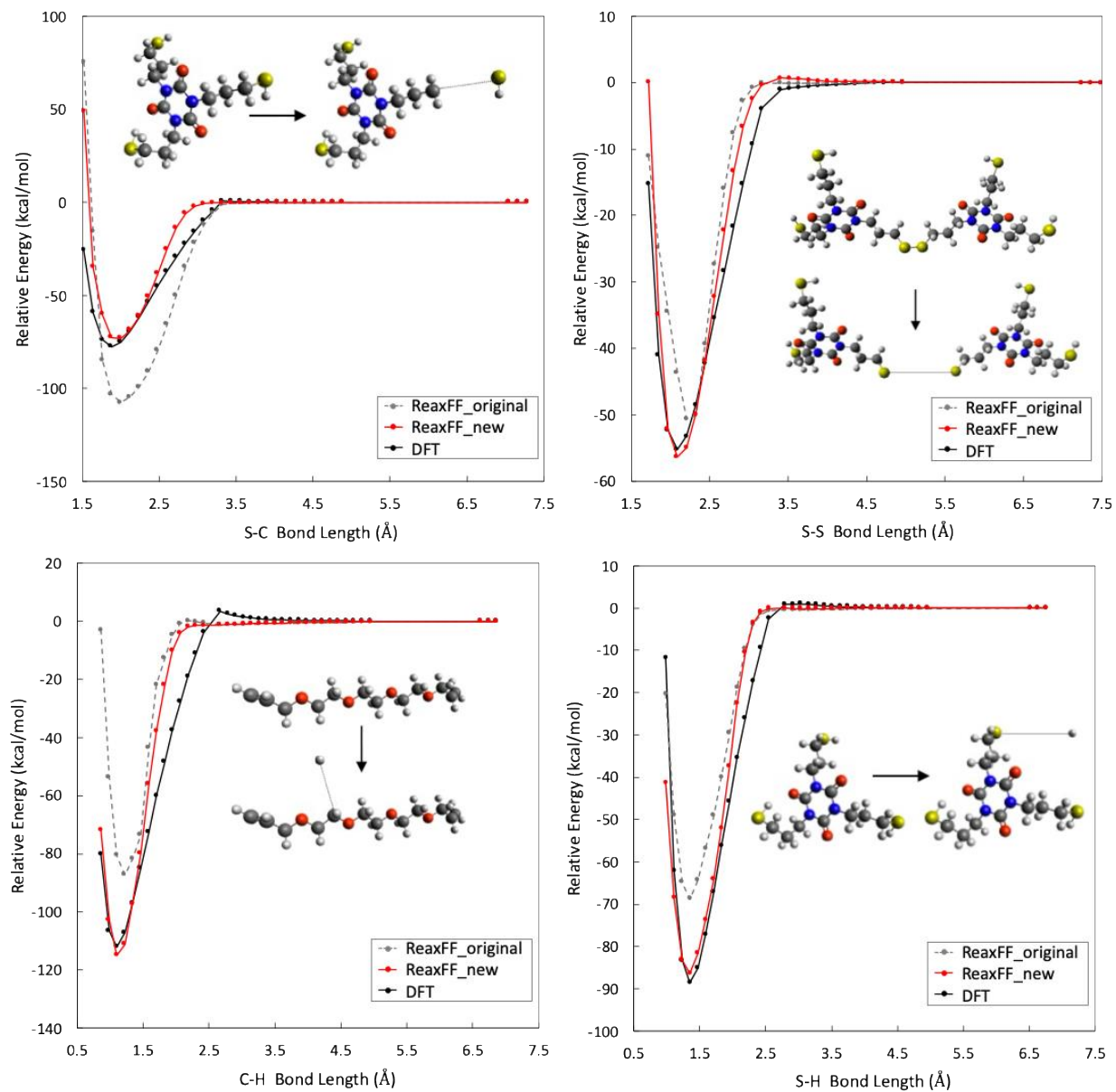
**Figure 4.5.** Average bonds lengths (top) and angles (bottom) from DFT, the original C/H/O/N/S/Si/Na/Al force field (ReaxFF\_original), and the optimized C/H/O/N/S force field (ReaxFF\_new). Lines show percent differences relative to DFT for ReaxFF\_original (dotted), and ReaxFF\_new (solid).

The optimized force field also improved agreement for bond energies relative to the original parameterization. The largest improvements were observed for S–C and S–H bond energies, where percent differences decreased from 39% and 22% to 6% and 2%, respectively. **Table 4.2** summarizes percent differences for relevant bond energies, and **Figure 4.6a, b** shows associated bond energy scans. While the percent error in the S–S bond energy increased slightly relative to the original force field, the equilibrium S–S bond length improved substantially, decreasing from 2.21 Å to 2.09 Å and matching the DFT value.

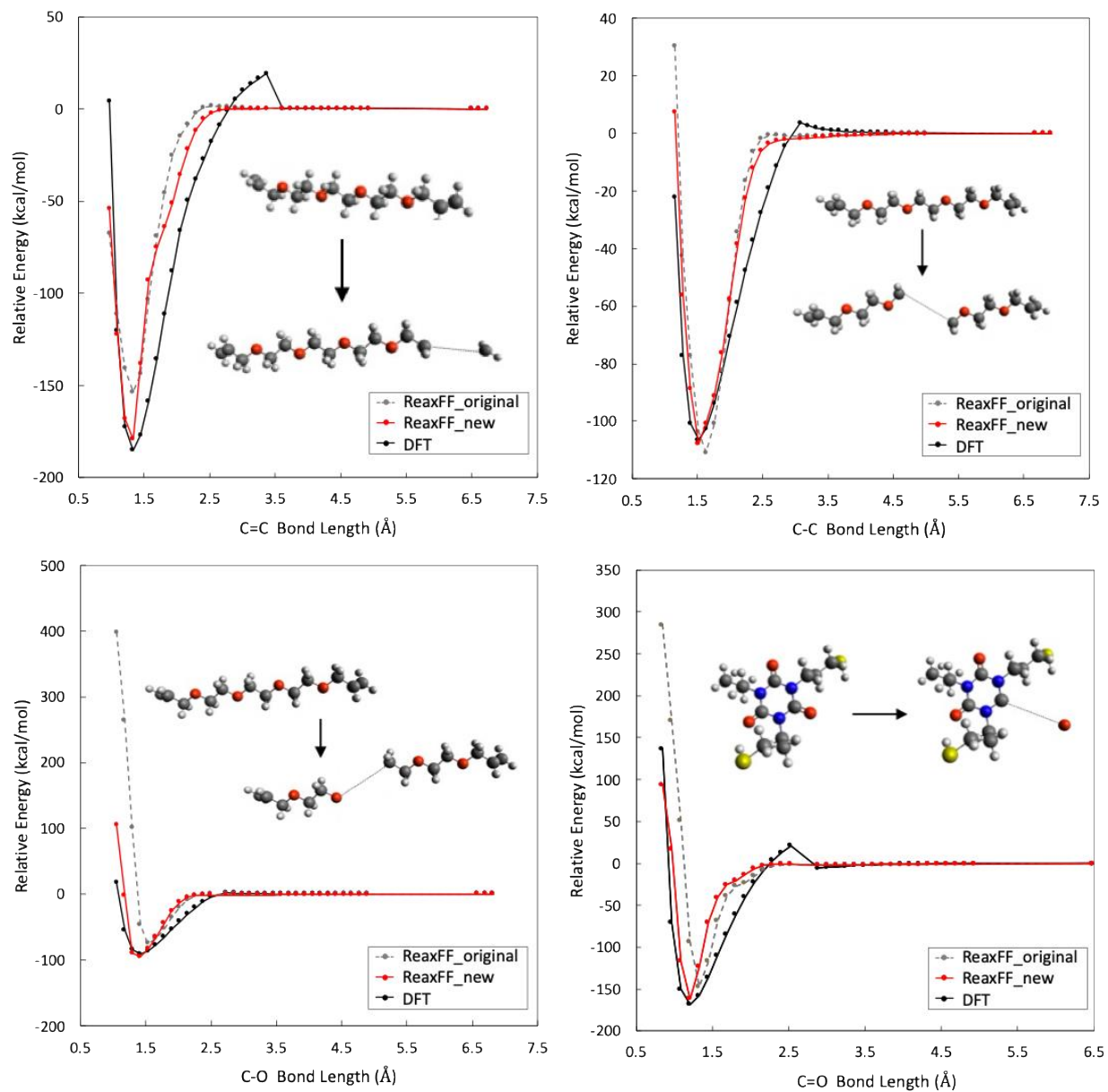
**Table 4.2.** Percent differences in selected bond energies for ReaxFF\_original and ReaxFF\_new relative to DFT.

| Model           | S-C | S-H | S-S | C=O | C-H | C-C | C-O | C=C |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| ReaxFF_original | 39  | 22  | 5   | 13  | 22  | 8   | 18  | 17  |
| ReaxFF_new      | 6   | 2   | 6   | 4   | 3   | 5   | 5   | 3   |

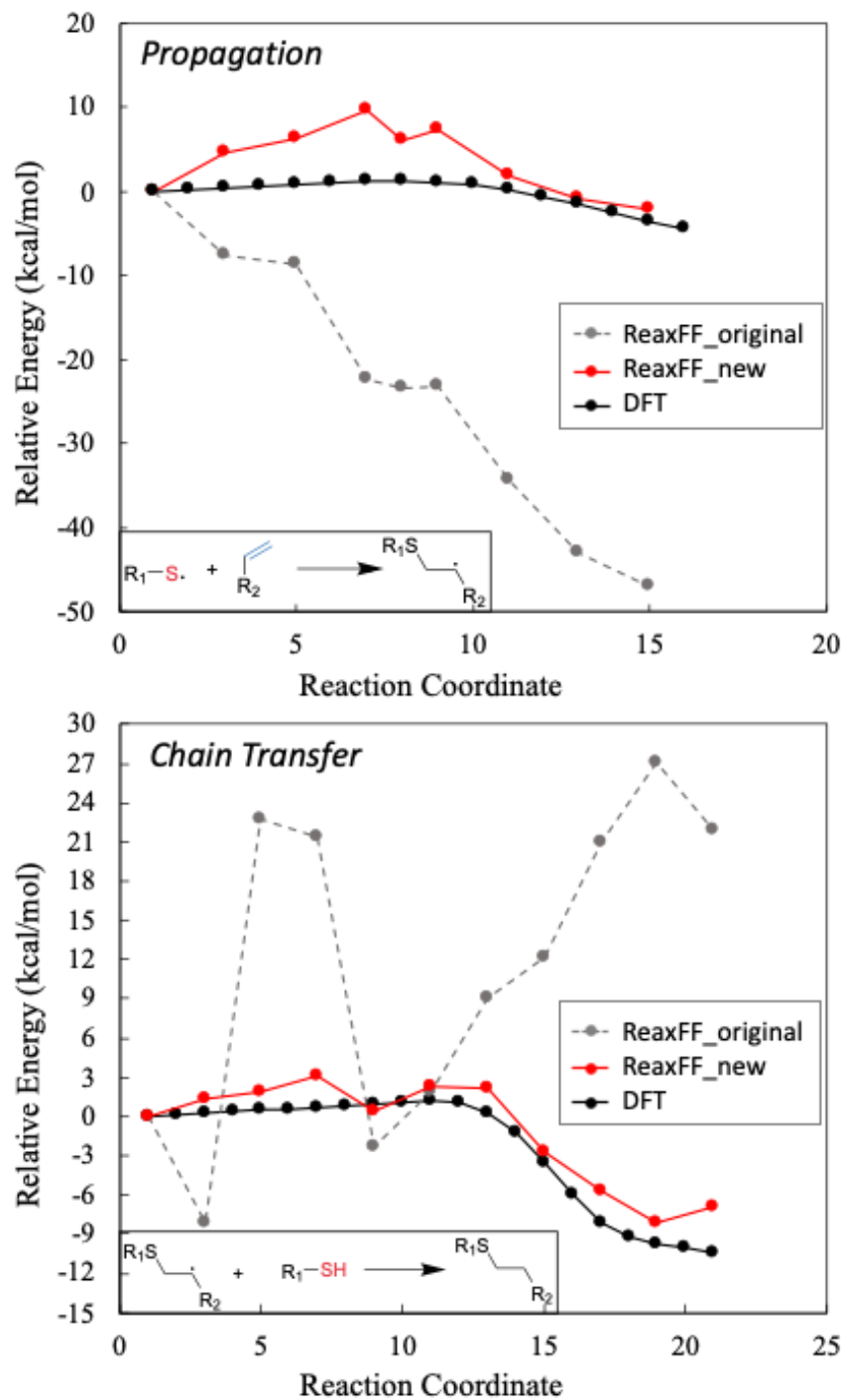
The original C/H/O/N/S/Si/Na/Al force field did not reproduce the overall shape of the reaction coordinate for the propagation and chain transfer steps. In contrast, the optimized C/H/O/N/S force field improved agreement with DFT for both reaction coordinates significantly (**Figure 4.7**), although activation energies were still overestimated, particularly for propagation. DFT predicted an activation energy of 1.22 kcal/mol for propagation, whereas ReaxFF\_new predicted 9.61 kcal/mol. Reaction energies for propagation were -4.45 kcal/mol (DFT) and -2.04 kcal/mol (ReaxFF\_new). For chain transfer, ReaxFF\_new predicted an activation barrier of 3.07 kcal/mol compared to 1.19 kcal/mol from DFT, and a reaction energy of -8.06 kcal/mol compared to -10.4 kcal/mol from DFT. Despite these discrepancies, propagation was observed in system-level simulations.



**Figure 4.6a.** Bond energy scans for S-C, S-S, C-H, and S-H bonds for ReaxFF\_original and developed ReaxFF\_new force fields relative to DFT.



**Figure 4.6b.** Bond energy scans for C=C, C-C, C-O, and C=O bonds for ReaxFF\_original and developed ReaxFF\_new force fields relative to DFT.



**Figure 4.7.** The intrinsic reaction coordinate for the (top) propagation and (bottom) chain transfer reactions calculated by the C/H/O/N/S/Si/Na/Al (ReaxFF\_original) and developed C/H/O/N/S (ReaxFF\_new) force fields, and DFT.

### 4.3.2 System-level Simulations: Pre-Initiation

Equilibrated liquid TME-ICN, TEGDAE, and a 1:1 mixture were evaluated with the optimized force field 300 K and 1 atm. Average densities and diffusion coefficients were computed from five simulations with independently generated initial configurations. Diffusion coefficients ( $D$ ) were obtained from the mean squared displacement (MSD) as:

$$\text{MSD}(t) = 6Dt = \frac{1}{N} \sum_{i=1}^N |r_i(t) - r_i(t_0)|^2. \quad (4.3.1)$$

Densities and diffusion coefficients are listed in **Table 4.3**. The C/H/O/N/S ReaxFF force field overestimated monomer densities by approximately 6%, suggesting mixture density is also likely overestimated. This increased density is consistent with steric crowding that suppresses reactivity. Diffusion coefficients further show that TEGDAE is substantially more mobile than the bulkier TME-ICN, indicating that TME-ICN can act as a relatively immobile obstacle while TEGDAE diffuses through the environment.

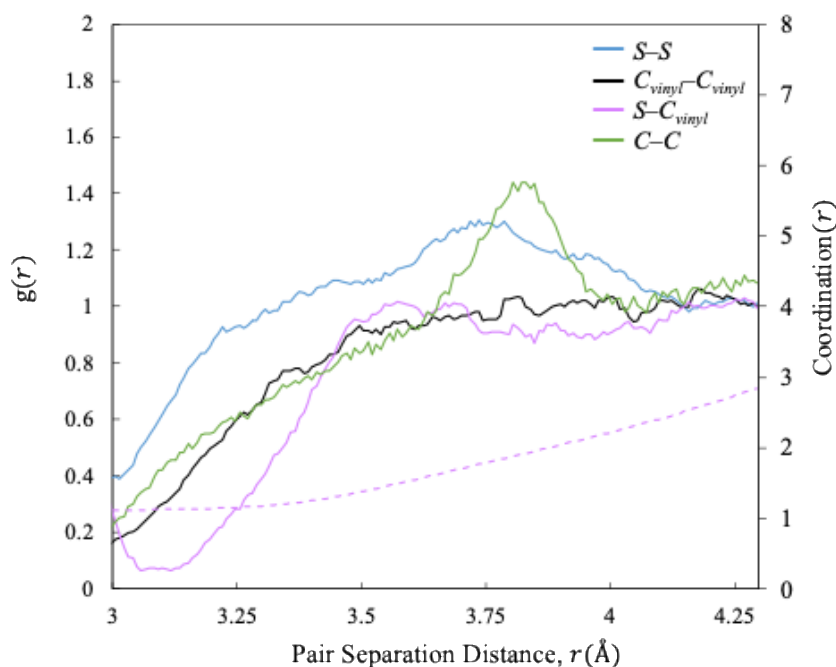
**Table 4.3.** Densities and diffusion coefficients for TEGDAE, TME-ICN, and a 1:1 mixture from the optimized C/H/O/N/S force field. Hyphens indicate where values were not measured.

|             | Density <sub>ReaxFF</sub> (cm <sup>3</sup> /g) | Density <sub>Exp.</sub> (cm <sup>3</sup> /g) | D <sub>ReaxFF</sub> (cm <sup>2</sup> /s) |
|-------------|------------------------------------------------|----------------------------------------------|------------------------------------------|
| TEGDAE      | 1.13 ± 0.1                                     | 1.07                                         | 2.7 × 10 <sup>-7</sup>                   |
| TME-ICN     | 1.41 ± 0.2                                     | 1.33                                         | 2.6 × 10 <sup>-8</sup>                   |
| 1:1 Mixture | 1.29 ± 0.2                                     | -                                            | -                                        |

RDFs was computed for vinyl carbon and sulfur atoms to assess accessibility using:

$$g(r) = \frac{\langle N(r, \Delta r) \rangle}{\rho_{bulk} \cdot 4\pi r^2 \Delta r}, \quad (4.3.2)$$

where  $\langle N(r, \Delta r) \rangle$  is the time-averaged number of particles in a spherical bin of width  $\Delta r$  at distance  $r$ . The coordination number ( $N_c$ ) for sulfur atoms near vinyl groups was computed by integrating  $g(r)$  and multiplying by the sulfur number density. **Figure 4.8** shows  $g(r)$  and coordination numbers for separations starting at 3 Å to focus on intermolecular distances. Although the simulation cell is 4 nm (40 Å), a short-range cutoff of 4.3 Å was used to isolate the first coordination shell.



**Figure 4.8.** Partial RDFs (solid lines) between selected atom pairs, and a cumulative coordination number for sulfur atoms near vinyl groups (dotted line). Distances start at 3 Å to emphasize intermolecular structure; a 4.3 Å cutoff was used to estimate the first coordination shell.

The RDFs indicate steric hindrance that can substantially limit reactivity. The  $C_{\text{vinyl}}-C_{\text{vinyl}}$  trace is near 1.0 at distances greater than 3.5 Å, consistent with a well-mixed system and reduced probability of homopolymerization. In contrast, the total C–C pair shows a peak at 3.8 Å, suggesting clustering and/or rigidity that can impede radical migration and render propagation diffusion-limited. The S–S RDF exhibits a broad peak with a maximum near 1.3 at approximately 3.75 Å, indicating sulfur clustering. Since S–S neighbors are about 30% more likely than in a random distribution, thiyl radicals may more frequently encounter each other and terminate by recombination than encounter a vinyl group, lowering conversion efficiency.

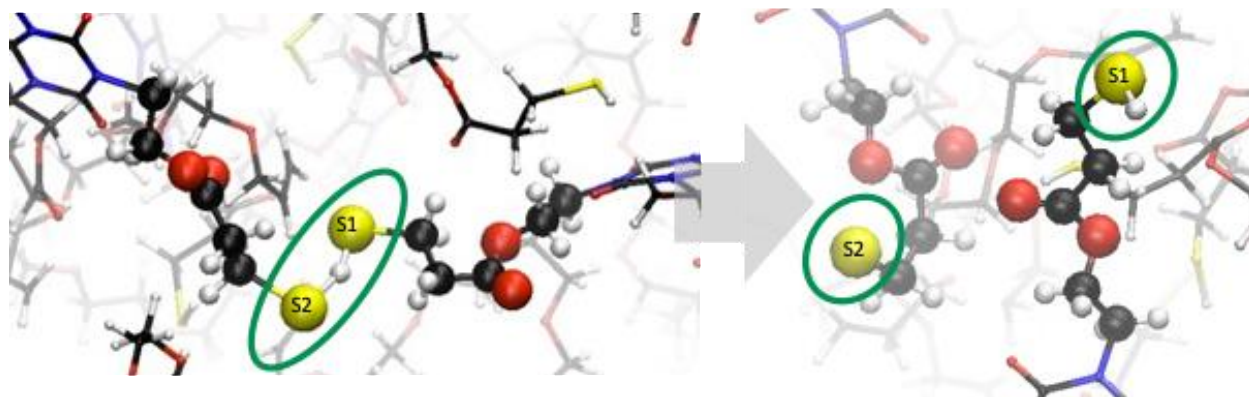
The S– $C_{\text{vinyl}}$  RDF approaches 1.0 at 3.54 Å, suggesting no specific attraction between the two monomers and indicating that propagation is entirely reliant on random diffusion. The pronounced dip in the S– $C_{\text{vinyl}}$  RDF ( $g(r) < 1.0$ ) between 3.6 and 4.1 Å coincides with the primary coordination peaks of S–S and C–C. This suggests competitive exclusion, where self-association of isocyanurate-containing species and dense backbone packing displace reactive vinyl and thiol groups from one another's immediate vicinity.

These physical barriers are further reflected in the number of thiols accessible to a vinyl carbon. The  $N_C$  analysis indicates that the number of sulfur molecules around vinyl carbons remains near 1.0 until nearly 4 Å. This plateau implies that once a radical center forms, it is statistically isolated, tethered to its initial reaction partner but lacking a secondary thiol neighbor within a viable reaction distance (less than 3.9 Å), which arrests the chain-transfer cycle.

#### 4.3.3 System-level Simulations: Initiation and Propagation

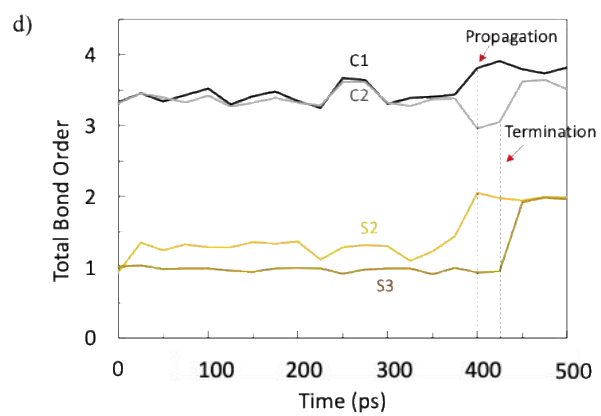
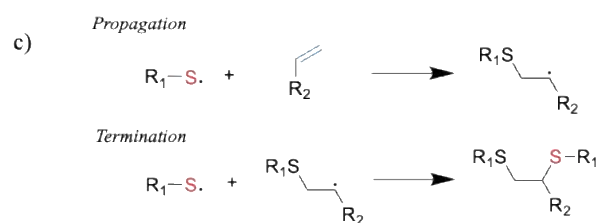
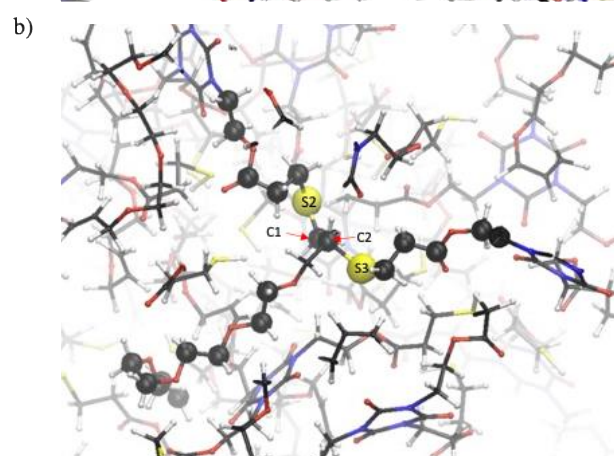
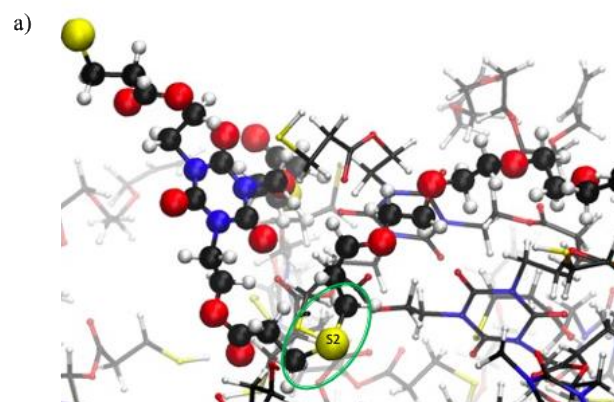
To probe reactivity, two sulfur radicals on separate TME-ICN molecules were generated in the equilibrated mixture and simulated with the optimized C/H/O/N/S force field at 800 K.

Three key reactions were observed under these conditions. First, a radical exchange between two sulfur atoms occurred at 64 ps. The bond order of sulfur atom S1 shifted from 0.94 (consistent with a sulfur radical bonded to carbon) to 1.91 after transferring its radical character to sulfur atom S2 in exchange for a hydrogen atom. In parallel, S2 changed from total bond order of 1.84 to 0.93, reflecting the loss of hydrogen and formation of a radical. This behavior is consistent with sulfur-mediated radical transfer akin to the chain-transfer step. **Figure 4.9** shows representative snapshots.



**Figure 9.** Snapshots of a radical-exchange event between a TME-ICN radical and an adjacent TME-ICN molecule. (Left) Frame immediately before S1 exchanges radical character to S2 in exchange for a hydrogen atom. (Right) subsequent frame after the exchange.

A propagation event and a termination event were observed at 400 and 425 ps, respectively. These reactions are evident from changes in bond orders of the reacting atoms. **Figure 10** shows snapshots and total bond orders as a function of simulation time. At 400 ps, the bond order of S2 and C1 increase while the total bond order for C2 decreases, consistent with formation of a S2–C1 bond and transfer of radical character to C2. At 425 ps, the total bond order of C2 increases as termination proceeds via bond formation between C2 and a nearby thiyl radical S3 on another TME-ICN molecule.



**Figure 10.** Snapshots of (a) propagation and (b) termination events. (c) Reaction schematics. (d) Total bond orders of the reacting atoms as a function of simulation time.

The observed dominance of radical-radical termination over the chain-transfer pathway can be rationalized using the calculated activation barriers. While chain transfer is energetically accessible with a relatively low activation barrier (3.07 kcal/mol in ReaxFF\_new), it is kinetically outcompeted by radical recombination. Termination between two radical species is typically considered effectively barrierless, making it strongly favored.

In this system, the probability that a radical center surmounts the chain transfer barrier is further reduced by the local coordination environment. As shown by the RDF analysis, thiyl radicals cluster in this system (peak S-S;  $g(r) \approx 1.3$ ), creating local regions of elevated radical density. Consequently, a carbon-centered radical generated by propagation is statistically more likely to encounter a nearby thiyl radical and terminate than it is to traverse sterically constrained environments to find a neutral thiol for chain transfer. This kinetic competition directs polymerization into a dead-end pathway, providing a molecular basis for the experimentally low modulus (0.12 MPa).<sup>7</sup>

A notable feature of this study is the contrast between the high simulation temperature (800 K) and the experimental glass transition temperature ( $T_g = -56\text{ }^\circ\text{C}$ ).<sup>7</sup> Although 800 K provides a substantial kinetic overpotential that might be expected to overcome activation barriers, the results indicate that the steric constraints, rather than energetic barriers, dominate reactivity. The  $g(r)$  and  $N_c$  analysis show isocyanurate-containing species remain clustered, rigid local structure (peak S-S;  $g(r) \approx 1.3$ ) and dense packing of backbones persists (peak C-C  $g(r) \approx 1.4$ ). This combination creates a physical caging effect that remains even at elevated

temperature. At 800 K, radical centers have high vibrational energy, but their effective mean free path is limited by the surrounding dense, largely unreactive architecture.

These physical barriers also explain the experimentally observed mechanical response. If reaction pathways are sterically hindered even at 800 K, polymerization is expected to be strongly suppressed at room temperature. The low modulus (0.12 MPa)<sup>7</sup> and high failure strain (293%)<sup>7</sup> are consistent with a very low crosslink density, suggesting that many TME-ICN and TEGDAE molecules remain unreacted or only singly linked, acting as internal plasticizers. Overall, the force field captures a kinetically frustrated system in which the isocyanurate ring architecture acts as an inherent inhibitor of network formation.

This demonstrates that the C/H/O/N/S force field effectively discriminates between chemically viable and sterically hindered pathways. The model reflects the physical reality of a packed monomer environment, making it a robust tool for screening monomer capability in high-density resin systems.

## 4.4 Conclusion

We developed an optimized C/H/O/N/S ReaxFF force field to probe molecular-scale kinetics in a TME-ICN/TEGDAE thiol-ene system. System-level simulations and structural analysis reveal a topological bottleneck that prevents efficient progression from propagation to chain transfer. Although chain transfer barrier is energetically accessible, RDF and coordination-number analysis show that steric crowding spatially isolates carbon-centered radicals from neutral thiol within a viable reaction radius. As a result, radical centers terminate prematurely with nearby clustered thiyl radicals (peak S-S;  $g(r) \approx 1.3$ ) limiting network formation and providing a mechanistic explanation for the experimentally observed low modulus (0.12 MPa)

and high failure strain (293%).<sup>7</sup> These results shift the interpretation of this resin from idealized alternating copolymerization toward a diffusion-limited, sterically constrained regime, where molecular architecture, rather than intrinsic electronic reactivity primarily governs macroscopic properties.

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## 4.5 Supplementary Data

Reactive MD-force field: c/h/o/n/s

```
39      ! Number of general parameters
50.0000 !Overcoordination parameter
9.5469 !Overcoordination parameter
1.6725 !Valency angle conjugation parameter
1.7224 !Triple bond stabilisation parameter
6.8702 !Triple bond stabilisation parameter
60.4850 !C2-correction
1.0588 !Undercoordination parameter
4.6000 !Triple bond stabilisation parameter
12.1176 !Undercoordination parameter
13.3056 !Undercoordination parameter
-70.5044 !Triple bond stabilization energy
0.0000 !Lower Taper-radius
10.0000 !Upper Taper-radius
2.8793 !Not used
33.8667 !Valency undercoordination
6.0891 !Valency angle/lone pair parameter
1.0563 !Valency angle
2.0384 !Valency angle parameter
6.1431 !Not used
6.9290 !Double bond/angle parameter
0.3989 !Double bond/angle parameter: overcoord
3.9954 !Double bond/angle parameter: overcoord
-2.4837 !Not used
5.7796 !Torsion/BO parameter
10.0000 !Torsion overcoordination
1.9487 !Torsion overcoordination
-1.2327 !Conjugation 0 (not used)
2.1645 !Conjugation
1.5591 !vdWaals shielding
0.1000 !Cutoff for bond order (*100)
1.7602 !Valency angle conjugation parameter
0.6991 !Overcoordination parameter
50.0000 !Overcoordination parameter
1.8512 !Valency/lone pair parameter
0.5000 !Not used
20.0000 !Not used
5.0000 !Molecular energy (not used)
0.0000 !Molecular energy (not used)
0.7903 !Valency angle conjugation parameter
12  ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
    alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.
    cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
```

ov/un;val1;n.u.;val3,vval4

|    |          |         |          |          |          |         |         |        |
|----|----------|---------|----------|----------|----------|---------|---------|--------|
| C  | 1.3744   | 4.0000  | 12.0000  | 1.6595   | 0.1825   | 0.8223  | 1.0410  | 4.0000 |
|    | 10.6733  | 2.5702  | 4.0000   | 41.4395  | 79.5548  | 5.6762  | 7.1801  | 0.0000 |
|    | 1.2114   | 0.0000  | 202.2908 | 10.4975  | 33.9206  | 12.4151 | 0.8563  | 0.0000 |
|    | -2.8825  | 2.6536  | 1.0564   | 4.0000   | 3.0130   | 0.0000  | 0.0000  | 0.0000 |
| H  | 0.9868   | 1.0000  | 1.0080   | 1.3751   | 0.0972   | 0.9297  | -0.1000 | 1.0000 |
|    | 7.5176   | 33.9225 | 1.0000   | 0.0000   | 121.1250 | 3.6172  | 10.8263 | 1.0000 |
|    | -0.1000  | 0.0000  | 55.1878  | 2.5901   | 2.3594   | 0.0003  | 1.0698  | 0.0000 |
|    | -22.0019 | 4.6264  | 1.0338   | 1.0000   | 2.9221   | 0.0000  | 0.0000  | 0.0000 |
| O  | 1.2450   | 2.0000  | 15.9990  | 2.2237   | 0.0939   | 1.0528  | 1.0548  | 6.0000 |
|    | 9.8625   | 12.7734 | 4.0000   | 36.9950  | 116.0768 | 8.4162  | 7.3260  | 2.0000 |
|    | 0.9049   | 0.4328  | 68.0152  | 21.9940  | 3.5799   | 0.2687  | 0.9745  | 0.0000 |
|    | -3.3263  | 2.5217  | 1.0493   | 4.0000   | 3.0395   | 0.0000  | 0.0000  | 0.0000 |
| N  | 1.2333   | 3.0000  | 14.0000  | 1.9324   | 0.1376   | 0.7921  | 1.1748  | 5.0000 |
|    | 10.0667  | 7.8431  | 4.0000   | 32.2482  | 100.0000 | 7.5795  | 6.3952  | 2.0000 |
|    | 1.0433   | 27.4290 | 119.9837 | 1.9457   | 4.2874   | 3.4869  | 0.9745  | 0.0000 |
|    | -4.3875  | 2.6192  | 1.0183   | 4.0000   | 2.8793   | 0.0000  | 0.0000  | 0.0000 |
| S  | 1.8241   | 2.0000  | 32.0600  | 2.3075   | 0.2007   | 1.0321  | 1.5354  | 6.0000 |
|    | 10.0456  | 6.1158  | 4.0000   | 54.0078  | 112.1416 | 4.9984  | 8.0917  | 2.0000 |
|    | 1.4601   | 8.3133  | 71.1843  | 5.4697   | 21.9314  | 13.7020 | 0.9745  | 0.0000 |
|    | -12.4489 | 2.2038  | 1.0338   | 6.2998   | 2.9659   | 0.0000  | 0.0000  | 0.0000 |
| Mg | 1.8315   | 2.0000  | 24.3050  | 2.2464   | 0.1806   | 0.5020  | 1.0000  | 2.0000 |
|    | 10.9186  | 27.1205 | 3.0000   | 38.0000  | 0.0000   | 0.9499  | 5.6130  | 0.0000 |
|    | -1.3000  | 0.0000  | 127.9160 | 49.9248  | 0.3370   | 0.0000  | 0.0000  | 0.0000 |
|    | -1.0823  | 2.3663  | 1.0564   | 6.0000   | 2.9663   | 0.0000  | 0.0000  | 0.0000 |
| P  | 1.5994   | 3.0000  | 30.9738  | 1.7000   | 0.1743   | 1.0000  | 1.3000  | 5.0000 |
|    | 9.1909   | 14.9482 | 5.0000   | 0.0000   | 0.0000   | 1.6676  | 7.0946  | 0.0000 |
|    | -1.0000  | 25.0000 | 125.6300 | 0.2187   | 21.4305  | 15.1425 | 0.0000  | 0.0000 |
|    | -3.9294  | 3.4831  | 1.0338   | 5.0000   | 2.8793   | 0.0000  | 0.0000  | 0.0000 |
| Na | 1.8000   | 1.0000  | 22.9898  | 2.8270   | 0.1872   | 0.4000  | -1.0000 | 1.0000 |
|    | 10.0000  | 2.5000  | 1.0000   | 0.0000   | 0.0000   | -0.9871 | 6.7728  | 0.0000 |
|    | -1.0000  | 0.0000  | 23.0445  | 100.0000 | 1.0000   | 0.0000  | 0.8563  | 0.0000 |
|    | -2.5000  | 3.9900  | 1.0338   | 8.0000   | 2.5791   | 0.0000  | 0.0000  | 0.0000 |
| Ti | 2.0254   | 4.0000  | 47.8800  | 2.2105   | 0.1574   | 0.4098  | 0.1000  | 4.0000 |
|    | 12.7041  | 16.6482 | 4.0000   | 0.1000   | 0.0000   | -4.6395 | 7.7218  | 0.0000 |
|    | -1.0000  | 0.0000  | 143.1770 | 19.9797  | 0.5782   | 0.0064  | 0.8563  | 0.0000 |
|    | -15.0000 | 1.5000  | 1.0338   | 6.2998   | 2.2632   | 0.0000  | 0.0000  | 0.0000 |
| Cl | 1.7140   | 1.0000  | 35.4500  | 1.9139   | 0.2000   | 0.3500  | -1.0000 | 7.0000 |
|    | 11.5345  | 10.1330 | 1.0000   | 0.0000   | 0.0000   | 9.9704  | 6.1703  | 0.0000 |
|    | -1.0000  | 1.2769  | 143.1770 | 6.2293   | 5.2294   | 0.1542  | 0.8563  | 0.0000 |
|    | -10.2080 | 2.9867  | 1.0338   | 6.2998   | 2.5791   | 0.0000  | 0.0000  | 0.0000 |
| F  | 1.2100   | 1.0000  | 18.9984  | 1.8601   | 0.1200   | 0.3000  | -0.1000 | 7.0000 |
|    | 11.5000  | 7.5000  | 4.0000   | 9.2533   | 0.2000   | 9.0000  | 15.0000 | 0.0000 |
|    | -1.0000  | 35.0000 | 1.5000   | 6.9821   | 4.1799   | 1.0561  | 0.0000  | 0.0000 |
|    | -7.3000  | 2.6656  | 1.0493   | 4.0000   | 2.9225   | 0.0000  | 0.0000  | 0.0000 |
| X  | -0.1000  | 2.0000  | 1.0080   | 2.0000   | 0.0000   | 1.0000  | -0.1000 | 6.0000 |

```

10.0000 2.5000 4.0000 0.0000 0.0000 8.5000 1.5000 0.0000
-0.1000 0.0000 -2.3700 8.7410 13.3640 0.6690 0.9745 0.0000
-11.0000 2.7466 1.0338 4.0000 2.8793 0.0000 0.0000 0.0000
58 ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
    pbe2;pbo3;pbo4;Etrip;pbo1;pbo2;ovcorr
1 1 155.3126 107.3606 78.0000 -0.6259 -0.4550 1.0000 37.6117 0.4147
    0.4537 -0.1000 8.2554 1.0000 -0.0988 5.6904 1.0000 0.0000
1 2 169.4760 0.0000 0.0000 -0.6083 0.0000 1.0000 6.0000 0.7652
    5.2290 1.0000 0.0000 1.0000 -0.0500 6.9136 0.0000 0.0000
2 2 153.3934 0.0000 0.0000 -0.4600 0.0000 1.0000 6.0000 0.7300
    6.2500 1.0000 0.0000 1.0000 -0.0790 6.0552 0.0000 0.0000
1 3 143.2031 111.6645 23.3059 -0.3762 -0.1613 1.0000 10.8851 1.0000
    0.3739 -0.3275 6.6476 1.0000 -0.1369 6.2542 0.0000 0.0000
3 3 60.1463 176.6202 51.1430 -0.2802 -0.1244 1.0000 29.6439 0.9114
    0.2441 -0.1239 7.6487 1.0000 -0.1302 6.2919 1.0000 0.0000
1 4 134.1215 140.2179 79.9745 0.0163 -0.1428 1.0000 27.0617 0.2000
    0.1387 -0.3681 7.1611 1.0000 -0.1000 5.0825 1.0000 0.0000
3 4 130.8596 169.4551 40.0000 0.3837 -0.1639 1.0000 35.0000 0.2000
    1.0000 -0.3579 7.0004 1.0000 -0.1193 6.8773 1.0000 0.0000
4 4 157.9384 82.5526 152.5336 0.4010 -0.1034 1.0000 12.4261 0.5828
    0.1578 -0.1509 11.9186 1.0000 -0.0861 5.4271 1.0000 0.0000
2 3 160.0000 0.0000 0.0000 -0.5725 0.0000 1.0000 6.0000 0.5626
    1.1150 1.0000 0.0000 0.0000 -0.0920 4.2790 0.0000 0.0000
2 4 185.3171 0.0000 0.0000 -0.3689 0.0000 1.0000 6.0000 0.2854
    7.6517 1.0000 0.0000 1.0000 -0.0408 6.0255 0.0000 0.0000
1 5 90.1571 50.8626 39.0716 0.0661 -0.4463 1.0000 31.1766 0.4530
    0.2459 -0.4387 4.7448 1.0000 -0.0810 7.9147 1.0000 0.0000
2 5 138.3881 0.0000 0.0000 -0.3268 0.0000 1.0000 6.0000 0.3803
    12.9209 1.0000 0.0000 1.0000 -0.1000 7.2275 1.0000 0.0000
3 5 0.0000 0.0000 0.0000 0.5848 -0.2406 1.0000 22.1005 0.2335
    0.7069 -0.2681 8.3465 1.0000 -0.0922 5.4651 1.0000 0.0000
4 5 0.0000 0.0000 0.0000 0.5000 -0.2000 1.0000 40.0000 0.3000
    0.4000 -0.2500 9.0000 1.0000 -0.1000 6.0000 1.0000 0.0000
5 5 149.9568 0.0000 0.0000 0.1787 -0.5000 1.0000 20.0000 1.0000
    0.2428 -0.2693 12.9767 1.0000 -0.1000 6.2884 1.0000 0.0000
2 6 58.6896 0.0000 0.0000 -0.0203 -0.1418 1.0000 13.1260 0.0230
    8.2136 -0.1310 0.0000 1.0000 -0.2692 6.4254 0.0000 24.4461
3 6 87.0227 0.0000 43.3991 0.0030 -0.3000 1.0000 36.0000 0.0250
    0.0087 -0.2500 12.0000 1.0000 -0.0439 6.6073 1.0000 24.4461
6 6 32.3808 0.0000 0.0000 -0.0076 -0.2000 0.0000 16.0000 0.2641
    4.8726 -0.2000 10.0000 1.0000 -0.0729 4.6319 0.0000 0.0000
1 7 110.0000 92.0000 0.0000 0.2171 -0.1418 1.0000 13.1260 0.6000
    0.3601 -0.1310 10.7257 1.0000 -0.0869 5.3302 1.0000 0.0000
2 7 0.1466 0.0000 0.0000 0.2250 -0.1418 1.0000 13.1260 0.6000
    0.3912 -0.1310 0.0000 1.0000 -0.1029 9.3302 0.0000 0.0000
3 7 201.0058 194.1410 0.0000 1.0000 -0.5000 1.0000 25.0000 0.4873

```

|   |    |          |         |         |         |         |         |         |        |        |
|---|----|----------|---------|---------|---------|---------|---------|---------|--------|--------|
|   |    |          | 0.4358  | -0.1571 | 15.8745 | 1.0000  | -0.2431 | 6.3823  | 1.0000 | 0.0000 |
| 4 | 7  | 130.0000 | 0.0000  | 0.0000  | 0.2171  | -0.1418 | 1.0000  | 13.1260 | 0.6000 |        |
|   |    |          | 0.3601  | -0.1310 | 10.7257 | 1.0000  | -0.0869 | 5.3302  | 1.0000 | 0.0000 |
| 6 | 7  | 0.1000   | 0.0000  | 0.0000  | 0.2500  | -0.5000 | 1.0000  | 35.0000 | 0.6000 |        |
|   |    |          | 0.5000  | -0.5000 | 20.0000 | 1.0000  | -0.2000 | 10.0000 | 1.0000 | 0.0000 |
| 7 | 7  | 0.0000   | 0.0000  | 0.0000  | 0.2171  | -0.5000 | 1.0000  | 35.0000 | 0.6000 |        |
|   |    |          | 0.5000  | -0.5000 | 20.0000 | 1.0000  | -0.2000 | 10.0000 | 1.0000 | 0.0000 |
| 1 | 8  | 0.0000   | 0.0000  | 0.0000  | -1.0000 | -0.3000 | 1.0000  | 36.0000 | 0.7000 |        |
|   |    |          | 10.1151 | -0.3500 | 25.0000 | 1.0000  | -0.1053 | 8.2003  | 1.0000 | 0.0000 |
| 2 | 8  | 0.0000   | 0.0000  | 0.0000  | -1.0000 | -0.3000 | 1.0000  | 36.0000 | 0.7000 |        |
|   |    |          | 10.1151 | -0.3500 | 25.0000 | 1.0000  | -0.1053 | 8.2003  | 1.0000 | 0.0000 |
| 3 | 8  | 45.8933  | 0.0000  | 0.0000  | -0.1511 | -0.3000 | 1.0000  | 36.0000 | 0.3105 |        |
|   |    |          | 5.8448  | -0.3500 | 25.0000 | 1.0000  | -0.0659 | 7.9140  | 1.0000 | 0.0000 |
| 4 | 8  | 0.0000   | 0.0000  | 0.0000  | -1.0000 | -0.3000 | 1.0000  | 36.0000 | 0.7000 |        |
|   |    |          | 10.1151 | -0.3500 | 25.0000 | 1.0000  | -0.1053 | 8.2003  | 1.0000 | 0.0000 |
| 5 | 8  | 0.0000   | 0.0000  | 0.0000  | -1.0000 | -0.3000 | 1.0000  | 36.0000 | 0.7000 |        |
|   |    |          | 10.1151 | -0.3500 | 25.0000 | 1.0000  | -0.1053 | 8.2003  | 1.0000 | 0.0000 |
| 6 | 8  | 0.0000   | 0.0000  | 0.0000  | 0.2500  | -0.5000 | 1.0000  | 35.0000 | 0.6000 |        |
|   |    |          | 0.5000  | -0.5000 | 20.0000 | 1.0000  | -0.2000 | 10.0000 | 1.0000 | 0.0000 |
| 7 | 8  | 0.0000   | 0.0000  | 0.0000  | 0.2500  | -0.5000 | 1.0000  | 35.0000 | 0.6000 |        |
|   |    |          | 0.5000  | -0.5000 | 20.0000 | 1.0000  | -0.2000 | 10.0000 | 1.0000 | 0.0000 |
| 8 | 8  | 64.4508  | 0.0000  | 0.0000  | -0.3738 | 0.3000  | 0.0000  | 25.0000 | 0.2158 |        |
|   |    |          | 0.9915  | -0.4000 | 12.0000 | 1.0000  | -0.0515 | 5.0000  | 0.0000 | 0.0000 |
| 4 | 6  | 50.0000  | 10.0901 | 0.0000  | -1.0000 | -0.3000 | 1.0000  | 36.0000 | 0.7058 |        |
|   |    |          | 0.8567  | -0.3487 | 17.4990 | 1.0000  | -0.0794 | 8.2232  | 1.0000 | 0.0000 |
| 1 | 9  | 0.0000   | 0.0000  | 0.0000  | -0.2872 | -0.3000 | 1.0000  | 36.0000 | 0.0082 |        |
|   |    |          | 1.7973  | -0.2500 | 20.0000 | 1.0000  | -0.2578 | 6.5219  | 1.0000 | 0.0000 |
| 2 | 9  | 0.0000   | 0.0000  | 0.0000  | -0.2872 | -0.3000 | 1.0000  | 36.0000 | 0.0082 |        |
|   |    |          | 1.7973  | -0.2500 | 20.0000 | 1.0000  | -0.2578 | 6.5219  | 1.0000 | 0.0000 |
| 3 | 9  | 121.6983 | 22.3803 | 0.0000  | 0.5110  | -0.3000 | 1.0000  | 36.0000 | 0.0100 |        |
|   |    |          | -0.0707 | -0.2493 | 16.1482 | 1.0000  | -0.1654 | 6.4224  | 1.0000 | 0.0000 |
| 4 | 9  | 0.0000   | 0.0000  | 0.0000  | -0.2872 | -0.3000 | 1.0000  | 36.0000 | 0.0082 |        |
|   |    |          | 1.7973  | -0.2500 | 20.0000 | 1.0000  | -0.2578 | 6.5219  | 1.0000 | 0.0000 |
| 5 | 9  | 0.0000   | 0.0000  | 0.0000  | -0.2872 | -0.3000 | 1.0000  | 36.0000 | 0.0082 |        |
|   |    |          | 1.7973  | -0.2500 | 20.0000 | 1.0000  | -0.2578 | 6.5219  | 1.0000 | 0.0000 |
| 6 | 9  | 0.0000   | 0.0000  | 0.0000  | -0.2872 | -0.3000 | 1.0000  | 36.0000 | 0.0082 |        |
|   |    |          | 1.7973  | -0.2500 | 20.0000 | 1.0000  | -0.2578 | 6.5219  | 1.0000 | 0.0000 |
| 7 | 9  | 0.0000   | 0.0000  | 0.0000  | -0.2872 | -0.3000 | 1.0000  | 36.0000 | 0.0082 |        |
|   |    |          | 1.7973  | -0.2500 | 20.0000 | 1.0000  | -0.2578 | 6.5219  | 1.0000 | 0.0000 |
| 8 | 9  | 0.1000   | 0.0000  | 0.0000  | 0.2500  | -0.5000 | 1.0000  | 35.0000 | 0.6000 |        |
|   |    |          | 0.5000  | -0.5000 | 20.0000 | 1.0000  | -0.2000 | 10.0000 | 1.0000 | 0.0000 |
| 9 | 9  | 80.1930  | 0.0000  | 0.0000  | -0.8469 | -0.2000 | 0.0000  | 16.0000 | 0.2022 |        |
|   |    |          | 0.7528  | -0.1924 | 14.9725 | 1.0000  | -0.0885 | 5.0000  | 0.0000 | 0.0000 |
| 1 | 10 | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |        |
|   |    |          | 1.0001  | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000 | 0.0000 |
| 2 | 10 | 98.9788  | 0.0000  | 0.0000  | -0.0572 | -0.2000 | 0.0000  | 16.0000 | 1.1523 |        |

|    |                                                            |          |         |         |         |         |         |         |        |
|----|------------------------------------------------------------|----------|---------|---------|---------|---------|---------|---------|--------|
|    |                                                            | 2.2822   | -0.2000 | 15.0000 | 1.0000  | -0.1093 | 5.1686  | 0.0000  | 0.0000 |
| 3  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 4  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 5  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 6  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 7  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 8  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 9  | 10                                                         | 0.0000   | 0.0000  | 0.0000  | 0.5000  | -0.2000 | 0.0000  | 16.0000 | 0.5000 |
|    |                                                            | 1.0001   | -0.2000 | 15.0000 | 1.0000  | -0.1000 | 10.0000 | 0.0000  | 0.0000 |
| 10 | 10                                                         | 0.2500   | 0.0000  | 0.0000  | 0.1803  | -0.2000 | 0.0000  | 16.0000 | 0.3356 |
|    |                                                            | 0.9228   | -0.2000 | 15.0000 | 1.0000  | -0.1178 | 5.6715  | 0.0000  | 0.0000 |
| 1  | 11                                                         | 237.8781 | 0.0000  | 0.0000  | -0.7438 | -0.5000 | 1.0000  | 35.0000 | 1.0460 |
|    |                                                            | 3.6661   | -0.2500 | 15.0000 | 1.0000  | -0.0800 | 5.4719  | 1.0000  | 0.0000 |
| 2  | 11                                                         | 0.0000   | 0.0000  | 0.0000  | -0.4643 | 0.0000  | 1.0000  | 6.0000  | 0.6151 |
|    |                                                            | 12.3710  | 1.0000  | 0.0000  | 1.0000  | -0.1008 | 8.5980  | 0.0000  | 0.0000 |
| 3  | 11                                                         | 0.0000   | 0.0000  | 0.0000  | -0.4643 | 0.0000  | 1.0000  | 6.0000  | 0.6151 |
|    |                                                            | 12.3710  | 1.0000  | 0.0000  | 1.0000  | -0.1008 | 8.5980  | 0.0000  | 0.0000 |
| 4  | 11                                                         | 0.0000   | 0.0000  | 0.0000  | -0.4643 | 0.0000  | 1.0000  | 6.0000  | 0.6151 |
|    |                                                            | 12.3710  | 1.0000  | 0.0000  | 1.0000  | -0.1008 | 8.5980  | 0.0000  | 0.0000 |
| 5  | 11                                                         | 0.0000   | 0.0000  | 0.0000  | -0.4643 | 0.0000  | 1.0000  | 6.0000  | 0.6151 |
|    |                                                            | 12.3710  | 1.0000  | 0.0000  | 1.0000  | -0.1008 | 8.5980  | 0.0000  | 0.0000 |
| 11 | 11                                                         | 250.0765 | 0.0000  | 0.0000  | 0.2298  | -0.3500 | 1.0000  | 25.0000 | 0.8427 |
|    |                                                            | 0.1167   | -0.2500 | 15.0000 | 1.0000  | -0.1506 | 7.3516  | 1.0000  | 0.0000 |
| 22 | ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2 |          |         |         |         |         |         |         |        |
| 1  | 2                                                          | 0.1239   | 1.4004  | 9.8467  | 1.1210  | -1.0000 | -1.0000 |         |        |
| 2  | 3                                                          | 0.0286   | 1.2995  | 8.4116  | 0.7036  | -1.0000 | -1.0000 |         |        |
| 2  | 4                                                          | 0.0687   | 1.5130  | 10.0094 | 0.9412  | -1.0000 | -1.0000 |         |        |
| 1  | 3                                                          | 0.1349   | 1.6053  | 9.0916  | 1.2866  | 0.9199  | 1.0637  |         |        |
| 1  | 4                                                          | 0.1447   | 1.8766  | 9.7990  | 1.3436  | 1.1885  | 1.1363  |         |        |
| 3  | 4                                                          | 0.1048   | 2.0003  | 10.1220 | 1.3173  | 1.1096  | 1.0206  |         |        |
| 1  | 5                                                          | 0.1408   | 1.8161  | 9.9393  | 1.7986  | 1.3021  | 1.4031  |         |        |
| 2  | 5                                                          | 0.0895   | 1.6239  | 10.0104 | 1.4640  | -1.0000 | -1.0000 |         |        |
| 3  | 5                                                          | 0.1962   | 1.7872  | 10.2319 | 1.4622  | 1.4025  | -1.0000 |         |        |
| 4  | 5                                                          | 0.1505   | 1.9000  | 10.5104 | 1.8000  | 1.4000  | -1.0000 |         |        |
| 2  | 6                                                          | 0.0100   | 1.6000  | 13.2979 | 1.8670  | -1.0000 | -1.0000 |         |        |
| 3  | 6                                                          | 0.0809   | 1.7000  | 11.4606 | 1.5177  | -1.0000 | -1.0000 |         |        |
| 3  | 7                                                          | 0.0534   | 1.7520  | 10.4281 | 1.8000  | 1.4498  | -1.0000 |         |        |
| 6  | 7                                                          | 0.1801   | 1.8566  | 9.8498  | 0.1000  | -1.0000 | -1.0000 |         |        |
| 3  | 8                                                          | 0.0825   | 1.5904  | 11.3396 | 1.5905  | -1.0000 | -1.0000 |         |        |
| 2  | 9                                                          | 0.1731   | 1.6201  | 12.1586 | 0.0100  | -1.0000 | -1.0000 |         |        |

|    |    |                                                   |          |         |         |          |         |                 |
|----|----|---------------------------------------------------|----------|---------|---------|----------|---------|-----------------|
| 3  | 9  | 0.1200                                            | 1.8000   | 10.5000 | 1.6486  | 1.4739   | -1.0000 |                 |
| 1  | 9  | 0.2035                                            | 1.7007   | 11.4530 | 0.0100  | -1.0000  | -1.0000 |                 |
| 2  | 10 | 0.0376                                            | 1.6671   | 9.6285  | 1.2123  | -1.0000  | -1.0000 |                 |
| 3  | 10 | 0.1945                                            | 2.2766   | 11.2353 | -1.0000 | -1.0000  | -1.0000 |                 |
| 1  | 11 | 0.1071                                            | 1.6243   | 11.0402 | 1.3176  | -1.0000  | -1.0000 |                 |
| 2  | 11 | 0.0431                                            | 1.7204   | 10.3632 | 0.5386  | -1.0000  | -1.0000 |                 |
| 83 |    | ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2 |          |         |         |          |         |                 |
| 1  | 1  | 1                                                 | 63.9222  | 39.9138 | 0.6671  | 0.0000   | 0.5999  | 6.6015 1.1910   |
| 1  | 1  | 2                                                 | 68.2535  | 13.1391 | 7.4491  | 0.0000   | 0.4034  | 0.0000 1.5236   |
| 2  | 1  | 2                                                 | 70.2607  | 25.2202 | 3.7312  | 0.0000   | 0.0050  | 0.0000 2.7500   |
| 1  | 2  | 2                                                 | 0.0000   | 0.0000  | 6.0000  | 0.0000   | 0.0000  | 0.0000 1.0400   |
| 1  | 2  | 1                                                 | 0.0000   | 3.4110  | 7.7350  | 0.0000   | 0.0000  | 0.0000 1.0400   |
| 2  | 2  | 2                                                 | 0.0000   | 27.9213 | 5.8635  | 0.0000   | 0.0000  | 0.0000 1.0400   |
| 1  | 1  | 3                                                 | 65.9327  | 9.4278  | 2.9996  | 0.0000   | 2.3840  | 46.3384 0.9634  |
| 3  | 1  | 3                                                 | 65.1523  | 32.7268 | 2.3197  | -27.8840 | 1.3492  | -48.4715 3.0133 |
| 1  | 1  | 4                                                 | 78.5538  | 21.4381 | 7.4715  | 0.0000   | 1.1046  | 50.0000 1.5275  |
| 3  | 1  | 4                                                 | 73.9544  | 12.4661 | 7.0000  | 0.0000   | 1.1046  | 0.0000 1.1880   |
| 4  | 1  | 4                                                 | 89.3168  | 20.2660 | 7.5000  | 0.0000   | 1.1046  | 0.0000 1.5403   |
| 2  | 1  | 3                                                 | 65.0000  | 16.3141 | 5.2730  | 0.0000   | 0.4448  | 0.0000 1.4077   |
| 2  | 1  | 4                                                 | 74.2929  | 31.0883 | 2.6184  | 0.0000   | 0.1000  | 0.0000 1.0500   |
| 1  | 2  | 4                                                 | 0.0000   | 0.0019  | 6.3000  | 0.0000   | 0.0000  | 0.0000 1.0400   |
| 1  | 3  | 1                                                 | 74.8592  | 45.3144 | 0.7950  | 0.0000   | 2.4841  | 0.0000 1.6485   |
| 1  | 3  | 3                                                 | 81.9029  | 32.2258 | 1.7397  | 0.0000   | 0.9888  | 68.1072 1.7777  |
| 1  | 3  | 4                                                 | 82.4890  | 31.4554 | 0.9953  | 0.0000   | 3.0000  | 0.0000 1.0783   |
| 3  | 3  | 3                                                 | 80.7324  | 30.4554 | 0.9953  | 0.0000   | 3.0000  | 50.0000 1.0783  |
| 3  | 3  | 4                                                 | 84.3637  | 31.4554 | 0.9953  | 0.0000   | 3.0000  | 0.0000 1.0783   |
| 4  | 3  | 4                                                 | 89.7071  | 31.4554 | 0.9953  | 0.0000   | 3.0000  | 0.0000 1.1519   |
| 1  | 3  | 2                                                 | 70.1101  | 13.1217 | 4.4734  | 0.0000   | 0.8433  | 0.0000 3.0000   |
| 2  | 3  | 3                                                 | 75.6935  | 50.0000 | 2.0000  | 0.0000   | 1.0000  | 0.0000 1.1680   |
| 2  | 3  | 4                                                 | 75.6201  | 18.7919 | 0.9833  | 0.0000   | 0.1000  | 0.0000 1.0500   |
| 2  | 3  | 2                                                 | 85.8000  | 9.8453  | 2.2720  | 0.0000   | 2.8635  | 0.0000 1.5800   |
| 1  | 4  | 1                                                 | 81.4699  | 7.2318  | 1.2608  | 0.0000   | 3.0000  | 0.0000 1.2127   |
| 1  | 4  | 3                                                 | 103.3204 | 33.0381 | 0.5787  | 0.0000   | 3.0000  | 0.0000 1.2127   |
| 1  | 4  | 4                                                 | 50.0000  | 25.0250 | 4.7651  | 0.0000   | 3.0000  | 0.0000 1.2028   |
| 3  | 4  | 3                                                 | 74.1978  | 42.1786 | 1.7845  | -18.0069 | 3.0000  | 0.0000 1.2127   |
| 3  | 4  | 4                                                 | 74.8600  | 43.7354 | 1.1572  | -0.9193  | 3.0000  | 0.0000 1.2127   |
| 4  | 4  | 4                                                 | 75.0538  | 14.8267 | 5.2794  | 0.0000   | 3.0000  | 0.0000 1.2127   |
| 1  | 4  | 2                                                 | 68.2294  | 29.6576 | 1.0533  | 0.0000   | 0.3481  | 0.0000 1.5443   |
| 2  | 4  | 3                                                 | 81.3686  | 40.0712 | 2.2396  | 0.0000   | 0.3481  | 0.0000 1.5443   |
| 2  | 4  | 4                                                 | 83.0104  | 43.4766 | 1.5328  | 0.0000   | 0.3481  | 0.0000 1.5443   |
| 2  | 4  | 2                                                 | 79.6336  | 17.7917 | 3.7832  | 0.0000   | 0.0222  | 0.0000 2.0238   |
| 1  | 2  | 3                                                 | 0.0000   | 25.0000 | 3.0000  | 0.0000   | 1.0000  | 0.0000 1.0400   |
| 1  | 2  | 4                                                 | 0.0000   | 0.0019  | 6.0000  | 0.0000   | 0.0000  | 0.0000 1.0400   |
| 1  | 2  | 5                                                 | 0.0000   | 0.0019  | 6.0000  | 0.0000   | 0.0000  | 0.0000 1.0400   |
| 3  | 2  | 3                                                 | 0.0000   | 15.0000 | 2.8900  | 0.0000   | 0.0000  | 0.0000 2.8774   |
| 3  | 2  | 4                                                 | 0.0000   | 0.0019  | 6.0000  | 0.0000   | 0.0000  | 0.0000 1.0400   |

|    |                                                               |    |         |         |         |         |         |         |        |        |
|----|---------------------------------------------------------------|----|---------|---------|---------|---------|---------|---------|--------|--------|
| 4  | 2                                                             | 4  | 0.0000  | 0.0019  | 6.0000  | 0.0000  | 0.0000  | 0.0000  | 0.0000 | 1.0400 |
| 2  | 2                                                             | 3  | 0.0000  | 8.5744  | 3.0000  | 0.0000  | 0.0000  | 0.0000  | 0.0000 | 1.0421 |
| 2  | 2                                                             | 4  | 0.0000  | 0.0019  | 6.0000  | 0.0000  | 0.0000  | 0.0000  | 0.0000 | 1.0400 |
| 1  | 1                                                             | 5  | 74.4180 | 33.4273 | 1.7018  | 0.1463  | 0.5000  | 0.0000  | 0.0000 | 1.6178 |
| 1  | 5                                                             | 1  | 79.7037 | 28.2036 | 1.7073  | 0.1463  | 0.5000  | 0.0000  | 0.0000 | 1.6453 |
| 2  | 1                                                             | 5  | 63.3289 | 29.4225 | 2.1326  | 0.0000  | 0.5000  | 0.0000  | 0.0000 | 3.0000 |
| 1  | 5                                                             | 2  | 85.9449 | 38.3109 | 1.2492  | 0.0000  | 0.5000  | 0.0000  | 0.0000 | 1.1000 |
| 1  | 5                                                             | 5  | 85.6645 | 40.0000 | 2.9274  | 0.1463  | 0.5000  | 0.0000  | 0.0000 | 1.3830 |
| 2  | 5                                                             | 2  | 83.8555 | 5.1317  | 0.4377  | 0.0000  | 0.5000  | 0.0000  | 0.0000 | 3.0000 |
| 2  | 5                                                             | 5  | 97.0064 | 32.1121 | 2.0242  | 0.0000  | 0.5000  | 0.0000  | 0.0000 | 2.8568 |
| 3  | 5                                                             | 3  | 81.0926 | 30.2268 | 6.4132  | -5.4471 | 2.5968  | 0.0000  | 0.0000 | 3.0000 |
| 1  | 5                                                             | 3  | 70.0000 | 35.0000 | 3.4223  | 0.0000  | 1.3550  | 0.0000  | 0.0000 | 1.2002 |
| 1  | 3                                                             | 5  | 57.3353 | 41.0012 | 1.0609  | 0.0000  | 1.3000  | 0.0000  | 0.0000 | 3.0000 |
| 3  | 3                                                             | 5  | 83.9753 | 31.0715 | 3.5590  | 0.0000  | 0.8161  | 0.0000  | 0.0000 | 1.1776 |
| 2  | 3                                                             | 5  | 89.8843 | 17.5000 | 3.3660  | 0.0000  | 2.0000  | 0.0000  | 0.0000 | 2.0734 |
| 2  | 6                                                             | 2  | 0.0000  | 49.8261 | 0.2093  | 0.0000  | 2.0870  | 0.0000  | 0.0000 | 2.2895 |
| 2  | 2                                                             | 6  | 0.0000  | 40.0366 | 3.1505  | 0.0000  | 1.1296  | 0.0000  | 0.0000 | 1.1110 |
| 6  | 2                                                             | 6  | 0.0000  | 0.5047  | 0.8000  | 0.0000  | 0.8933  | 0.0000  | 0.0000 | 4.6650 |
| 2  | 6                                                             | 6  | 0.0000  | 8.7037  | 0.0827  | 0.0000  | 3.5597  | 0.0000  | 0.0000 | 1.1198 |
| 3  | 6                                                             | 3  | 0.0000  | 9.2317  | 0.1000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.0920 |
| 6  | 3                                                             | 6  | 0.0008  | 25.0000 | 8.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 3.0000 |
| 2  | 3                                                             | 6  | 66.0423 | 5.0000  | 1.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.2500 |
| 2  | 6                                                             | 3  | 0.0000  | 0.5000  | 0.1000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 3.0000 |
| 3  | 3                                                             | 6  | 70.0000 | 20.0000 | 1.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.2500 |
| 3  | 7                                                             | 3  | 90.0000 | 18.4167 | 0.6799  | -8.0000 | 0.1310  | 0.0000  | 0.0000 | 2.2321 |
| 2  | 3                                                             | 7  | 72.6004 | 9.6150  | 0.8905  | 0.0000  | 3.5473  | 0.0000  | 0.0000 | 1.0400 |
| 3  | 3                                                             | 7  | 60.0000 | 40.0000 | 4.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.0400 |
| 3  | 2                                                             | 7  | 0.0000  | 10.0000 | 1.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.0400 |
| 6  | 3                                                             | 7  | 41.0995 | 3.2207  | 7.3523  | 0.0000  | 0.1101  | 0.0000  | 0.0000 | 1.0947 |
| 7  | 3                                                             | 7  | 62.1312 | 7.5931  | 0.1000  | 0.0000  | 0.5154  | 0.0000  | 0.0000 | 2.1744 |
| 1  | 3                                                             | 7  | 74.1394 | 8.5687  | 1.7132  | 0.0000  | -0.6553 | 0.0000  | 0.0000 | 2.2323 |
| 2  | 7                                                             | 3  | 75.0000 | 25.0000 | 2.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.2500 |
| 3  | 7                                                             | 7  | 70.0000 | 25.0000 | 2.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.2500 |
| 3  | 9                                                             | 3  | 86.0504 | 40.0000 | 2.6582  | 0.0000  | 0.4104  | 0.0000  | 0.0000 | 1.4546 |
| 9  | 3                                                             | 9  | 90.0000 | 7.9508  | 4.6213  | 0.0000  | 2.0000  | 0.0000  | 0.0000 | 1.7772 |
| 3  | 3                                                             | 9  | 60.1752 | 17.8642 | 0.5300  | 0.0000  | 0.7799  | 0.0000  | 0.0000 | 1.1839 |
| 3  | 9                                                             | 9  | 14.8518 | 35.2791 | 0.9053  | 0.0000  | 2.0000  | 0.0000  | 0.0000 | 2.2837 |
| 2  | 3                                                             | 9  | 74.4898 | 20.0000 | 4.3622  | 0.0000  | 2.0000  | 0.0000  | 0.0000 | 2.1145 |
| 1  | 3                                                             | 9  | 90.0000 | 7.6430  | 0.2869  | 0.0000  | 1.8647  | 0.0000  | 0.0000 | 4.0000 |
| 3  | 2                                                             | 10 | 0.0000  | 0.0100  | 0.0100  | 0.0000  | 0.0000  | 0.0000  | 0.0000 | 1.1456 |
| 11 | 1                                                             | 11 | 77.8443 | 49.0744 | 5.9913  | 0.0000  | 0.7835  | 0.0000  | 0.0000 | 2.3020 |
| 1  | 11                                                            | 1  | 0.0000  | 19.9962 | 3.2299  | 0.0000  | 2.1012  | 0.0000  | 0.0000 | 1.1537 |
| 1  | 11                                                            | 11 | 0.0000  | 25.0000 | 1.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.0400 |
| 11 | 1                                                             | 2  | 69.6421 | 10.0000 | 2.0000  | 0.0000  | 1.0000  | 0.0000  | 0.0000 | 1.0400 |
| 58 | ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n |    |         |         |         |         |         |         |        |        |
| 1  | 1                                                             | 1  | 1       | -0.2288 | 32.0663 | 0.0352  | -4.2551 | -1.2672 | 0.0000 | 0.0000 |

|   |   |   |   |         |          |         |          |         |        |        |
|---|---|---|---|---------|----------|---------|----------|---------|--------|--------|
| 1 | 1 | 1 | 2 | -0.2655 | 28.3548  | 0.3551  | -4.6980  | -1.7630 | 0.0000 | 0.0000 |
| 2 | 1 | 1 | 2 | -0.2601 | 36.5651  | 0.3494  | -3.9596  | -2.3355 | 0.0000 | 0.0000 |
| 1 | 1 | 1 | 3 | 1.3805  | 14.5821  | -0.6613 | -2.1128  | -1.0000 | 0.0000 | 0.0000 |
| 2 | 1 | 1 | 3 | 1.9159  | 19.8113  | 0.7914  | -4.6995  | -1.0000 | 0.0000 | 0.0000 |
| 3 | 1 | 1 | 3 | -1.4477 | 16.6853  | 0.6461  | -4.9622  | -1.0000 | 0.0000 | 0.0000 |
| 1 | 1 | 3 | 1 | 0.3850  | 18.9073  | -0.0062 | -2.7168  | -1.0000 | 0.0000 | 0.0000 |
| 1 | 1 | 3 | 2 | 1.2044  | 80.0000  | -0.3139 | -6.1481  | -1.0000 | 0.0000 | 0.0000 |
| 2 | 1 | 3 | 1 | -3.0535 | 25.1061  | 0.6084  | -2.8220  | -3.1846 | 0.0000 | 0.0000 |
| 2 | 1 | 3 | 2 | -2.4875 | 70.8145  | 0.7582  | -4.2274  | -3.0000 | 0.0000 | 0.0000 |
| 1 | 1 | 3 | 3 | -0.3566 | 10.0000  | 0.0816  | -2.6110  | -1.9631 | 0.0000 | 0.0000 |
| 2 | 1 | 3 | 3 | -1.4383 | 80.0000  | 1.0000  | -3.6877  | -2.8000 | 0.0000 | 0.0000 |
| 3 | 1 | 3 | 1 | -1.3224 | 77.8326  | -0.1109 | -4.0881  | -3.8965 | 0.0000 | 0.0000 |
| 3 | 1 | 3 | 2 | -2.5000 | 70.3345  | -1.0000 | -5.5315  | -3.0000 | 0.0000 | 0.0000 |
| 3 | 1 | 3 | 3 | -2.0234 | 80.0000  | 0.1684  | -3.1568  | -2.6174 | 0.0000 | 0.0000 |
| 1 | 3 | 3 | 1 | 1.1637  | -17.3637 | 0.5459  | -3.6005  | -2.6938 | 0.0000 | 0.0000 |
| 1 | 3 | 3 | 2 | -2.1289 | 12.8382  | 1.0000  | -5.6657  | -2.9759 | 0.0000 | 0.0000 |
| 2 | 3 | 3 | 2 | 2.5000  | -22.9397 | 0.6991  | -3.3961  | -1.0000 | 0.0000 | 0.0000 |
| 1 | 3 | 3 | 3 | 2.5000  | -25.0000 | 1.0000  | -2.5000  | -1.0000 | 0.0000 | 0.0000 |
| 2 | 3 | 3 | 3 | -2.5000 | -2.5103  | -1.0000 | -2.5000  | -1.0000 | 0.0000 | 0.0000 |
| 3 | 3 | 3 | 3 | -2.5000 | -25.0000 | 1.0000  | -2.5000  | -1.0000 | 0.0000 | 0.0000 |
| 0 | 1 | 2 | 0 | 0.0000  | 0.0000   | 0.0000  | 0.0000   | 0.0000  | 0.0000 | 0.0000 |
| 0 | 2 | 2 | 0 | 0.0000  | 0.0000   | 0.0000  | 0.0000   | 0.0000  | 0.0000 | 0.0000 |
| 0 | 2 | 3 | 0 | 0.0000  | 0.1000   | 0.0200  | -2.5415  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 1 | 1 | 0 | 0.0000  | 50.0000  | 0.3000  | -4.0000  | -2.0000 | 0.0000 | 0.0000 |
| 0 | 3 | 3 | 0 | 0.5511  | 25.4150  | 1.1330  | -5.1903  | -1.0000 | 0.0000 | 0.0000 |
| 0 | 1 | 4 | 0 | 1.7932  | 141.5515 | 0.9686  | -4.2368  | -1.9727 | 0.0000 | 0.0000 |
| 0 | 2 | 4 | 0 | -1.5000 | 0.1032   | 0.0100  | -5.0965  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 3 | 4 | 0 | 1.1397  | 61.3225  | 0.5139  | -3.8507  | -3.0000 | 0.0000 | 0.0000 |
| 0 | 4 | 4 | 0 | 0.7265  | 44.3155  | 1.0000  | -4.4046  | -2.0000 | 0.0000 | 0.0000 |
| 4 | 1 | 4 | 4 | -0.0949 | 8.7582   | 0.3310  | -7.9430  | -2.0000 | 0.0000 | 0.0000 |
| 0 | 1 | 5 | 0 | 3.3423  | 30.3435  | 0.0365  | -2.7171  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 5 | 5 | 0 | -0.0555 | -5.0000  | 0.1515  | -2.2056  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 2 | 5 | 0 | 0.0000  | 0.0000   | 0.0000  | 0.0000   | 0.0000  | 0.0000 | 0.0000 |
| 2 | 3 | 5 | 3 | 2.5000  | 2.5000   | 0.2237  | -10.0000 | -1.0000 | 0.0000 | 0.0000 |
| 0 | 3 | 5 | 0 | -2.5000 | 50.0000  | -0.5000 | -10.0000 | -1.0000 | 0.0000 | 0.0000 |
| 0 | 6 | 6 | 0 | 0.0000  | 0.0000   | 0.1200  | -2.4426  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 2 | 6 | 0 | 0.0000  | 0.0000   | 0.1200  | -2.4847  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 3 | 6 | 0 | 0.0000  | 0.0000   | 0.1200  | -2.4703  | 0.0000  | 0.0000 | 0.0000 |
| 1 | 1 | 3 | 3 | -0.0002 | 20.1851  | 0.1601  | -9.0000  | -2.0000 | 0.0000 | 0.0000 |
| 1 | 3 | 3 | 1 | 0.0002  | 80.0000  | -1.5000 | -4.4848  | -2.0000 | 0.0000 | 0.0000 |
| 3 | 1 | 3 | 3 | -0.1583 | 20.0000  | 1.5000  | -9.0000  | -2.0000 | 0.0000 | 0.0000 |
| 1 | 1 | 1 | 7 | -0.3232 | 14.3871  | 0.1823  | -9.8682  | -1.7255 | 0.0000 | 0.0000 |
| 7 | 1 | 1 | 7 | -0.1452 | 50.0000  | -0.1915 | -8.0773  | -1.7255 | 0.0000 | 0.0000 |
| 0 | 1 | 7 | 0 | 4.0000  | 45.8264  | 0.9000  | -4.0000  | 0.0000  | 0.0000 | 0.0000 |
| 0 | 7 | 7 | 0 | 4.0000  | 45.8264  | 0.9000  | -4.0000  | 0.0000  | 0.0000 | 0.0000 |
| 2 | 1 | 3 | 7 | -1.5000 | 18.9285  | 0.3649  | -6.1208  | 0.0000  | 0.0000 | 0.0000 |

|    |                                                  |    |    |         |         |         |          |         |        |        |
|----|--------------------------------------------------|----|----|---------|---------|---------|----------|---------|--------|--------|
| 2  | 3                                                | 7  | 3  | 1.5000  | -1.0000 | 0.2575  | -6.2100  | 0.0000  | 0.0000 | 0.0000 |
| 1  | 3                                                | 7  | 3  | -1.4375 | -0.8700 | 0.9861  | -2.5424  | 0.0000  | 0.0000 | 0.0000 |
| 7  | 3                                                | 7  | 3  | -1.5000 | 21.5086 | -1.0000 | -4.8869  | 0.0000  | 0.0000 | 0.0000 |
| 2  | 1                                                | 3  | 9  | 0.0000  | 84.3556 | 0.1000  | -3.1953  | 0.0000  | 0.0000 | 0.0000 |
| 1  | 1                                                | 3  | 9  | 0.0000  | 51.0461 | 0.1059  | -7.2043  | 0.0000  | 0.0000 | 0.0000 |
| 2  | 3                                                | 9  | 3  | 0.0000  | 0.1000  | -0.3000 | -4.3862  | 0.0000  | 0.0000 | 0.0000 |
| 1  | 1                                                | 1  | 11 | 0.5000  | 0.1000  | 0.4683  | -11.5274 | -1.7255 | 0.0000 | 0.0000 |
| 2  | 1                                                | 1  | 11 | 0.0000  | 49.3871 | 0.2000  | -10.5765 | -1.7255 | 0.0000 | 0.0000 |
| 11 | 1                                                | 1  | 11 | -0.5000 | 95.4727 | -0.2080 | -4.8579  | -1.7255 | 0.0000 | 0.0000 |
| 0  | 1                                                | 11 | 0  | 4.0000  | 45.8264 | 0.9000  | -4.0000  | 0.0000  | 0.0000 | 0.0000 |
| 0  | 11                                               | 11 | 0  | 4.0000  | 45.8264 | 0.8897  | -4.0000  | 0.0000  | 0.0000 | 0.0000 |
| 9  | ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1 |    |    |         |         |         |          |         |        |        |
| 3  | 2                                                | 3  |    | 2.1200  | -3.5800 | 1.4500  | 19.5000  |         |        |        |
| 3  | 2                                                | 4  |    | 1.6787  | -3.9601 | 1.4500  | 19.5000  |         |        |        |
| 4  | 2                                                | 3  |    | 1.5585  | -3.9305 | 1.4500  | 19.5000  |         |        |        |
| 4  | 2                                                | 4  |    | 1.9336  | -5.8831 | 1.4500  | 19.5000  |         |        |        |
| 3  | 2                                                | 5  |    | 1.5000  | -2.0000 | 1.4500  | 19.5000  |         |        |        |
| 4  | 2                                                | 5  |    | 1.5000  | -2.0000 | 1.4500  | 19.5000  |         |        |        |
| 5  | 2                                                | 3  |    | 1.5000  | -2.0000 | 1.4500  | 19.5000  |         |        |        |
| 5  | 2                                                | 4  |    | 1.5000  | -2.0000 | 1.4500  | 19.5000  |         |        |        |
| 5  | 2                                                | 5  |    | 1.5000  | -2.0000 | 1.4500  | 19.5000  |         |        |        |

## Chapter 5

### 5 Summary & Outlook

This dissertation establishes a mechanistic framework for understanding how local chemical architecture governs the long-term performance of reactive and degradable polymer systems. Across both high-performance flat-flex cable adhesives and UV-cured thiol-ene resins, the central finding is that macroscopic behavior is controlled not simply by overall composition, but by the local molecular environment that directs reaction pathways, constrains structural rearrangement, and determines how chemistry is translated into functional performance.

For flat-flex cable assemblies, this work identifies butyl acrylate-co-acrylonitrile (BA-AN) as the life-limiting polymeric component under humid aging conditions. Accelerated aging following by high potential breakdown and peel testing showed substantial losses in both dielectric and mechanical performance, reaching 15.4% and 62.2%, respectively after 140 days at 70 °C and 70% relative humidity. ATR-FTIR analysis of the cable polymerics revealed that degradation signatures arise in BA-AN rather than in PMDA-ODA, directly implicating the adhesive as the origin of macroscopic property loss. The spectral evolution further showed that hydrolysis occurs primarily at the ester carbonyl and nitrile functionalities, generating a chemically heterogeneous population that includes acids, alcohols, amides, and amidines. Kinetic modeling based on water diffusion and time-resolved ATR-FTIR measurements yielded apparent activation barriers of nominally 40 kcal/mol for both ester and nitrile hydrolysis. However, a mechanistic model demonstrated that only nitrile hydrolysis is strongly coupled to dielectric and peel strength decay, whereas ester hydrolysis is comparatively benign. This distinction provides a predictive basis for service-life estimation and leads to the projection that cables exposed for

five years at 25 °C and 70% relative humidity will experience approximately 14% dielectric loss and 50% peel strength loss.

The computational studies in this dissertation explain why nitrile hydrolysis is uniquely damaging. By combining steered molecular dynamics with a DFTB framework, conformational sampling with CREST, and DFT-based spectral and electronic analysis, this work resolves both the likely sequence architecture of the adhesive and the reactive pathways accessible within that environment. Comparison between computed and experimental spectra indicates that a 5:12 BA:AN molar ratio, corresponding to a 1:1 weight formulation, provides the most realistic description of the unaged adhesive. Within this architecture, short AN-rich blocks create a crowded local environment that suppresses simple terminal hydrolysis and instead promotes sequence-dependent nitrile reactivity. Although ester hydrolysis is more favorable thermodynamically, nitrile hydrolysis becomes kinetically privileged because the local sequence environment selectively channels reaction toward nitrogen-rich intermediates. In particular, the pathway to cyclic amidine formation emerges as the dominant branch, even though it requires substantial non-equilibrium structural work. This result shows that the decisive barrier in the aged adhesive is not purely chemical, but mechanostructural, namely the energetic cost of reorganizing the polymer matrix to enable reaction. Once formed, amidine species become trapped intermediates, preventing complete conversion to terminal acid products and preserving a chemically and electronically distinct aged state.

This trapped amidine-rich state also provides the molecular origin of dielectric instability. Deconvolution of the aged ATR-FTIR spectrum using computed product spectra reproduces the dominant nitrogenous product distribution and captures the disparity between overall chemical degradation and measured property loss. Electronic-structure analysis shows that the aged 5:12

architecture experiences only a modest reduction in average band gap, but a much larger increase in transition dipole moment. This identifies dipolar amplification, rather than gap collapse, as the dominant contributor to dielectric decay. The resulting electronic quality factor closely reproduces the experimentally measured reduction in breakdown strength, demonstrating that sequence-specific hydrolysis products can be linked quantitatively to macroscopic electrical failure. More broadly, these results show that the same local sequence architecture that governs hydrolysis also determines whether degradation remains chemically diffuse or becomes concentrated into electronically and mechanically damaging intermediates.

The outlook for the cable-aging work is clear. Future studies should examine the role of copper transport within the assembly and its coupling to adhesive degradation. Copper migration may contribute directly to the discrepancy between spectroscopically inferred degradation and the larger mechanically inferred loss, and it may also provide the dominant kinetics governing cable lifetime. Establishing the interplay among water ingress, adhesive hydrolysis, and metal transport will therefore be essential for building a more complete predictive model of flat-flex cable service life.

The second major outcome of this dissertation is the development of a reactive force field for UV-cured thiol-ene chemistry relevant to volumetric additive manufacturing. Here, a C/H/O/N/S ReaxFF framework was parameterized against DFT reference data to model photo-initiated radical polymerization in a TME-ICN/TEGDAE resin system. The resulting force field captures the sterically hindered reactive environment of the resin and provides a mechanistic explanation for the experimentally observed tensile response. In particular, the simulations indicate that steric crowding limits efficient propagation and promotes premature termination, thereby suppressing network formation. This behavior is fully consistent with the measured low

modulus and high strain-to-failure. The force field therefore serves not only as a fitted computational model, but as a mechanistic tool for interpreting how monomer structure controls polymerization dynamics and final material properties. Extending this framework to less sterically congested thiol-ene systems will provide an important next step in establishing its generality and utility for resin design.

Together, the results of this dissertation show that molecular-scale environment is the decisive mediator between chemistry and performance. In degradative systems, local architecture determines which reactions occur, which intermediates accumulate, and which properties fail first. In reactive systems, local steric and electronic structure governs how efficiently polymer networks form and, therefore, how mechanical properties emerge. The broader implication is that thermodynamic favorability alone is often insufficient to predict material behavior. Instead, sequence distribution, steric confinement, transport limitations, and non-equilibrium structural work must all be considered as determinants of performance. By integrating experiment with predictive simulation, this dissertation provides both a mechanistic explanation of existing materials behavior and a transferable framework for the design of more durable adhesives and more effective photopolymer resins.