Analytical guidelines for coating formulation

FROM TRIAL-AND-ERROR TO PREDICTIVE MODELING

COOCK+ ADDBIO

DELIVERABLE D3.2



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2. Stepwise guidance tool
3. Analytical techniques

Introduction

Introduction

ANALYTICAL COATING DESIGN

- Implementing an **analytical coating formulation approach** means formulating coatings based on measured chemical, physical, and performance data rather than trial-and-error experimentation. Analytical chemistry becomes the foundation for understanding composition–structure–property relationships and optimizing formulations. Implementing an analytical coating formulation approach involves shifting coating development from a predominantly empirical, trial-and-error process toward a data-driven methodology based on scientific understanding of composition, structure, processing, and performance relationships. In this approach, analytical chemistry and material characterization techniques provide quantitative information that guides formulation decisions, accelerates development, reduces raw material consumption, and improves product robustness.

- For predictive coating design, **additive–matrix interactions** are often more important than the additive concentration itself. In an epoxy coating, a dispersant, toughener, silane, wax, corrosion inhibitor, or bio-based additive only works because it changes the epoxy network, interphase, filler dispersion, or transport properties. The real power of an analytical coating formulation approach is not characterization itself—it's using analytical data to predict coating performance before running long-term tests.

Introduction

PERFORMANCE = CONTROLLING ADDITIVE VERSUS BINDER INTERACTIONS

Weak interaction → Acts as a filler → Small property change → Migration possible → Poor long-term durability

Strong interaction → Becomes part of the network → Large property change → Stable incorporation → Better long-term durability

Mechanism	Example	Possible effects
Hydrogen bonding (intermolecular forces between polar groups)	Cellulose in acrylic, lignin in polyurethane, tannin in epoxy, starch in polyester	Higher modulus (e.g. storage modulus E'), higher Tg, reduced chain mobility, better barrier performance, reduced permeability, BUT higher viscosity, moisture sensitivity
Covalent bonding (additive becomes chemically incorporated into the network)	Silane coupling agent	Higher crosslinking density, improved adhesion, lower water uptake, better stress transfer, improved corrosion resistance
Ionic interaction (Electrostatic attraction between charged groups)	Functional dispersant, waterborne coatings, bio-based dispersions, latex systems	Stronger film formation, better adhesion, improved dispersion stability, BUT strong pH sensitivity
Physical entanglement (Polymer chains interpenetrate each other)	Polymer toughener in epoxy (e.g. epoxidized vegetable oilsbio-polyolselastomer modifiers)	Higher impact resistance, improved flexibility, crack resistance, BUT possible Tg reduction
Interfacial adsorption	Pigment dispersant (dispersants, wetting agents)	Lower viscosity, better gloss, improved color development, higher storage stability, BUT migration

Introduction

FROM EMPIRICAL FORMULATION TO KNOWLEDGE-BASED DESIGN

- Traditional coating formulation often relies on iterative adjustments of binders, pigments, fillers, solvents, and additives until the desired performance is achieved. While effective, this approach can be time-consuming and may not reveal the underlying reasons for success or failure.

- **An analytical formulation strategy seeks to answer fundamental questions such a**s:
    - What is the exact chemical composition of the coating?
    - How are the components distributed within the film?
    - How do molecular interactions influence rheology, film formation, and curing?
    - Which formulation parameters most strongly affect durability, adhesion, barrier properties, or appearance?
    - How can performance be predicted before extensive testing?
    - By understanding these relationships, formulators can design coatings with greater precision and confidence.

Introduction

BUILDING COMPOSITION–STRUCTURE–PROPERTY RELATIONSHIPS

Composition

- Resin/binder chemistry
- Crosslinkers and curing agents
- Pigments and fillers
- Solvents or water phase
- Functional additives
- Surface modifiers

Microstructure

- Particle size distribution
- Pigment dispersion quality
- Crosslink density
- Porosity
- Surface roughness
- Phase separation
- Interfacial interactions

Properties

Mechanical Properties

- Hardness
- Impact resistance
- Elasticity
- Scratch resistance

Physical Properties

- Viscosity
- Glass transition
- Surface energy
- Thermal stability

Chemical Properties

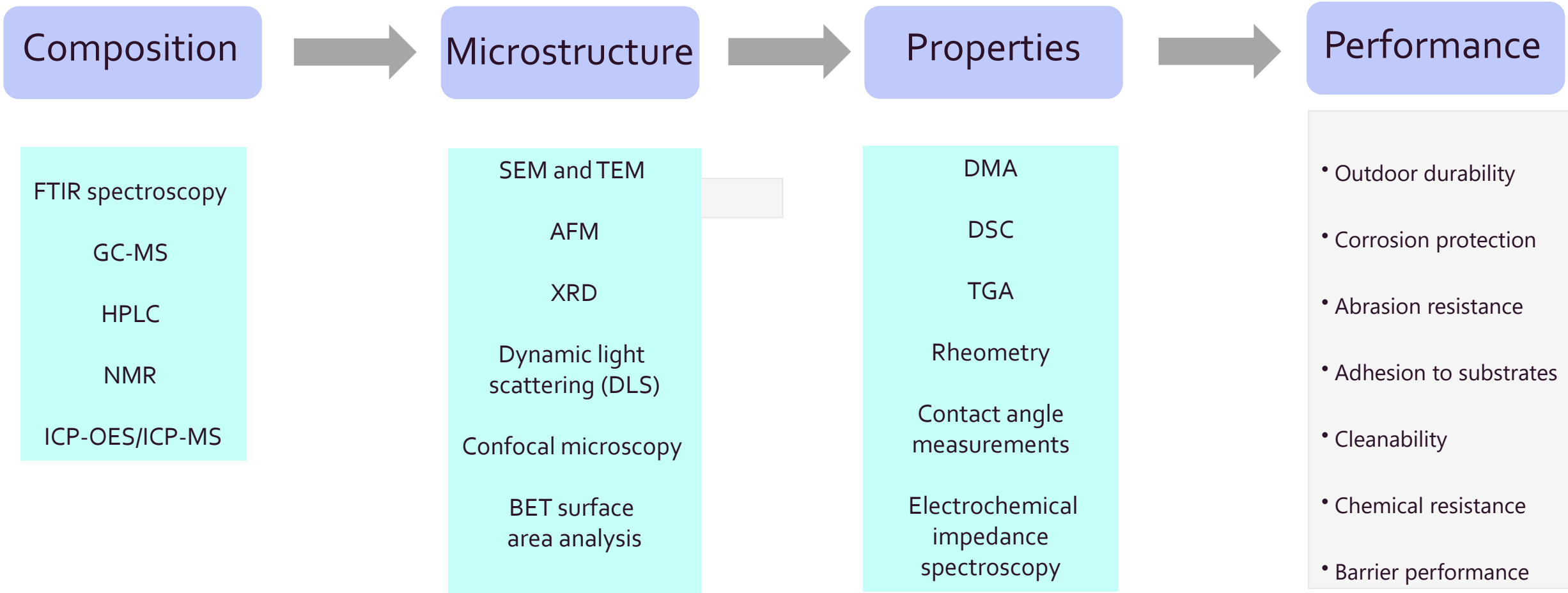
- Solvent resistance
- UV stability
- Corrosion resistance
- Water uptake

Performance

- Outdoor durability
- Corrosion protection
- Abrasion resistance
- Adhesion to substrates
- Cleanability
- Chemical resistance
- Barrier performance

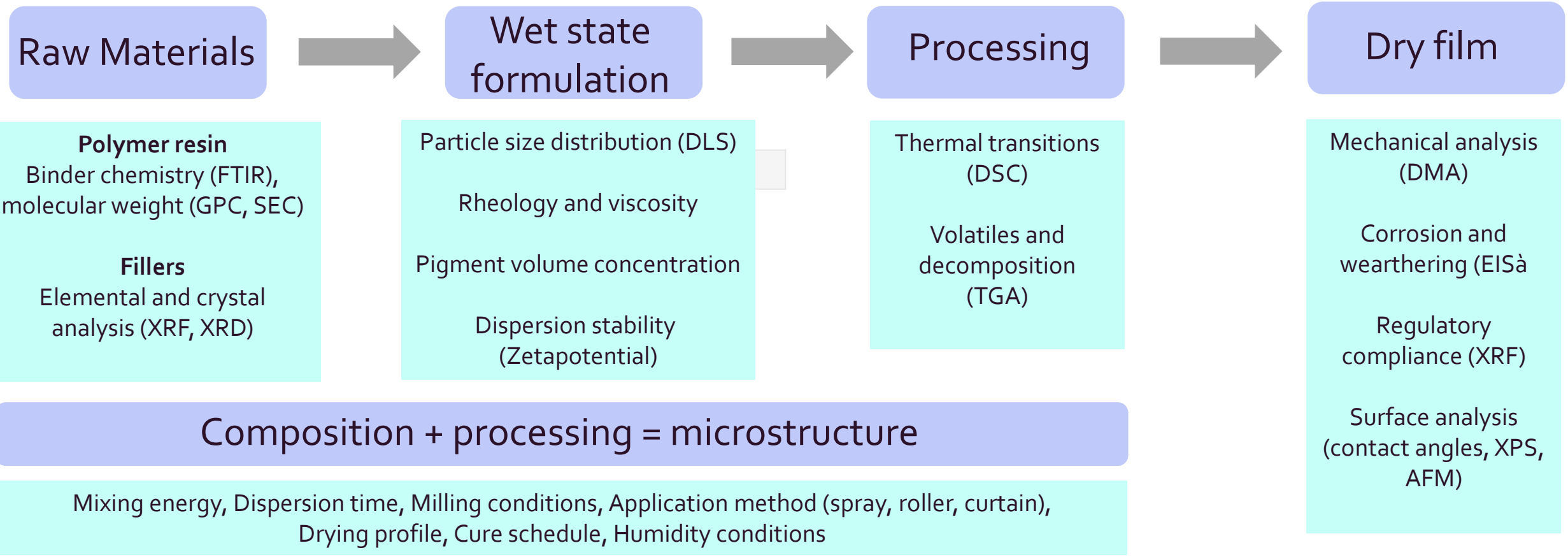
Introduction

BUILDING COMPOSITION–STRUCTURE–PROPERTY RELATIONSHIPS



Introduction

ANALYTICAL PROCEDURES DURING COATING FORMULATION AND APPLICATION



Introduction

BUILD A HIERARCHY OF PREDICTIVE PARAMETERS

Most coating failures originate from a limited number of underlying material parameters. The goal is to identify measurable analytical descriptors that drive performance.

Performance property	Direct test	Predictive analytical parameters
Corrosion protection	Salt spray	Crosslink density, water uptake, porosity
Adhesion	Pull-off test	Surface energy, functionality, cure degree
Scratch resistance	Scratch test	Tg, modulus, crosslink density
UV stability	Weathering	Chemical bond composition, stabilizer concentration
Water barrier	Immersion	Free volume, hydrophobicity
Chemical resistance	Solvent rub	Network density, polarity
Durability	Outdoor exposure	Combination of above

Practical example

BUILDING COMPOSITION–STRUCTURE–PROPERTY RELATIONSHIPS

Consider the development of a waterborne anti-corrosion coating incorporating bio-based binders and additives. Instead of testing dozens of formulations randomly, the analytical approach would:

- Characterize binder chemistry by **FTIR** and **NMR**.
- Measure **particle size** and dispersion quality.
- Monitor curing by **DSC** and rheology.
- Determine crosslink density using **DMA**.
- Evaluate barrier properties using **EIS**.
- Correlate analytical data with salt-spray performance.
- Build predictive models linking formulation parameters to corrosion protection.

By correlating laboratory measurements with field results, predictive models can be developed that reduce the need for extensive long-term testing. The result is a scientifically optimized coating developed faster, with fewer experiments and a deeper understanding of performance drivers.

DoE appraoch

DATA-DRIVEN FORMULATION OPTIMIZATION

- Rather than changing one component at a time, analytical formulation uses structured experimentation.
- Design of Experiments (DoE) allows simultaneous investigation of multiple formulation variables:

Variable	Examples
Binder content	25–40 wt%
Filler loading	10–35 wt%
Dispersant level	0.1–2 wt%
Crosslinker ratio	0.8–1.2 stoichiometric ratio

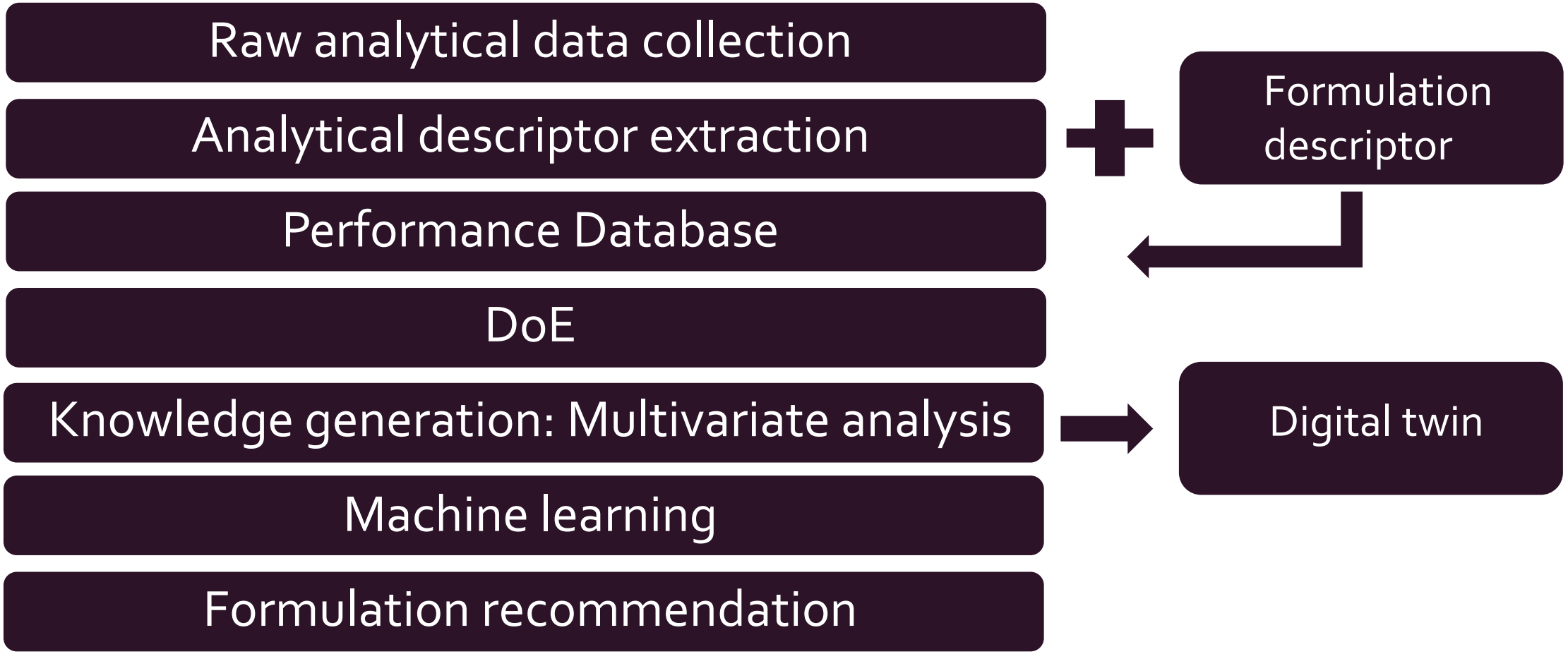
Statistical analysis identifies:

- Significant factors
- Interactions between components
- Optimal formulation windows

This approach dramatically reduces the number of experimental trials required.

DoE appraoch

DATA HIERARCHY AND DIGITALIZATION: FROM ANALYTICS TO DIGITAL FORMULATION



DoE appraoch

INTEGRATION OF ADVANCED ANALYTICS

Modern coating development increasingly incorporates

Multivariate Data Analysis

Large datasets generated by analytical measurements can be processed using:

- Principal Component Analysis (PCA): Which variables move together?
- Partial Least Squares Regression (PLS): Which analytical parameters drive performance?
- Machine Learning algorithms: Formulation+Analytics+Performance

These methods uncover hidden relationships between chemistry and performance that may not be visible through conventional analysis.

Example:

A PLS model may reveal that corrosion resistance is more strongly influenced by pigment particle size distribution and crosslink density than by total pigment loading.

Once sufficient analytical and performance data have been collected, **predictive models can estimate:**

- Viscosity
- Cure behavior
- Mechanical strength
- Barrier properties
- Corrosion resistance
- Service life

before a formulation is physically prepared.

This significantly accelerates product development and reduces material waste.

Examples for functional coating design

Example: corrosion resistance

Chemical descriptors

- FTIR
- XPS
- DSC
- EIS

Key parameters

- Crosslink density
- OH concentration
- Epoxy conversion
- Water absorption

Possible predictive model

Corrosion resistance (hours SST) =

X + 12 × crosslink density - 8 × water uptake + 5 × coating thickness – 10 x porosity

numbers are indicative

Example: water barrier properties

Chemical descriptors

- FTIR
- DSC
- Sorption measurement

Key parameters

- Tg
- Hydroxyl content
- Polarity
- Crystallinity
- Diffusion coefficient

More OH groups
↓
More water absorption
↓
Higher permeability
↓
Lower protection

Examples for functional coating design

Example: scratch and abrasion resistance

Chemical descriptors

- DSC
- DMA
- Hardness
- Nanoindentation

Key parameters

- Tg
- Storage modulus
- Elastic modulus
- Loss modulus
- tan δ
- Crosslink density

Possible predictive model

Scratch resistance

= 0.4 x Tg + 0.5 x storage modulus

+ 0.1 x crosslink density

numbers are indicative

Example: coating adhesion

Chemical descriptors

- FTIR
- XPS
- Contact angles
- Topography

Key parameters

- Functional groups
- Polarity, surface energy
- Roughness

Adhesion = f (surface energy match, functional group density, cure degree, roughness)

Benefits for Sustainable Coating Development

Reduced Experimental Waste

- Fewer trial batches
- Lower raw material consumption
- Reduced solvent use
- Less analytical rework

Improved Resource Efficiency

- Higher first-time-right success rates
- Optimized additive loading
- Reduced over-engineering

Facilitation of Renewable Materials

For bio-based and circular raw materials, analytical characterization is particularly important because these feedstocks often exhibit greater variability than fossil-based products. Detailed measurement of:

- Functional group content
- Molecular weight distributions
- Impurity profiles
- Thermal behavior

helps ensure consistent coating performance despite renewable feedstock variability.

Conclusion

Formulate → Test → Reformulate → Retest

An analytical coating formulation approach transforms coating development from an empirical art into a predictive science. By leveraging analytical chemistry, material characterization, statistical design, and data analytics, formulators can establish robust composition–structure–property relationships, optimize formulations more efficiently, reduce development costs, and accelerate innovation.

This methodology is particularly valuable for advanced sustainable coatings, bio-based materials, and circular economy applications, where understanding material variability and performance mechanisms is essential for successful product development.

A shift from data to prediction

Measure → Predict → Optimize → Validate

Raw materials → Analytics → Database → DoE → ML → Optimized formulation

Stepwise guidance tools

Step 1: Define coating performance targets

Start by translating customer requirements into measurable properties:

- Adhesion
- Corrosion resistance
- Scratch resistance
- UV durability
- Water barrier properties
- Gloss and appearance
- VOC content
- Cure speed
- Rheology and application behavior

These become your Critical Quality Attributes (CQAs).

Step 2: Build a formulation knowledge matrix

For every raw material, characterize:

Component	Analytical Technique	Information Obtained
Resin/binder	FTIR, NMR, GPC/SEC	Functional groups, molecular weight
Pigments	XRF, XRD, ICP-OES	Elemental and crystalline composition
Additives	HPLC, GC-MS	Identity and concentration
Fillers	Particle size analysis, SEM	Morphology and size distribution
Solvents	GC-FID, GC-MS	Purity and composition

Techniques such as FTIR, chromatography, particle-size analysis, and X-ray methods are widely used for coating characterization and formulation development.

Step 3: Establish structure-property relationships

Measure:

- Molecular weight (GPC)
- Glass transition temperature (DSC)
- Particle size (laser diffraction)
- Viscosity (rheometer)

Correlate with:

- Film formation
- Hardness
- Block resistance
- Adhesion

Develop predictive models such as

Hardness = f(Tg, crosslink density)

Gloss = f(particle size distribution)

Corrosion resistance = f(film porosity)

Viscosity = f(solid content + dispersant dosage)

This creates an analytical foundation for formulation decisions instead of empirical adjustments.

Step 4: Apply Design of Experiment (DoE)

Select formulation factors:

- Resin concentration
- Additive concentrations
- Pigment volume concentration (PVC)
- Dispersant level
- Rheology modifier dosage
- Crosslinker ratio

Measure responses:

- Viscosity
- Gloss
- Adhesion
- Salt spray performance
- Drying time

Use statistical software to generate predictive equations and identify optimal formulation windows.

This is analogous to an Analytical Quality by Design (AQbD) framework.

Step 5: Implement advanced analytical monitoring

Chemical composition (FTIR)
- Verify resin chemistry
- Monitor curing degree
- Detect monomeric residues
- Detect solvent residues
- Detect degradation
- Check crosslink density
- Verify additive/matrix interactions

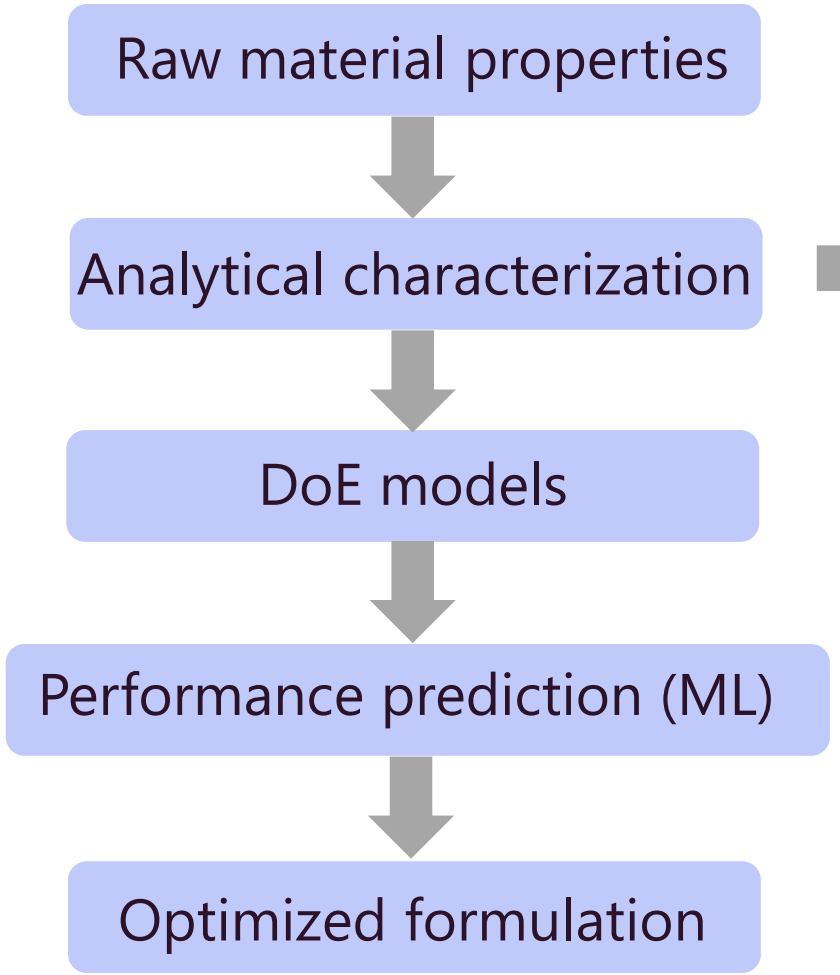
Thermal behavior (DSC, DMA)
- Glass transition temperature
- Melting temperature
- Degree of cure
- Unreacted species
- Crystallinity
- Crosslink density
- Additive interactions

Surface chemistry (XPS/AES, FTIR)
- Surface contamination
- Surface functionalization
- Surface activity/activation
- Adhesion failure mechanisms
- Surface oxidation

Morphology (SEM)
- Pigment dispersion
- Coating defects: pinholes, voids, cracks
- Cross-sectional analysis: delamination, interface adhesion

Rheology (rotational, oscillatory)
- Sag resistance
- Leveling
- Storage stability
- Application performance

Step 6: Develop predictive models



Create an analytical formulation database, including

- Raw material analytical data
- Formulation compositions
- Rheological profiles
- FTIR fingerprints
- Mechanical test results
- Durability data

This allows future formulations to be designed from historical analytical knowledge rather than starting from scratch.

Examples:

- Machine learning (ML) prediction of corrosion resistance, weatherability, barrier performance from analytical descriptors
- PVC optimization from pigment characteristics
- Viscosity prediction from particle size distribution
- Durability prediction from crosslink density

Step 6: Develop predictive models

EXAMPLE WORKFLOW FOR A BIO-BASED PROTECTIVE COATING

Characterize bio-based resin:

- FTIR
- GPC
- DSC

Characterize fillers:

- XRF
- FTIR
- PSD
- SEM

Build regression model, e.g.:

Corrosion resistance = 0.45(crosslink density)

+ 0.30(filler aspect ratio) - 0.25(water uptake)

Formulate using DoE:

- Resin/filler ratio
- Crosslinker level
- Dispersant dosage

Measure:

- Rheology
- Adhesion
- Water uptake
- Corrosion resistance

Analytical Techniques

Analytical Techniques

OVERVIEW OF SELECTED TECHNIQUES FOR ASSISTED COATING FORMULATION

- **Chemical Properties**
  Structural: FTIR, XRD
  Elemental/compositional: XRF, ICP-OES/ICP-MS, GC/MS, Pyr-GC/MS, HPLC, LC-MS
  Advanced mapping: Raman, ToF-SIMS
- **Thermal Properties**
  DSC, TGA
- **Thermo-Mechanical Properties**
  DMA
- **Mechanical properties**
  Nanoindentation, hardness
- **Physico-chemical Properties**
  PSD, Zetapotential
  Rheology
  Contact angles
  BET surface analysis

FTIR

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Coating binder

- Polymer functionality
  e.g. acrylate, epoxy, PUR
- Polymer conversion ratio (epoxy, PUR)
  e.g. C=O, NCO, epoxy peak area
- Crosslinking with hardener (network formation)
- Residual solvent
- Free hardener/resin
- Free/bonded hydrogen groups (reactivity)
- Matrix degradation (processing)

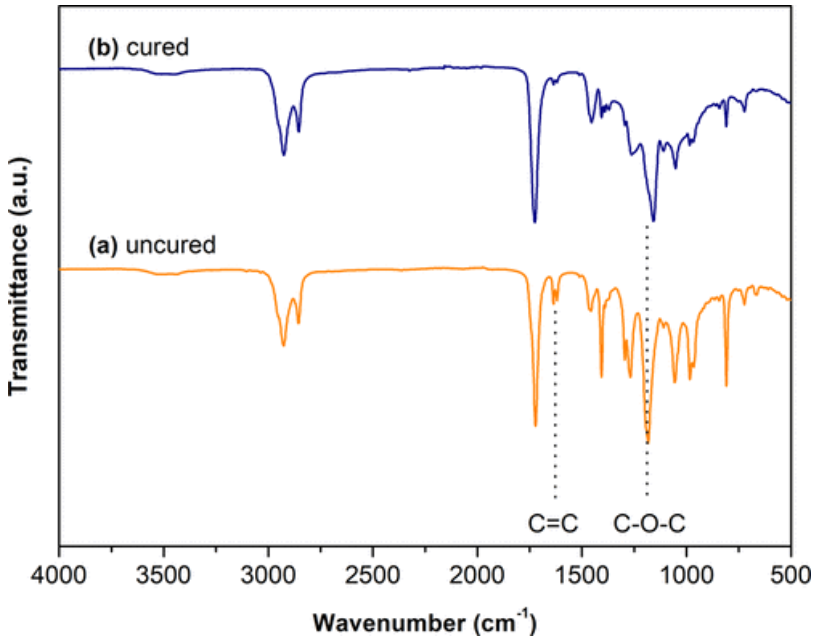
Mostly quantitatively or relatively, except after extensive calibration

Coating additives

- Surface functionalization
  e.g. siloxane
- Chemical identity (class)
- Crystallinity
- Chemical interaction with matrix:
  e.g. physical OH bonding (H bonding index), chemical covalent bonding

FTIR

EXAMPLE: CROSSLINKING OF ACRYLATE COATINGS



UV curing of acrylate coating:

- Reduction in C=C double bond at 1627, 1407, 806 cm^{-1}
- Shifting of C-O-C ester group from 1188 to 1156 cm^{-1}

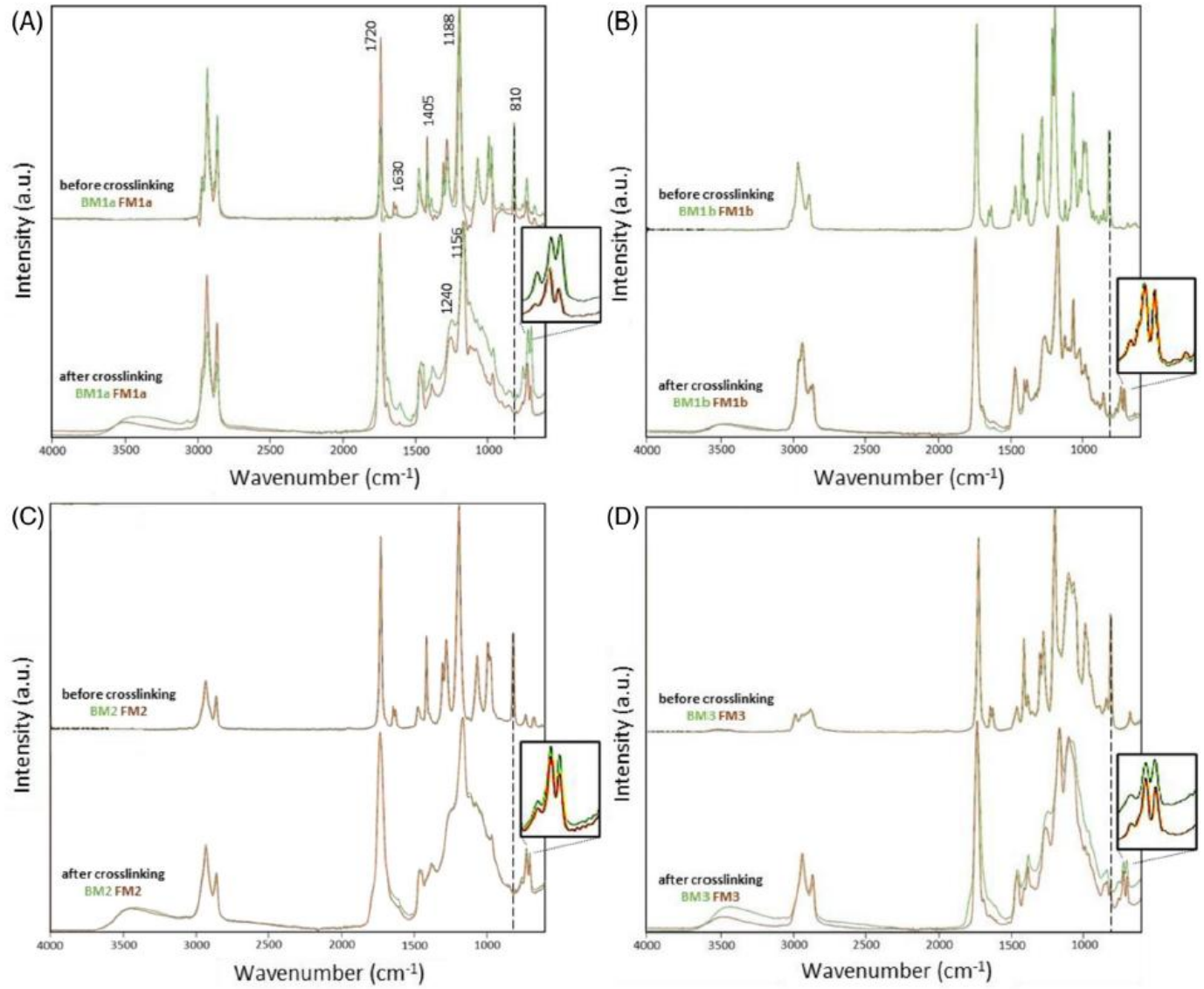


FIGURE 9 FTIR spectra before and after photochemical crosslinking of bio-based acrylates (green lines) and fossil-based acrylates (brown line) of different composition, (A) BM1a and FM1a, (B) BM1b and FM1b, (C) BM2 and FM2, (D) BM3 and FM3.

DSC

DIFFERENTIAL SCANNING CALORIMETRY: THERMAL SCAN OR ISOTHERMAL

Coating binder

- Glass transition temperature
- Melting temperature
- Crystallinity
- Crosslinking degree (degree of cure)
- Curing energy (thermal)
- Heat capacity (Δcp)
- Enthalpy (ΔHm)
- Free resin/hardener
- Crosslinking (curing) kinetics
- Aging effects
- Polymer structure (copolymer segments)

Coating additives

- Interactions with matrix

  e.g. fostering or hindering curing
- Miscibility, compatibility and blending, mixing homogeneity

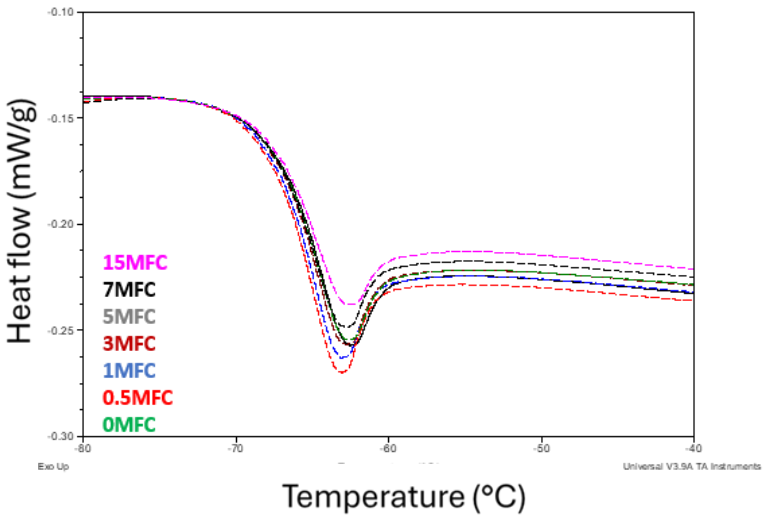
  e.g. double or single melting peaks and/or Tg
- Plasticizing effect (Tg decrease)
- Nucleating effect
- Release properties
- (Thermal and oxidative stability)

DSC

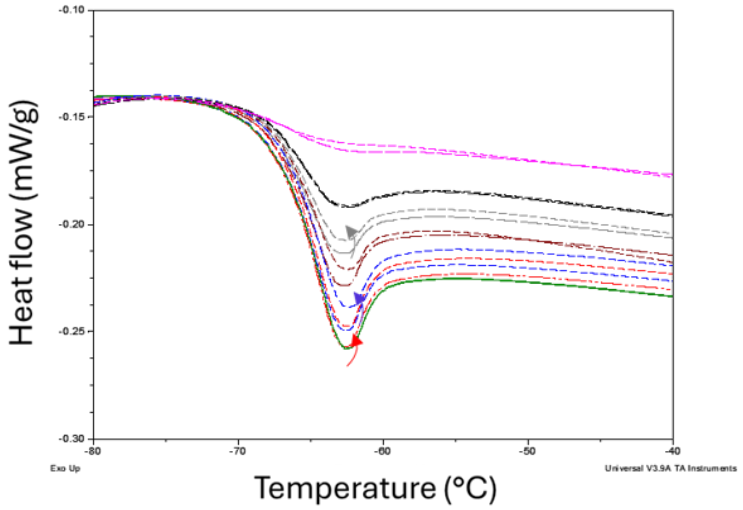
EXAMPLE: FILLER-MATRIX INTERACTIONS FOR NANOCELLULOSE AND DIFFERENT BINDERS (CURING)

Natural rubber with nanocellulose (non-cured latex mixture)

DSC first scan, non-cured NR+MFC



DSC first and second scan, non-cured NR+mMFC



Very minor but consistent variations in Tg transition related to reinforcement in the matrix and reactivity under curing of natural rubber with different nanocellulose grades and concentrations

P. Samyn, unpublished results

Bio-epoxy coating with nanocellulose grades CNF, mMFC, CNC

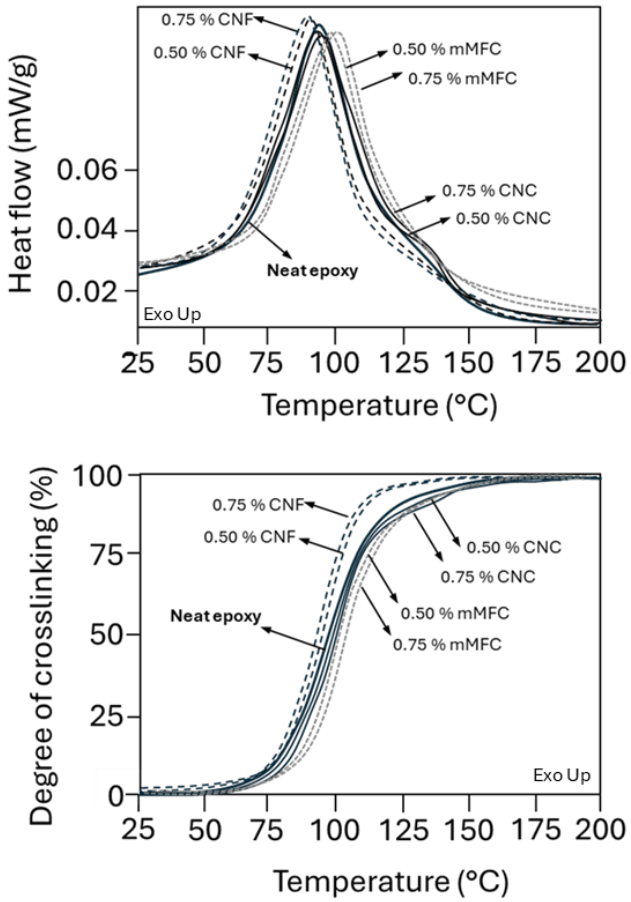


Figure 3. DSC measurements on liquid epoxy resin samples with different micro- and nanocellulose additives at 0.5 and 0.75 wt.% concentrations, including the (**a**) exothermal reaction peak and (**b**) degree of conversion.

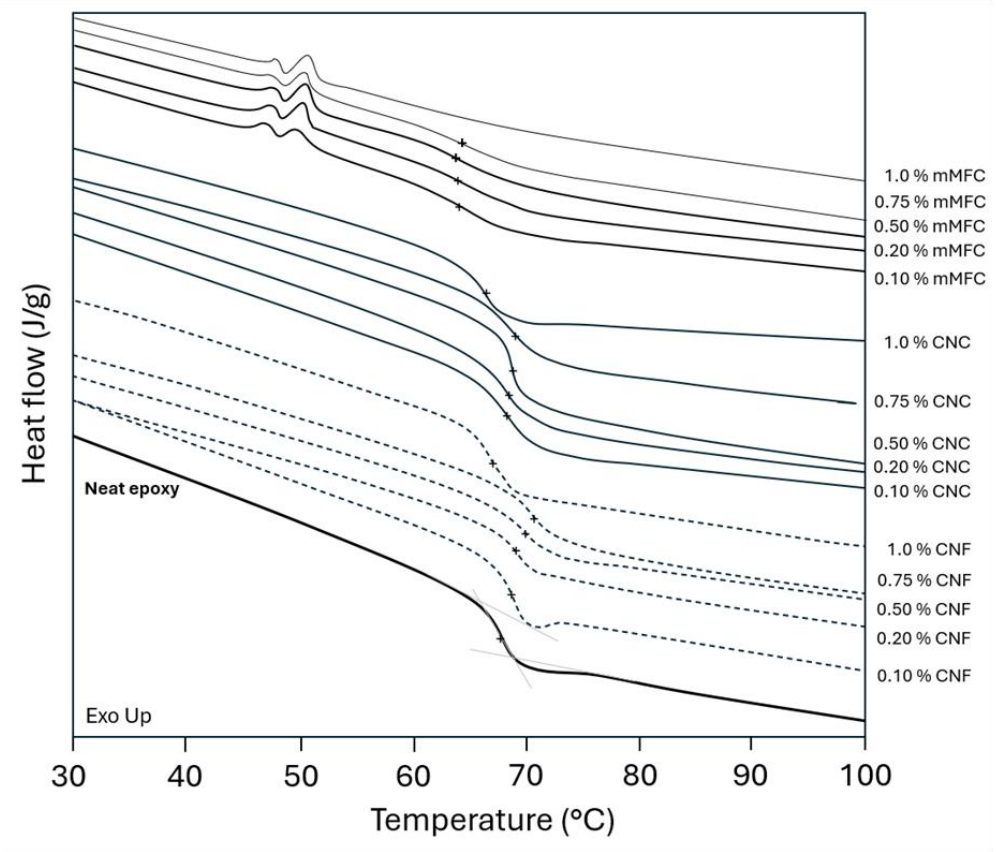
innovation forward

P. Samyn et al., Nanocellulose grades with different morphologies and surface modification as additives for waterborne epoxy coatings. Polymers **2024**, 16, 1095

DSC

EXAMPLE: EFFECT OF NANOCELLULOSE FILLERS ON CURING PROPERTIES

vb. Bio-epoxy coating met nanocelluloe



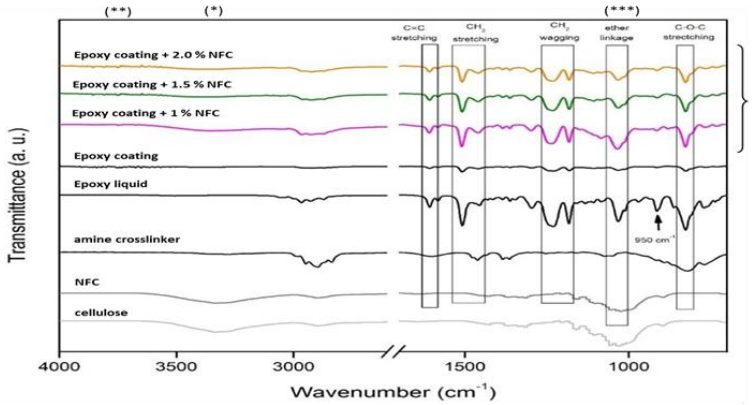
Monitoring of curing and degree of crosslinking

Structure vs. property relationships

Glass transition temperature relates to the coating hardness and mechanical properties !!



Chemical interactions between the additives and the binder improve mechanical robustness

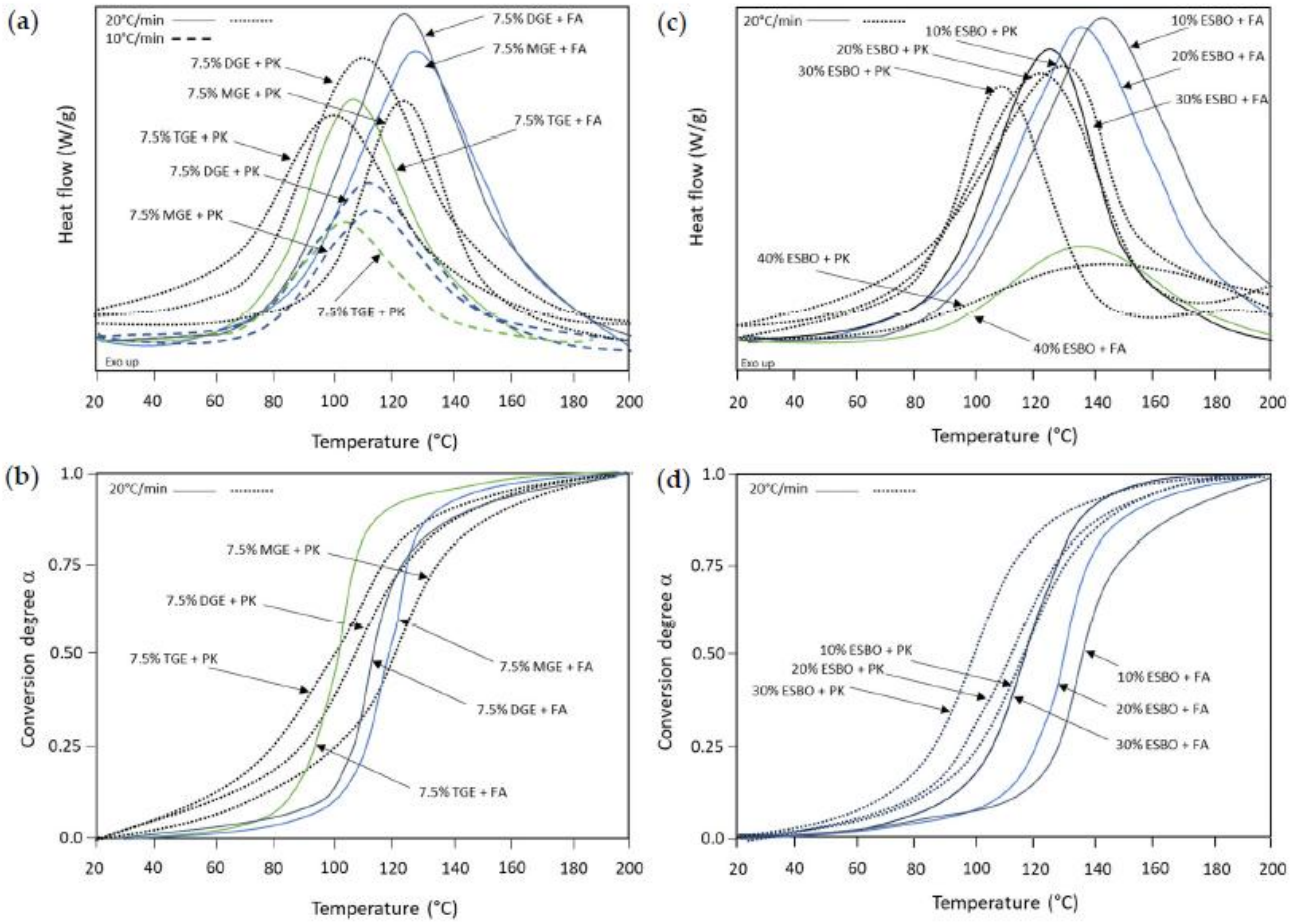


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P. Samyn et al., Nanocellulose grades with different morphologies and surface modification as additives for waterborne epoxy coatings. Polymers **2024**, 16, 1095

DSC

EXAMPLE: CURING KINETICS OF AN BIO-EPOXY COATING WITH DIFFERENT TYPES OF DILUENTS



Non-isothermal DSC thermographs with exothermal reaction and calculated conversion degree from monitoring the crosslinking reaction of epoxy resin with different diluents and crosslinkers:

(**a,b**) influence of diglycidyl ether diluents with different crosslinkers and (**c,d**) influence of vegetable oil with different crosslinkers

$$\frac{d\alpha}{dt} = k(T)(1-a)^n \quad (3)$$

$$k(T) = A\, e^{-\frac{Ea}{RT}} \quad (4)$$

Table 4. Thermal and kinetic factors for curing of epoxy coatings with a selection of diluents and crosslinkers.

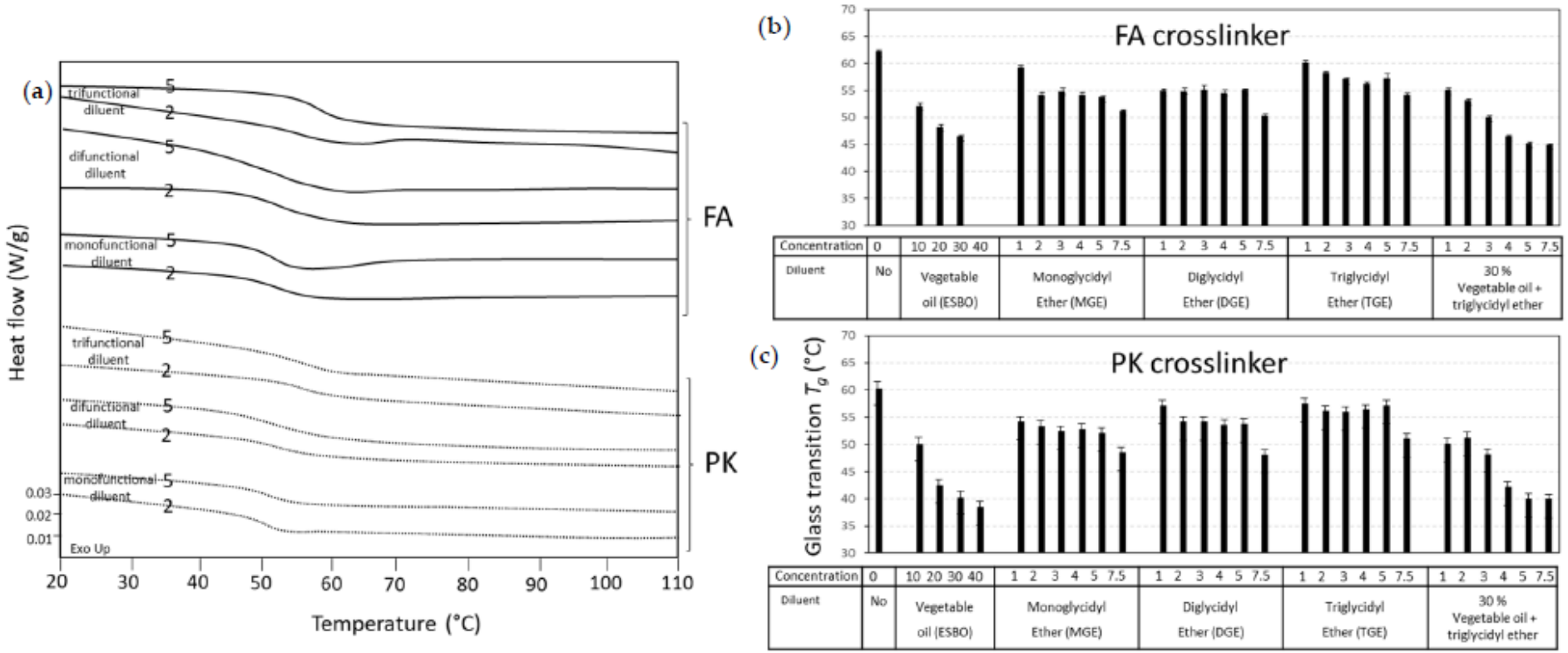
	FA-Epoxy					PK-Epoxy				
	DH_R (J/g)	T_p (°C)	E_a (kJ/mol)	A (min^{-1})	n (-)	DH_R (J/g)	T_p (°C)	E_a (kJ/mol)	A (min^{-1})	n (-)
DGEBA	295	128	64.2	2.5×10^6	0.999	281	132	52.3	2.8×10^6	0.995
DGEBA + 2 wt.-% MGE	270	127	50.3	1.6×10^6	0.998	228	121	38.3	0.9×10^6	0.998
DGEBA + 5 wt.-% MGE	265	126	49.8	1.5×10^6	0.998	212	122	40.2	1.0×10^6	0.996
DGEBA + 2 wt.-% DGE	310	122	46.2	2.1×10^6	0.975	254	110	35.2	1.3×10^6	0.998
DGEBA + 5 wt.-% DGE	286	122	47.5	2.2×10^6	0.988	232	112	39.5	1.2×10^6	0.986
DGEBA + 2 wt.-% TGE	232	106	56.2	1.1×10^6	0.993	215	99.5	42.2	0.7×10^6	0.999
DGEBA + 5 wt.-% TGE	245	108	58.2	1.0×10^6	0.998	205	106	45.1	0.6×10^6	0.991
DGEBA + 20 wt.-% ESBO	194	133	83.4	1.3×10^6	0.998	165	128	76.8	0.9×10^6	0.990
DGEBA + 30 wt.-% ESBO	185	141	84.2	0.9×10^6	0.997	159	122	80.8	0.7×10^6	0.994

innovation forward

P. Samyn et al. Role of bio-based and fossil-based reactive diluents in epoxy coatings with amine and phenalkamine crosslinker. Polymers **2023,** 15, 3856.

DSC

EXAMPLE: GLASS TRANSITION TEMPERATURE AND MOBILITY OF BIO-EXPO COATING WITH DIFFERENT TYPES OF DILUENTS



Glass transition temperature Tg of crosslinked bio-epoxy resing with different diluents and crosslinkers, (a) details from DSC thermographs of some compositions, (b) Tg values for FA (fossil amine)-epoxy and different diliuents, (c) Tg values for PK (phenalkamine)-epoxy and different diluents

P. Samyn et al. Role of bio-based and fossil-based reactive diluents in epoxy coatings with amine and phenalkamine crosslinker. Polymers **2023**, 15, 3856.

TGA

THERMOGRAVIMETRIC ANALYSIS

Coating binder

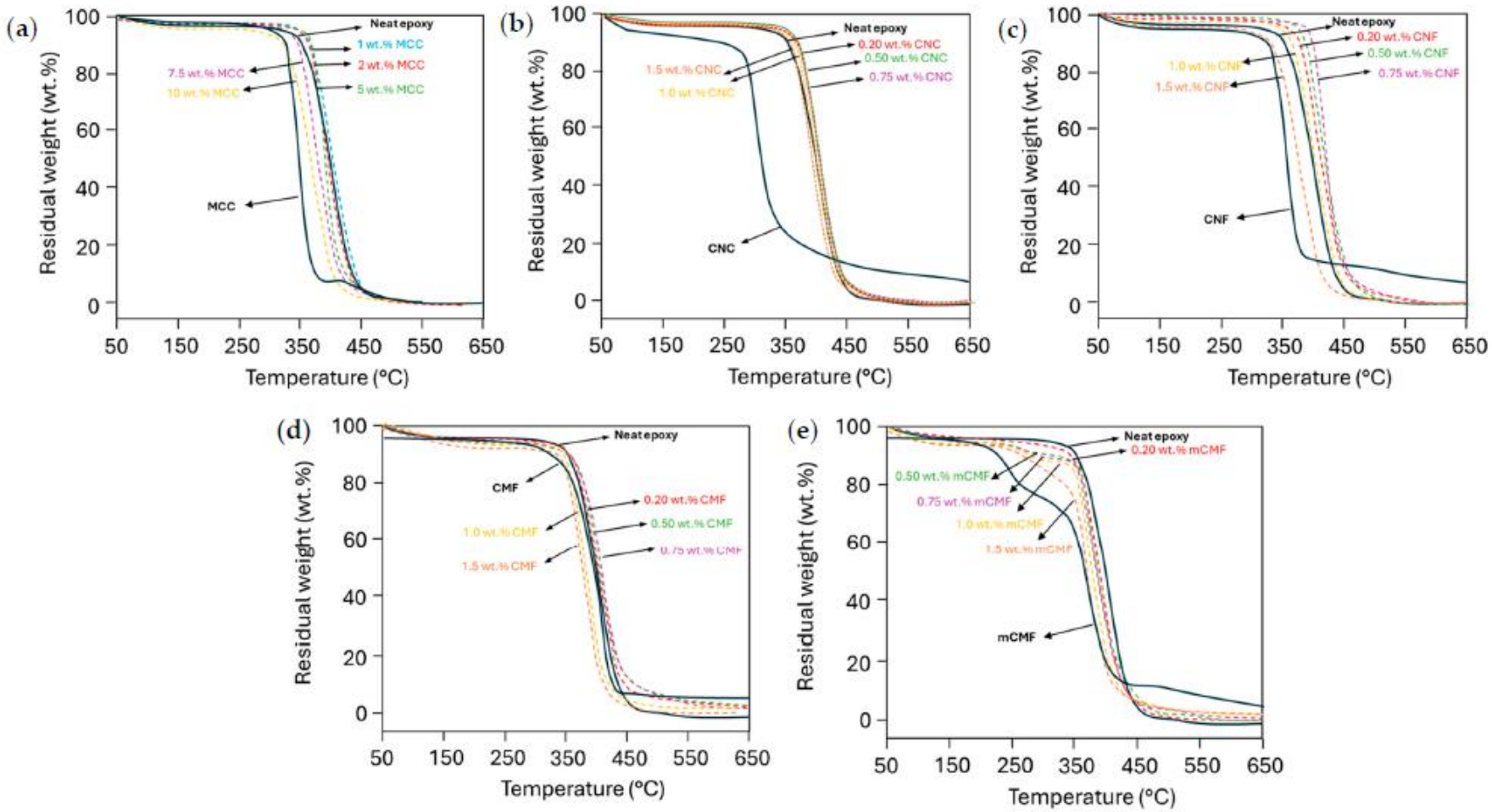
- Thermal and oxidative stability
- Polymer degradation
- Depolymerization/decomposition mechanism
- Binder content
- Char formation
- Moisture and volatile content
  - e.g. residual solvent, monomer, volatiles,
  - low-molecular weight species
- Degradation after aging
- Polymer structure (copolymer segments)

Coating additives

- Ash residue and content
  - e.g. talc, silica, TiO_2, glass fibers,…
- Organic vs. inorganic (mineral) phase (%)
  - e.g. talc loading,
- Crystallinity of inorganic phase
  - e.g. stepwise CaCO3 decomposition
- Thermal and oxidative stability
  - e.g. antioxidant properties
- Additive content (indirect quantification)
- Effectiveness of flame retardants
- Pyrolysis properties (char)

TGA

EXAMPLE: INTERACTIONS OF NANOCELLUSE WITH A BIO-EPOXY COATING MATRIX



TGA measurements on cured epoxy coatings with different micro- and nanocellulose additives at various concentrations, including (**a**) MCC, (**b**) CNC, (**c**) CNF, (**d**) CMF, and (**e**) mCMF.

P. Samyn et al., Nanocellulose grades with different morphologies and surface modification as additives for waterborne epoxy coatings. Polymers **2024**, 16, 1095

DMA

DYNAMIC MECHANICAL ANALYSIS

Coating binder

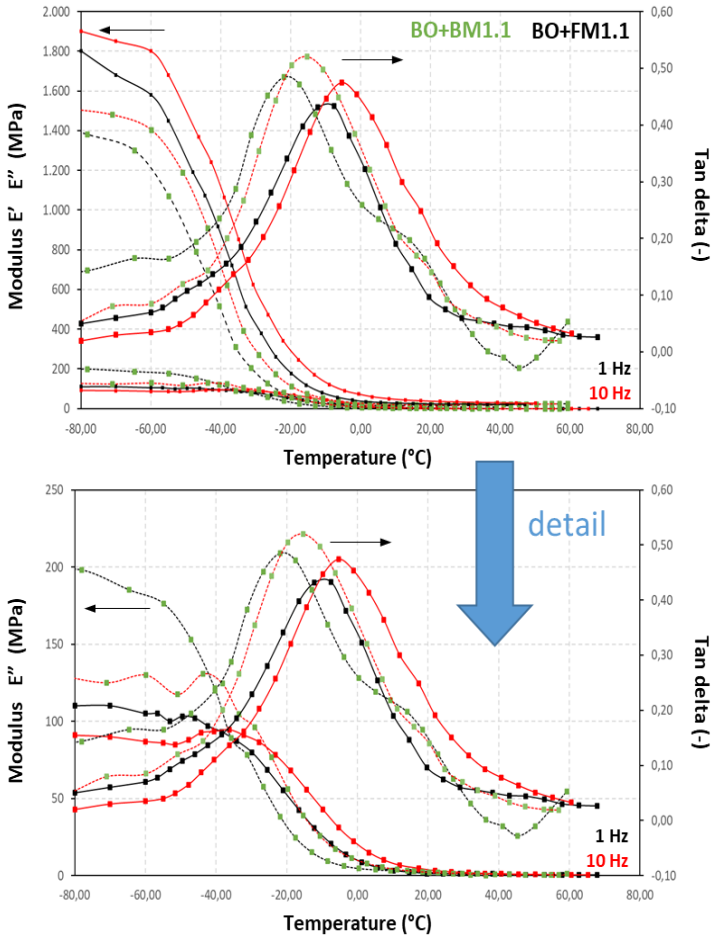
- Mechanical properties (stiffness)
- Storage modulus (elastic properties)
- Loss modulus, tan d (visco-elastic properties)
- Crosslinking density
- Glass transition
  e.g. Tg appears as a sharp drop in storage modulus, a peak in loss modulus and tan δ
- Long-term creep properties, relaxation
- Yield stress/strain

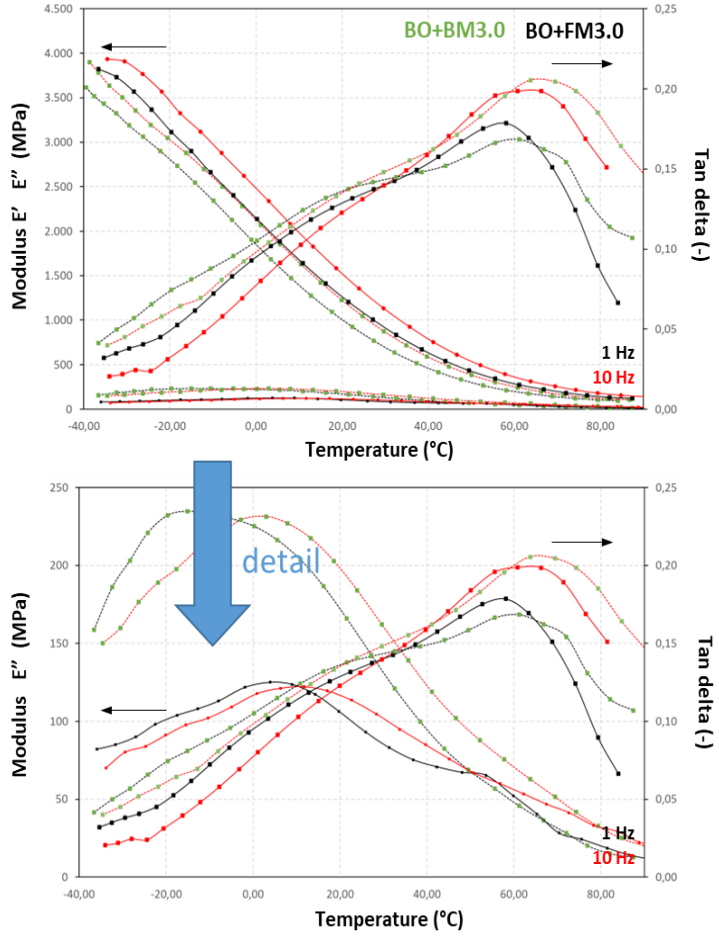
Coating additives

- Reinforcement effects/efficiency
  e.g. talc, glass fibers, cellulose fibers, silica nanoparticles typically increase storage modulus (E'), increase stiffness, and maintain modulus at higher temperatures
- Plasticizing effects
  e.g. citrates, phthalates, vegetable oil derivatives typically reduce storage modulus, increase flexibility, reduce stiffness
- Mechanical dampening properties
- Polymer-additive interactions
- Release properties

DMA

NETWORK FORMATION ON UV-CURABLE ACRYLATE COATINGS WITH FOSSIL AND BIO-BASED MONOMERS





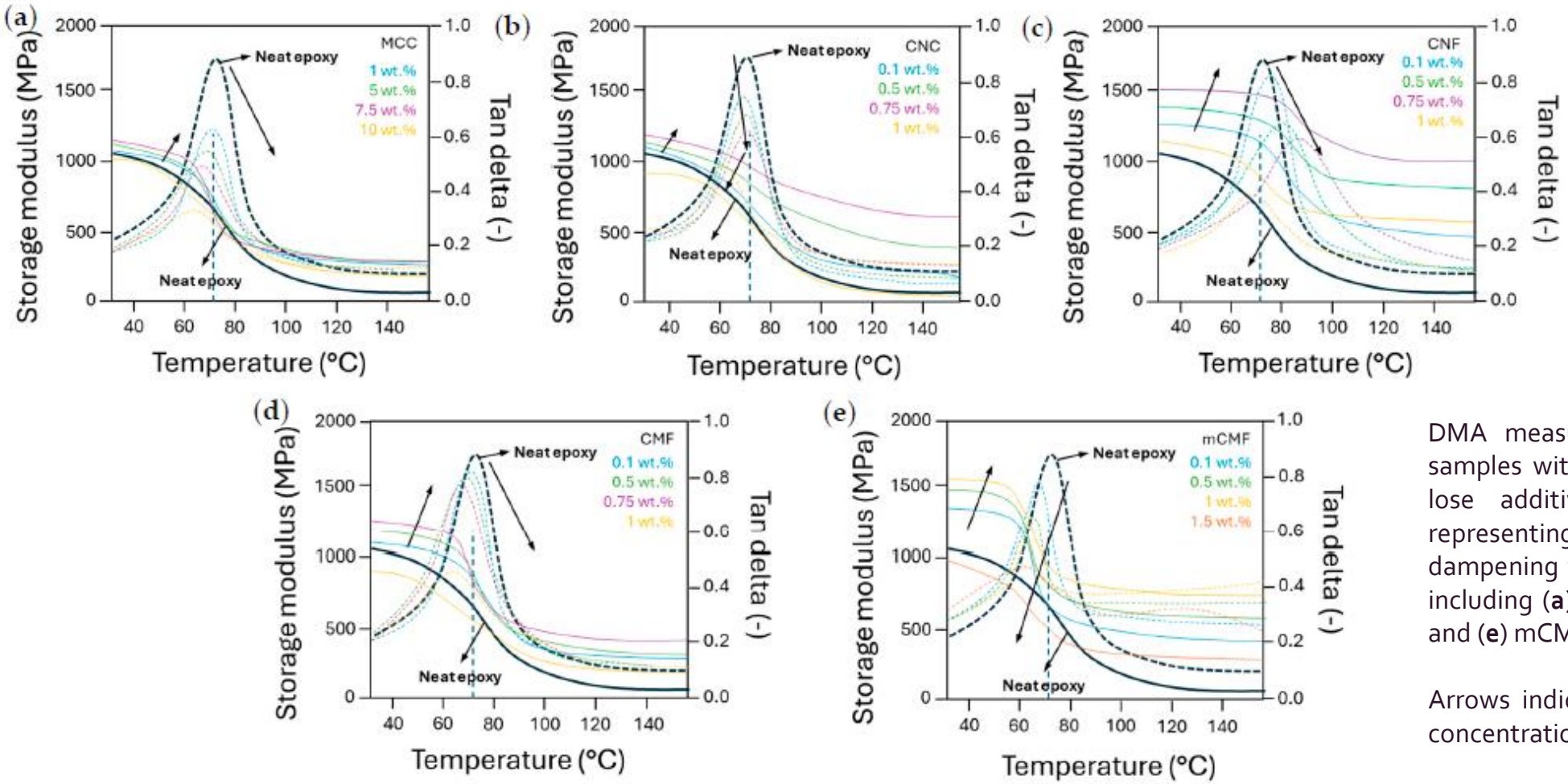
- The **bio-based** coatings have **lower elastic modulus** (E') and are **softer**, which may improve the lubricity during the wear testing.

- The **bio-based** coatings have **higher viscous modulus** (E") and higher dampening factor (tan delta) in the operational window. The data on mechanical dampening provides unique information as it is a measure for the uptake of mechanical energy. The higher dampening for bio-based coatings is in parallel with the **more ductile** properties and benefits for **improved lubricity** during mechanical testing. The higher dampening factor intrinsically relates to a molecular structure with more rotational freedom of the polymer chain segments, where the structure of bio-based polymers might have a fraction of molecules with smaller molecular weight.

P. Samyn et al., (Thermo)mechanical and chemical characteristics of photochemically crosslinked acrylates from bio- and fossil-based origin, Journal of Polymer 62 (2024), 3511-3527.

DMA

ELASTIC AND VISCOELASTIC PROPERTIES OF EPOXY COATING WITH DIFFERENT TYPES AND CONCENTRATION OF NANOCELLULOSE ADDITIVE



DMA measurements on cured epoxy resin samples with different micro- and nanocellulose additives at various concentrations, representing modulus E′ (full lines) and dampening factor tan δ = E″/E′ (dotted lines), including (**a**) MCC, (**b**) CNC, (**c**) CNF, (**d**) CMF, and (**e**) mCMF.

Arrows indicate curve shifts as a function of concentration.

P. Samyn et al., Nanocellulose grades with different morphologies and surface modification as additives for waterborne epoxy coatings. Polymers **2024**, 16, 1095

Rheology

ROTATIONAL OR OSCILLATING RHEOLOGY

Coating binder

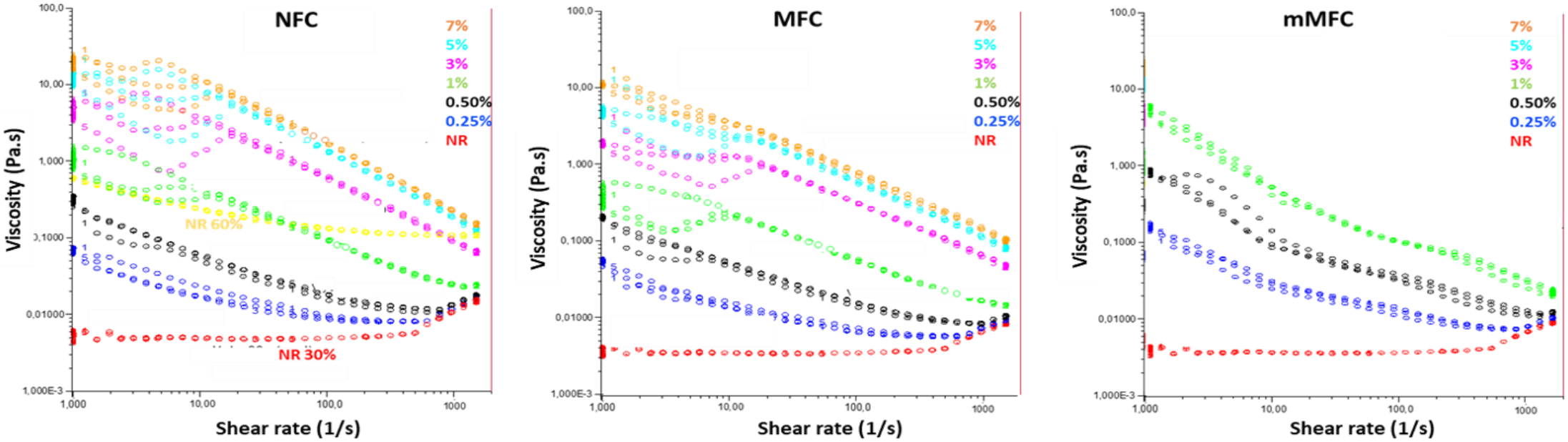
- Viscosity profile
- Zero-shear viscosity
- High-shear viscosity
- Yield stress
- Shear-thinning index
- Storage modulus (G')
- Loss modulus (G'')
- tan δ
- Determination processing parameters
- Gel point, cure rate, crosslinking reactions
- Melt strength

Coating additives

- Shear properties
- Stability regime
  - e.g. sedimentation, particle settling, filler separation, storage stability
- Dispersion quality
  - e.g.well-dispersed, agglomerated, forming network structure
- Homogeneous mixing/demixing regime
- Concentration limits for processing, optimum filler loading
- Filler network formation (critical concentration)
- Processability
- Polymer-additive interactions
  - e.g. Increased viscosity, increased elasticity, formation of structure, weak interactions cause smaller rheological changes in presence of coupling agents, compatibilizers, surface treatments, reactive additives
- Mixing energy requirementd

Rheology

EXAMPLE: MIXING OF DIFFERENT NANOCELLULOSE GRADES IN NATURAL RUBBER LATEX COATING (ROTATIONAL RHEOLOGY)



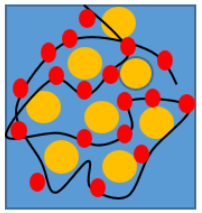
Flow properties depending on degree of fibrillation and phase/interfase compatibility

NFC / MFC



The viscosity is dominated by the shear thinning effect of the NFC and MFC fibers, indicating the formation of a not-fully penetrating and **partially phase-separated** fiber network.
This is more prevalent for NFC than for MFC.

mMFC

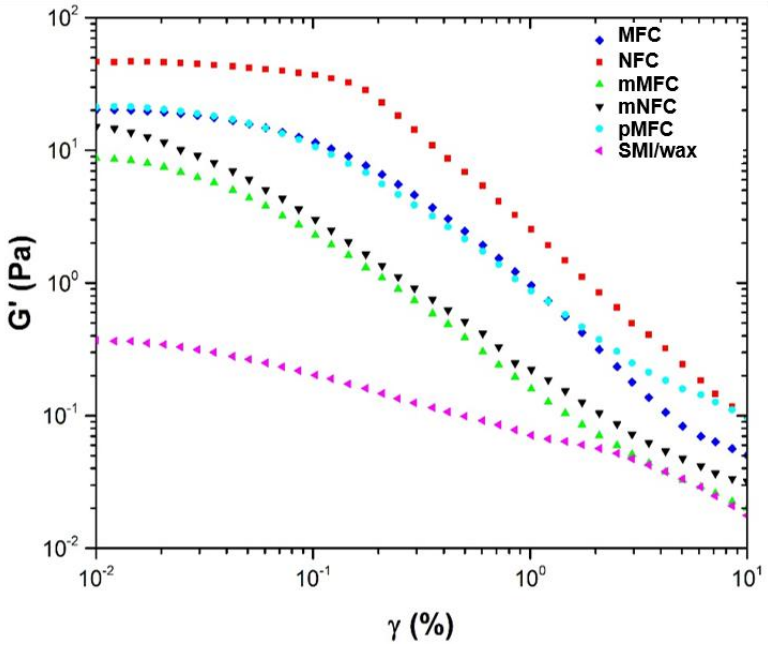


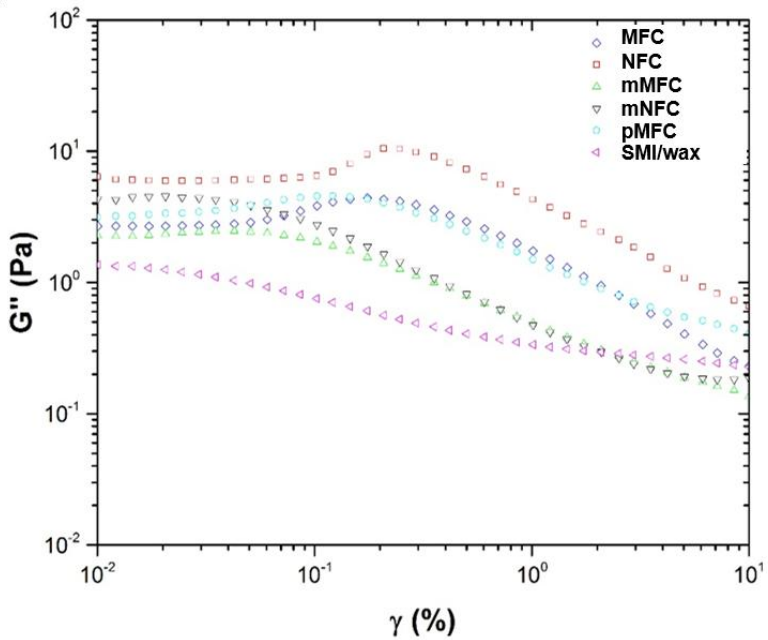
Significant increase in viscosity at same concentrations,
=
Indication for degree of compatibility and dispersion between NR + mMFC that , which improves due to **immobilization** of the rubber particles in the aqueous phase through the interdispersed fiber network,
e.g. 'liquid binding' or immobilization of the fiber network.

P. Samyn, unpublished results

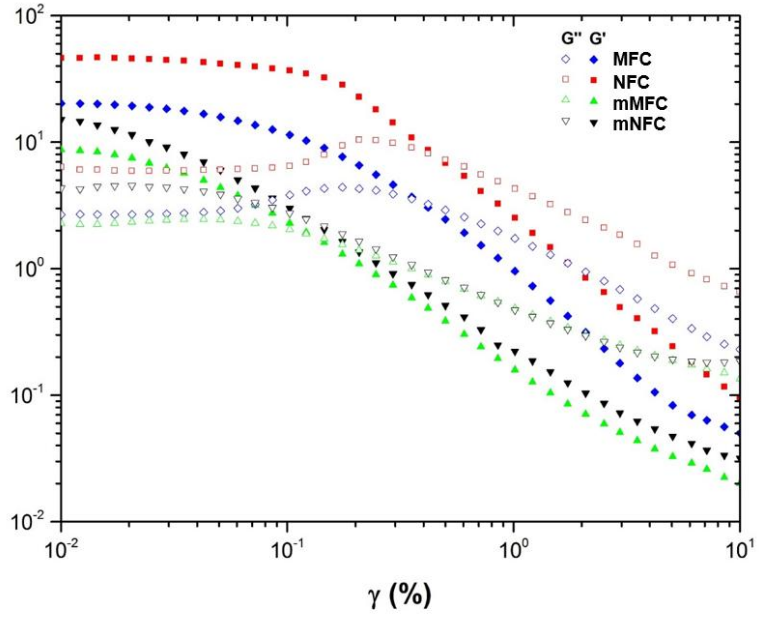
Rheology

EXAMPLE: NETWORK FORMATION OF NANOCELLULOSE ADDITIVES IN AQUEOUS COATING SUSPENSION (OSCILLATORY RHEOLOGY)





Cross-over point where G' < G" at lower strains for mMFC/mNFC



(data measured at variable stress τ, frequency f = 0.1 Hz)

For SMI/wax : G' < G" **liquid-like** due to flow behaviour

For (m)MFC, (m)NFC : G' > G" **gel-like** due to network formation

→ Decrease in G' at higher strain due to breakdown of the entangled fiber network

→ Weakening of visco-elastic properties (G') for mMFC/mNFC due to lower fiber interactions and re-duced tendency of network formation (electrostatic / hydrophobic stabilitzation): the fully different shape confirms different types of global fiber organization in the netwok (no G" transition).

innovation forward

P. Samyn et al. Rheology of fibrillated cellulose suspensions after surface modification by organic nanoparticle deposits, Journal of Materials Science 51 (2016), 9830-9848,

GC/MS, Pyr-GC/MS

GAS CHROMATOGRAPHY, PYROLYSIS GAS CHROMATOGRAPHY

Coating binder

- Binder identification (indirectly)
- Residual solvents and VOC
- Degradation products

  e.g. oxidation products after weathering, fragmented fractions after UV exposure, weathering, thermal aging, oxidation
- Contamination analysis

  e.g. silicone contamination, oil contamination, cleaning-agent residues, unwanted additives, processing contaminants leading to cratering, fish-eyes, poor adhesion, cure inhibition
- Quality control, failure analysis
- Reverse engineering

Coating additives

- Identification of organic additives (molecular fingerprint)

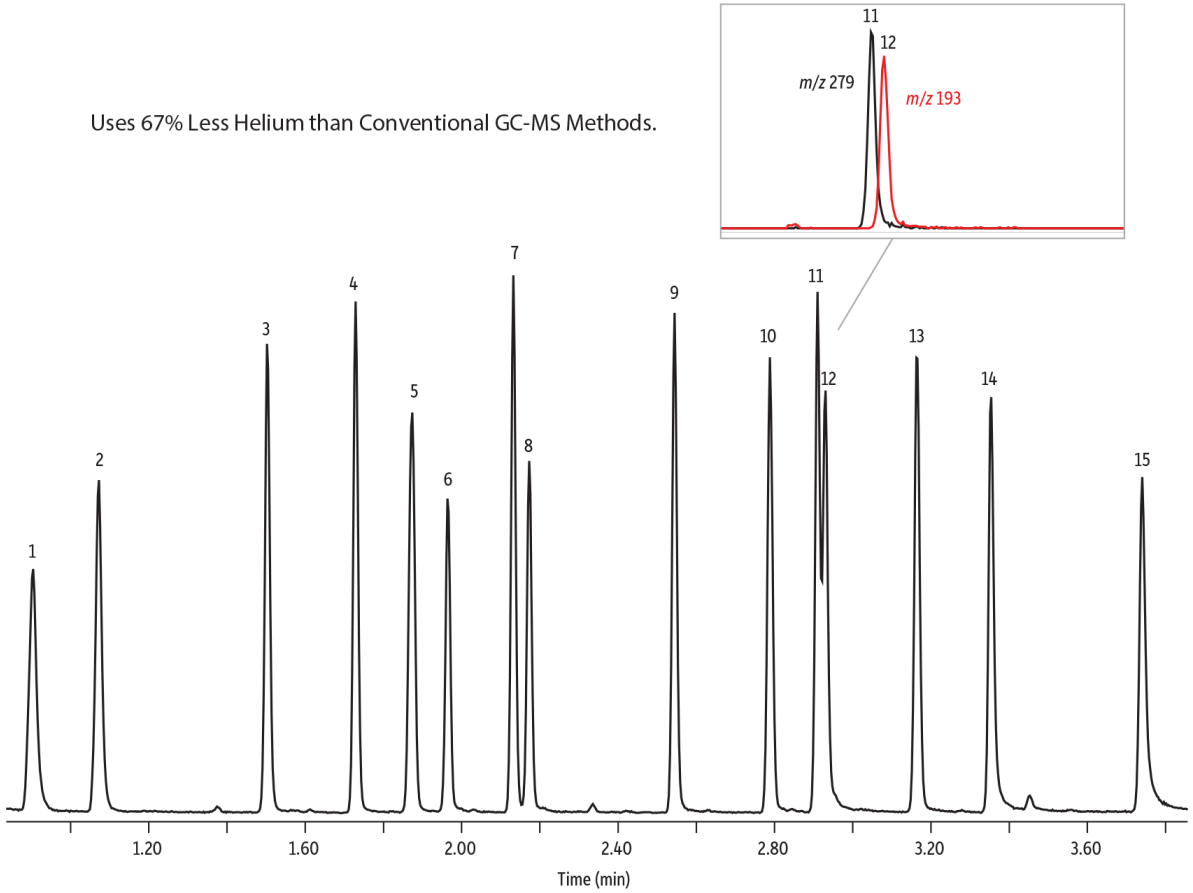
  e.g. plasticizers, flow modifiers, dispersants, defoamers, UV stabilizers, light stabilizers, antioxidants, residual solvents, residual monomers, processing aids
- Additive concentration (calibrated)
- Migration and leaching of additives

  e.g. migrate to the surface, evaporation, leaching into surrounding materials, plasticizer loss, surface blooming, additive depletion
- Additive degradation after aging

GC/MS, Pyr-GC/MS

EXAMPLE: GC/MS OF PHTHALATES

Uses 67% Less Helium than Conventional GC-MS Methods.



Column	LPGC Rxi-35Sil MS, includes Rxi-35Sil MS 10 m 0.32 mm 0.25 µm w/ 5 m 0.15 mm ID Rxi restrictor connected via SilTite connector (cat.# 11806)
Standard/Sample	EPA method 8061A phthalate esters mixture (cat.# 33227)
Diluent:	Hexane
Conc.:	100 µg/mL
Injection	
Inj. Vol.:	1 µL split (split ratio 10:1)
Liner:	Topaz, splitless, single taper inlet liner, 4.0 mm x 6.5 x 78.5 (cat.# 23303)
Inj. Temp.:	280 °C
Oven	
Oven Temp.:	180 °C (hold 0.5 min) to 200 °C at 75 °C/min to 300 °C at 35 °C/min (hold 5 min)
Carrier Gas	He, constant flow
Flow Rate:	0.9 mL/min

Detector	MS
Mode:	Scan
Scan Program:	

Group	Start Time (min)	Scan Range (amu)	Scan Rate (scans/sec)
1	0.5	55-300	9.7

Transfer Line Temp.:	300 °C
Analyzer Type:	Quadrupole
Source Temp.:	230 °C
Quad Temp.:	150 °C
Electron Energy:	70 eV
Instrument	Agilent 7890B GC & 5977A MSD
Sample Preparation	The standard was diluted with hexane to 100 ppm; analyzed in a 2 mL, short-cap, screw-thread vial (cat.# 21143); and capped with a short-cap, screw-vial closure (cat.# 24495).

Peaks	t_R (min)	Conc. (ppm)
1. Dimethyl phthalate	0.904	10
2. Diethyl phthalate	1.073	10
3. Diisobutyl phthalate	1.504	10
4. Di-n-butyl phthalate	1.73	10
5. Bis(2-methoxyethyl) phthalate	1.873	10
6. Bis[4-methyl-2-pentyl] phthalate isomers	1.964	10
7. Di-n-pentyl phthalate	2.133	10

Peaks	t_R (min)	Conc. (ppm)
8. Bis(2-ethoxyethyl) phthalate	2.173	10
9. Di-n-hexyl phthalate	2.545	10
10. Butyl benzyl phthalate	2.789	10
11. Bis(2-ethylhexyl) phthalate	2.911	10
12. Bis(2-butoxyethyl) phthalate	2.931	10
13. Dicyclohexyl phthalate	3.166	10
14. Di-n-octyl phthalate	3.357	10
15. Dinonyl phthalate	3.741	10

https://www.restek.com/global/en/chromatogram-detail/GC_GN1239?srsltid=AfmBOopIvpr_FtdfMMqS5Ly8ThEFrywIJsA-B5hoMEkmJWgl37fN6Yg3

HPLC, LC/MS

LIQUID CHROMATOGRAPHY

Coating binder

- Binder composition
  e.g. oligomers, resin components/fragments, additives dissolved in the binders, unreacted monomers, surfactants, crosslinking agents
- Binder degradation products
  e.g. fragments of UV aging, thermal aging, weathering, hydrolysis
- Molecular weight distribution (SEC, GPC)
  e.g. average molecular weight (Mn), weight-average molecular weight (Mw), polydispersity provide insight into binder processability, film-forming properties, mechanical performance
- Residual monomers
  e.g. acrylic acid, methyl methacrylate, butyl acrylate, styrene
- Crosslinkers and reactive species
  e.g. melamine crosslinkers, isocyanate derivatives, epoxy curing agents, amines helps determine binder formulation accuracy, storage stability, cure potential

Coating additives

- Identification of unknown additives
  e.g. UV absorbers HALS (Hindered Amine Light Stabilizers), antioxidants, biocides, wetting agents, dispersants, flow modifiers, crosslinkers
- Additive degradation during aging
  e.g. oxidized UV stabilizers, HALS degradation products, antioxidant breakdown compounds, hydrolysis products
- Surfactants and dispersants
- Migration
  e.g. plasticizer migration, UV absorber blooming, surfactant migration
- Leachables and extractables

HPLC, LC/MS

EXAMPLE: EXTRACTABLES AND LEACHABLES

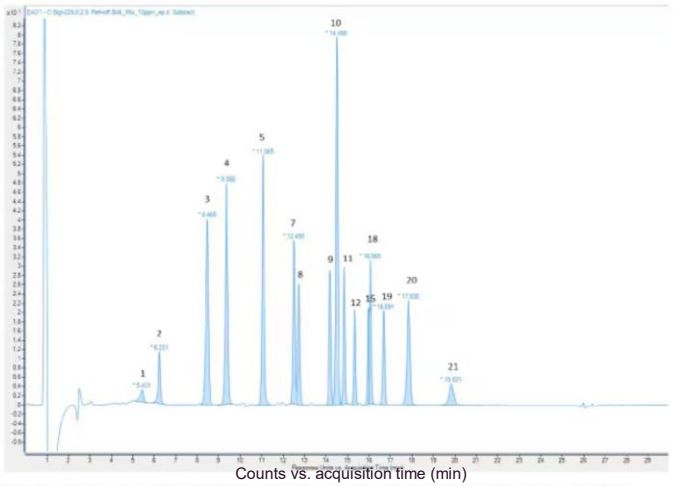


Figure 1. Extractables and Leachables Screening Standard for LC, UV (220nm), 10 mg/L in acetonitrile.

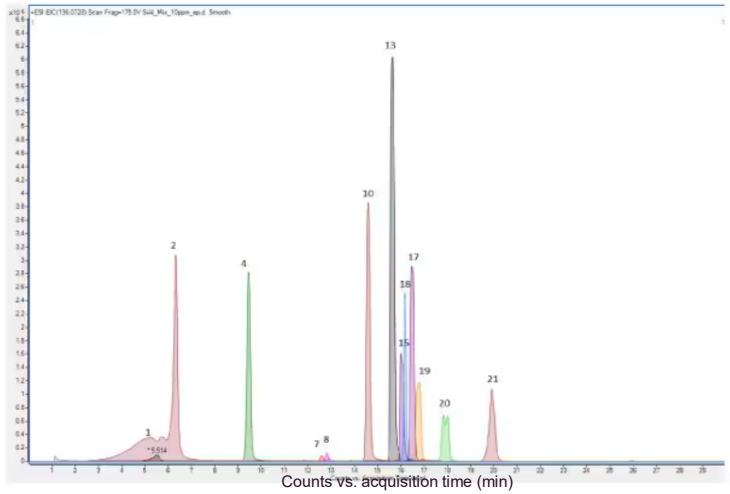


Figure 2. Extractables and Leachables Screening Standard for LC, ESI positive, 10 mg/L in acetonitrile.

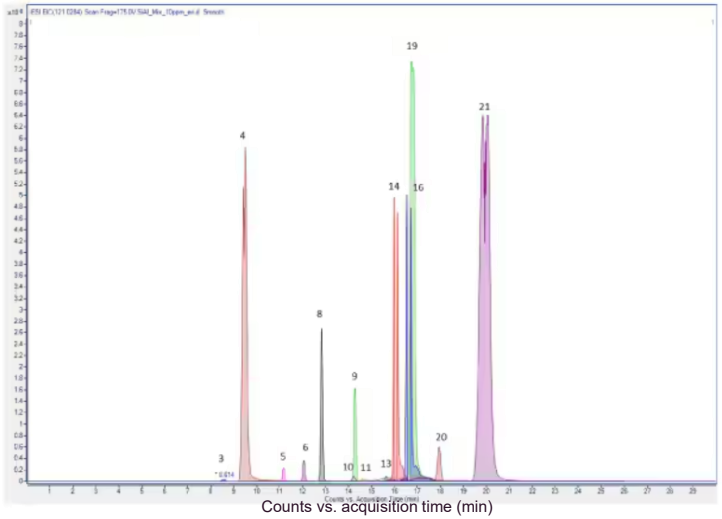


Figure 3. Extractables and Leachables Screening Standard for LC, ESI negative, 10 mg/L in acetonitrile.

Peak	Compound	CAS	Molecular Formula	m/z	UV absorption at 220 nm	Most prominent adducts		RT [min]
						ESI pos	ESI neg	
1	ε-Caprolactam	105-60-2	$C_6H_{11}NO$	136.0728	very weak	$[M+H]^+$	-	5.43
2	Dibenzylamine	103-49-1	$C_{14}H_{15}N$	198.1279	yes	$[M+H]^+$	-	6.23
3	Benzoic acid	65-85-0	$C_7H_6O_2$	121.0284	yes	-	$[M-H]^-$	8.48
4	2-Mercaptobenzothiazole (2-MBT)	149-30-4	$C_7H_5NS_2$	167.9931 165.9788	yes	$[M+H]^+$	$[M-H]^-$	9.36
5	Bisphenol A (BPA)	80-05-7	$C_{15}H_{16}O_2$	227.1077	yes	-	$[M-H]^-$	11.1
6	2-Ethylhexanoic acid	149-57-5	$C_8H_{16}O_2$	143.1082	no	-	$[M-H]^-$	12.1
7	Bis(4-chlorophenyl) sulfone	80-07-9	$C_{12}H_8Cl_2O_2S$	308.9519	yes	$[M+H]^+$	-	12.5
8	3,5-Di-*tert*-butyl-4-hydroxybenzyl alcohol	88-26-6	$C_{15}H_{24}O_2$	259.1672 235.1705	yes	$[M+Na]^+$	$[M-H]^-$	12.7
9	2,4-Di-*tert*-butylphenol	96-76-4	$C_{14}H_{22}O$	205.1597	yes	-	$[M-H]^-$	14.2
10	2-(2-Hydroxy-5-methylphenyl)benzotriazole	2440-22-4	$C_{13}H_{11}N_3O$	226.0972 224.0826	yes	$[M+H]^+$	$[M-H]^-$	14.5
11	Butylhydroxytoluene (BHT)	128-37-0	$C_{15}H_{24}O$	219.1754	yes	-	$[M-H]^-$	14.9
12	1,3-Di-*tert*-butylbenzene	1014-60-4	$C_{14}H_{22}$	-	yes	-	-	15.3
13	Oleamide	301-02-0	$C_{18}H_{35}NO$	282.2795 280.2643	very weak	$[M+H]^+$	$[M-H]^-$	15.6
14	Palmitic acid	57-10-3	$C_{16}H_{32}O_2$	255.2331	no	-	$[M-H]^-$	16.1
15	Bis(2-ethylhexyl) phthalate (DEHP)	117-81-7	$C_{24}H_{38}O_4$	391.2839	yes	$[M+H]^+$	-	16.0
16	Stearic acid	57-11-4	$C_{18}H_{36}O_2$	283.2644	no	-	$[M-H]^-$	16.5
17	Erucamide	112-84-5	$C_{22}H_{43}NO$	338.3417	very weak	$[M+H]^+$	-	16.5
18	Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate	27676-62-6	$C_{48}H_{69}N_3O_6$	806.5084	yes	$[M+Na]^+$	-	16.1
19	Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)	6683-19-8	$C_{73}H_{108}O_{12}$	1199.7770 1175.7726	yes	$[M+Na]^+$	$[M-H]^-$	16.7
20	Tris(2,4-di-*tert*-butylphenyl)phosphate	95906-11-9	$C_{42}H_{63}O_4P$	685.4365 661.4378	yes	$[M+Na]^+$	$[M-H]^-$	17.8
21	Octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate	2082-79-3	$C_{35}H_{62}O_3$	553.4597 529.4624	yes	$[M+Na]^+$	$[M-H]^-$	19.8

Table 2. Peak IDs, selected ions, and retention times of compounds

innovation forward

https://www.sigmaaldrich.com/BE/en/technical-documents/technical-article/analytical-chemistry/calibration-qualification-and-validation/extractables-study-with-lc-uv-ms

HPLC – LC/MS

EXAMPLE: RESIDUAL MONOMER FRACTIONS IN PHOTOCURED FOSSIL-BASED AND BIO-BASED ACRYLATE COATINGS

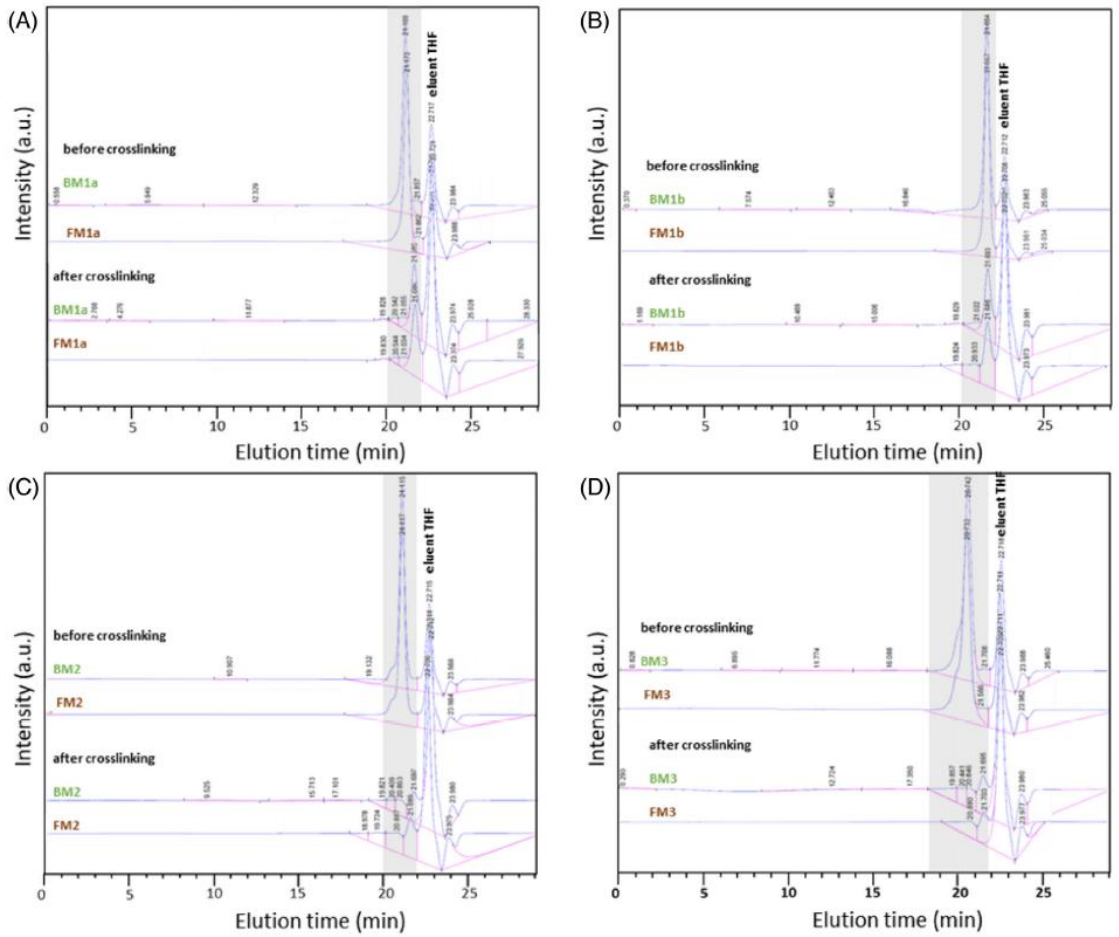


FIGURE 11 SEC chromatograms before and after photochemical crosslinking of bio-based acrylates and fossil-based acrylates of different composition, (A) BM1a and FM1a, (B) BM1b and FM1b, (C) BM2 and FM2, (D) BM3 and FM3.

The results from size exclusion chromatography (SEC) of BM and FM monomers with different functionalities before crosslinking and after dissolving the crosslinked films in THF, are presented. Before crosslinking, the main elution peaks at 21.17 to 20.70 min for BM and FM monomers are very similar and do not indicate significant variation in molecular structure of the main fraction in the monomer. Also, there is no indication of various impurity fractions in the BM and FM monomers, as they also did not show up in FTIR analysis. However, the BM monomers consistently present additional molecular fractions at lower elution times representing inherently highmolecular weight fractions. The chromatograms of crosslinked acrylates are taken on an extractable (soluble) polymer fraction of the photochemically crosslinked films. The intensity of elution peaks for extracted acrylate films is consequently lower (relatively to the THF solvent elution peak) due to the high conversion degree, and intensities further reduce for crosslinked monomers with higher functionality.

innovation forward

P. Samyn et al., (Thermo)mechanical and chemical characteristics of photochemically crosslinked acrylates from bio- and fossil-based origin, Journal of Polymer 62 (2024), 3511-3527.

XRD

X-RAY DIFFRACTION

Coating binder

- XRD is generally less informative as most coating binders are usually rather amorphous:
  e.g. can determine whether the binder contains crystalline regions, semi-crystalline regions, completely amorphous regions
- Crystal structure and crystal size
  e.g. crystal phases, crystal lattice type, polymorphs for semi-crystalline binders, together with crystallite size, crystal growth behavior
- Phase separation
  e.g. soft domains, hard domains, multiple polymer phases
- Orientation of the polymer chains

Coating (inorganic) additives

- Identification of crystalline additives: crystallinity and phase identification
  e.g. talc, calcium carbonate (calcite, aragonite), titanium dioxide (rutile, anatase), barium sulfate, silica (crystalline forms), zinc oxide, mica, kaolin, wollastonite
- Crystallite size and dimensions
  e.g. nano-TiO_2, nano-ZnO, nano-$CaCO_3$
- Quantification of Crystalline Phases
  e.g. relative amounts calcite, talc, rutile TiO2
- Degree of Dispersion of Layered Additives
  e.g. nanoclays, graphite, graphene oxide with stacked, Inter-calated, exfoliated layers
- Additive-binder interactions
  e.g. processing effects, nucleating agent, crystal growth modifier
- Weathering and Stability of Additives
  e.g. phase transformations, crystal growth, decomposition products

XRD

EXAMPLE: CRYSTALLINITY OF COATING ADDITIVES

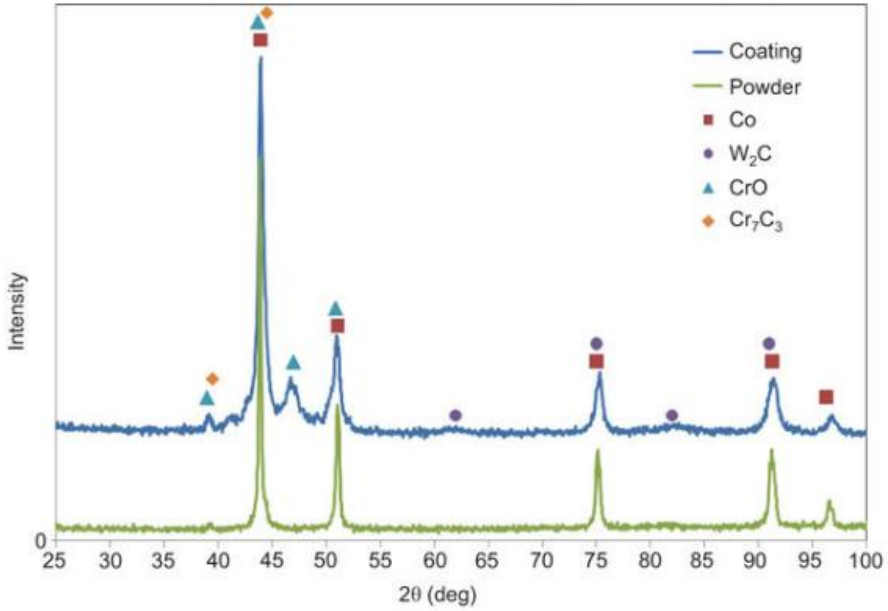


Figure 3: X-ray diffraction (XRD) analysis of Stellite-6 powder and coating with supersonic laser deposition (SLD).

https://researchgate.net/publication/260174470_Hardfacing_steel_with_nanostructured_coatings_of_Stellite-6_by_supersonic_laser_deposition/figures?lo=1&utm_source=google&utm_medium=organic

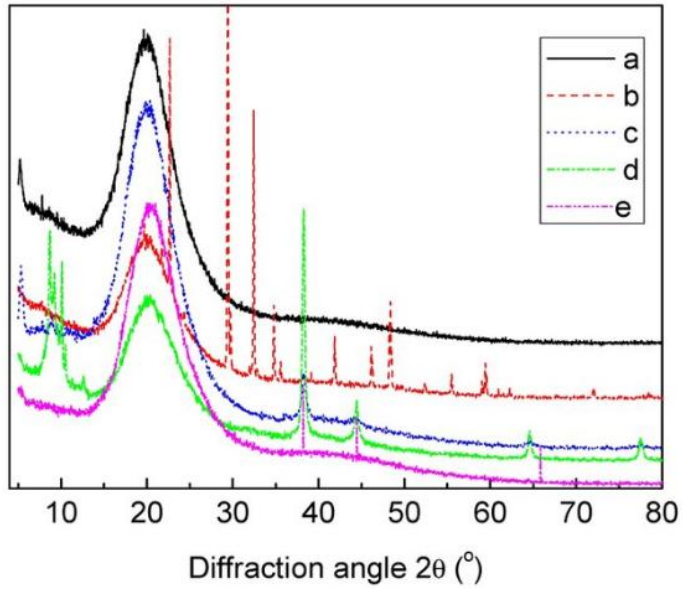


Figure 4. X-ray Diffraction curves for polyurethane (a) unmodified; and loaded with (b) 10% (w/w) AgNO3; (c) 1% (w/w) Ag lactate; (d) 10% (w/w) Ag lactate; and (e) Ag nanoparticles.

https://www.researchgate.net/publication/263324449_Antimicrobial_Mechanical_and_Thermal_Studies_of_Silver_Particle-Loaded_Polyurethane/figures?lo=1

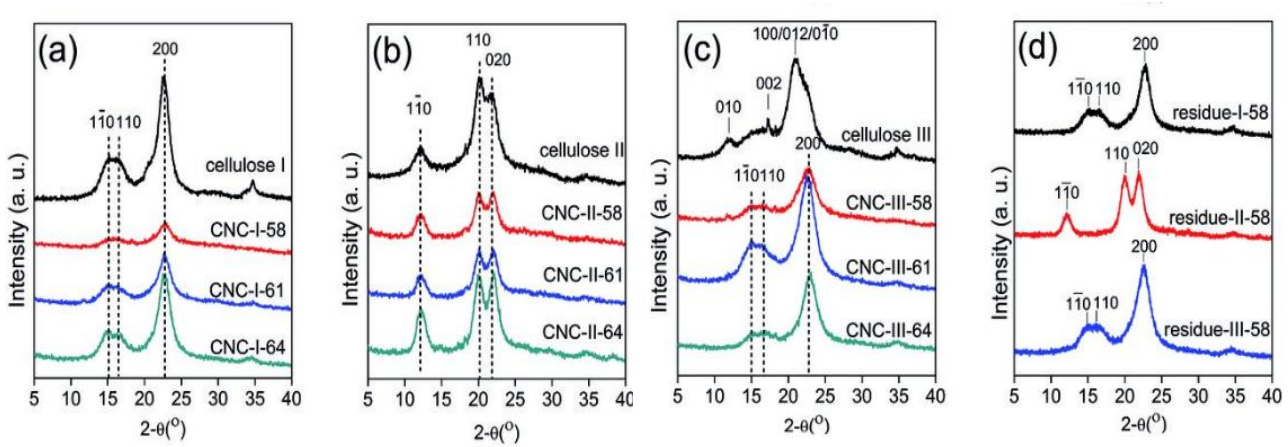


Figure 2: XRD patterns for cellulose I and CNC-I (a), XRD patterns for cellulose II and CNC-II (b), XRD patterns for cellulose III and CNC-III (c), and XRD patterns for residues generated in the centrifugation process of CNCs preparation in 58 wt% H2SO4 (d)

https://www.researchgate.net/publication/318112561_Research_on_cellulose_nanocrystals_produced_from_cellulose_sources_with_various_polymorphs/figures?lo=1

XRD

EXAMPLE: NANOSCALE ORDERED DOMAIN STRUCTURES IN PHOTOCURED ACRYLATE COATINGS

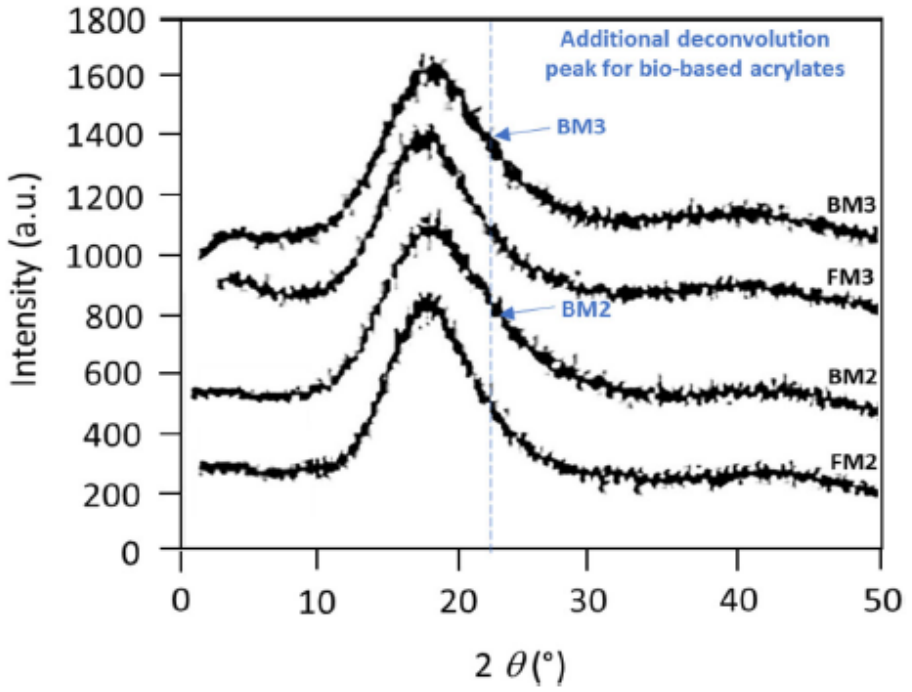


FIGURE 8 Wide-angle X-ray diffraction spectra for selected acrylates of functionality $f = 2, 3$, including BM2/FM2, and BM3/FM3.

TABLE 3 Analysis of nanomorphology with calculation of cluster sizes D_c for bio-based and fossil-based acrylates according to XRD.

	Peak 1		Peak 2		Peak 3		Peak 4	
	2θ	D_c	2θ	D_c	2θ	D_c	2θ	D_c
BM2	6.7	3.2	18.1	1.1	21.0	0.6	41.5	1.4
FM2	6.9	3.8	19.2	1.6	-	-	41.6	1.5
BM3	5.6	2.3	18.2	1.0	21.2	0.8	41.9	1.4
FM3	5.8	2.6	19.1	1.4	-	-	41.8	1.3

heterogeneity of the material. The highest variation in cluster sizes between the different acrylate materials is measured for the large clusters according to the "peak 1." However, the bio-based acrylates present a slightly different diffractogram with an additional "peak 3" after deconvolution of the central peak, corresponding to a smaller appar-

innovation forward

P. Samyn et al., (Thermo)mechanical and chemical characteristics of photochemically crosslinked acrylates from bio- and fossil-based origin, Journal of Polymer 62 (2024), 3511-3527.

XRF

X-RAY FLUORESCENCE

Coating binder

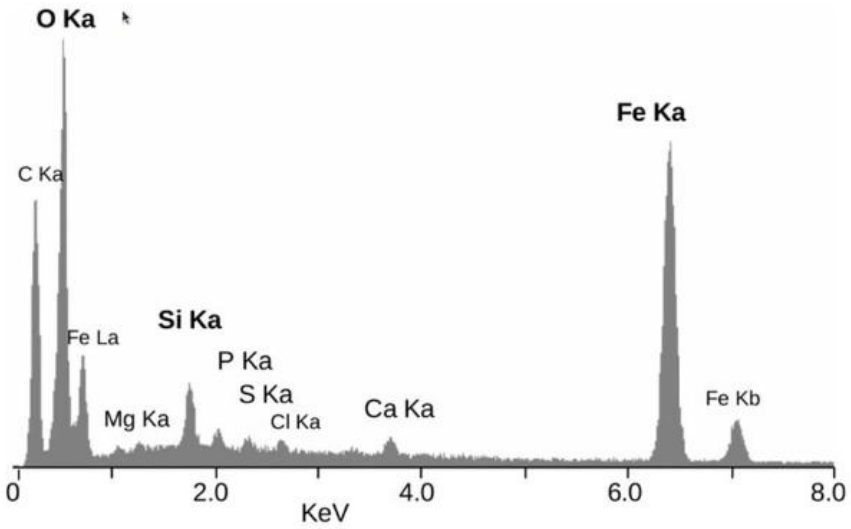
- Elemental composition (not organic)
- Inorganic components associated with the binder
  e.g. catalyst residues, crosslinking catalysts, metal dryers, pigment dispersions, mineral fillers
- Dryer and catalyst analysis
  e.g. important in alkyd coatings, polyurethane coatings, epoxy systems, it can detect catalytic metals such as cobalt, manganese, zirconium, zinc
- Contaminant detection
  e.g. iron contamination, heavy metals Pb, Cd, Cr, Hg, As), processing contamination, recycled-content impurities

Coating additives

- Elemental composition (not organic)
  e.g. Ti, Ca, Zn, Ba, Si, Al, Fe, Mg, P, S, Cl
- Inorganic filler identification and/or concentration (after calibration)
  e.g. calcium carbonate, talc, silica, barium sulfate, zinc oxide
- Pigment additive identification
  e.g. TiO_2, iron oxide red, chromium oxide green, zinc oxide
- Flame retardant additive identification
  e.g. aluminum hydroxide, magnesium hydroxide, zinc borate, phosphorous, brominated retardants

XRF

EXAMPLE: ELEMENTAL ANALYSIS



Elemental Analysis

X-Ray Fluorescence (XRF) analysis is a simple, highly accurate test method used to determine a material's chemical composition. Each of the elements present in a sample produces a unique set of characteristic x-rays that is a "fingerprint" for that specific element. XRF analyzers determine the chemistry of a sample by measuring the spectrum of the characteristic x-ray emitted by the different elements in the sample when it is illuminated by x-rays. XRF provides both qualitative and quantitative information on a wide variety of sample types. It can quantify elements from beryllium (Be) up to americium (Am) in concentrations from 100% down to sub-ppm level.

https://lab-solutions.dksh.com/testing-services/elemental-analysis/

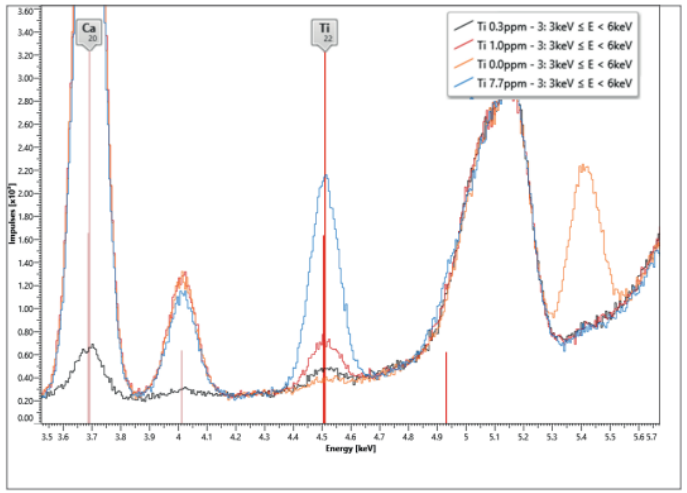


Figure 6: Measurement spectra recorded for four plastic compacts with different Ti contents (0, 0.3, 1.0, and 7.7 mg/kg), measuring time: 150 sec

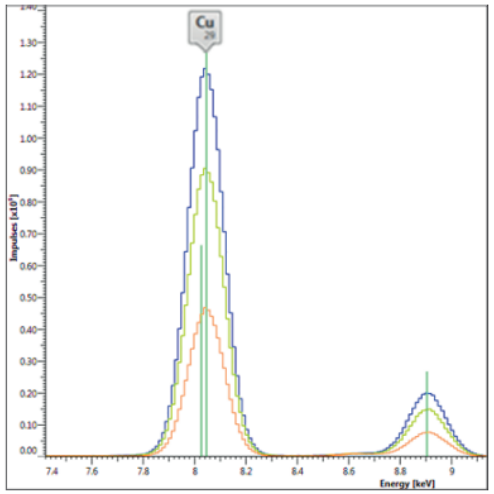


Figure 8: Measurement spectra recorded for three polyamide samples with Cu contents between about 1.6 and 5%

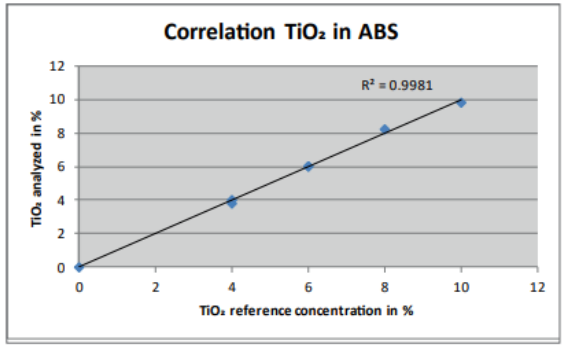


Figure 11: Calibration for TiO_2 in ABS

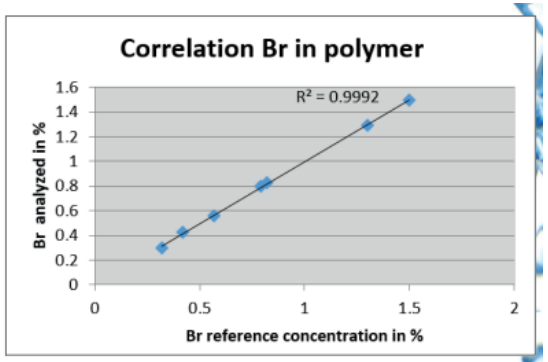


Figure 13: Calibration for Br in polystyrene

https://extranet.spectro.com/-/media/4F5AE97B-2F24-4720-B6F1-2F66E66CB62E.pdf

ICP-OES / ICP-MS

INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROSCOPY

Coating binder

- Catalyst residues (concentration)
  e.g. Ti, Sn, Zn, Zr,
- Metallic driers in coatings (concentration)
  e.g. Co, Mn, Zr, Ca, Zn
- Inorganic contamination (concentration)
  e.g. Fe, Cu, Cr, Ni, …
- Trace elements/contaminants
- Heavy metals
  e.g. Pb, Cd, Cr, Hg, As
- Purity / impurities after recycling
  e.g. Ti, Zn, Fe, Al, ….

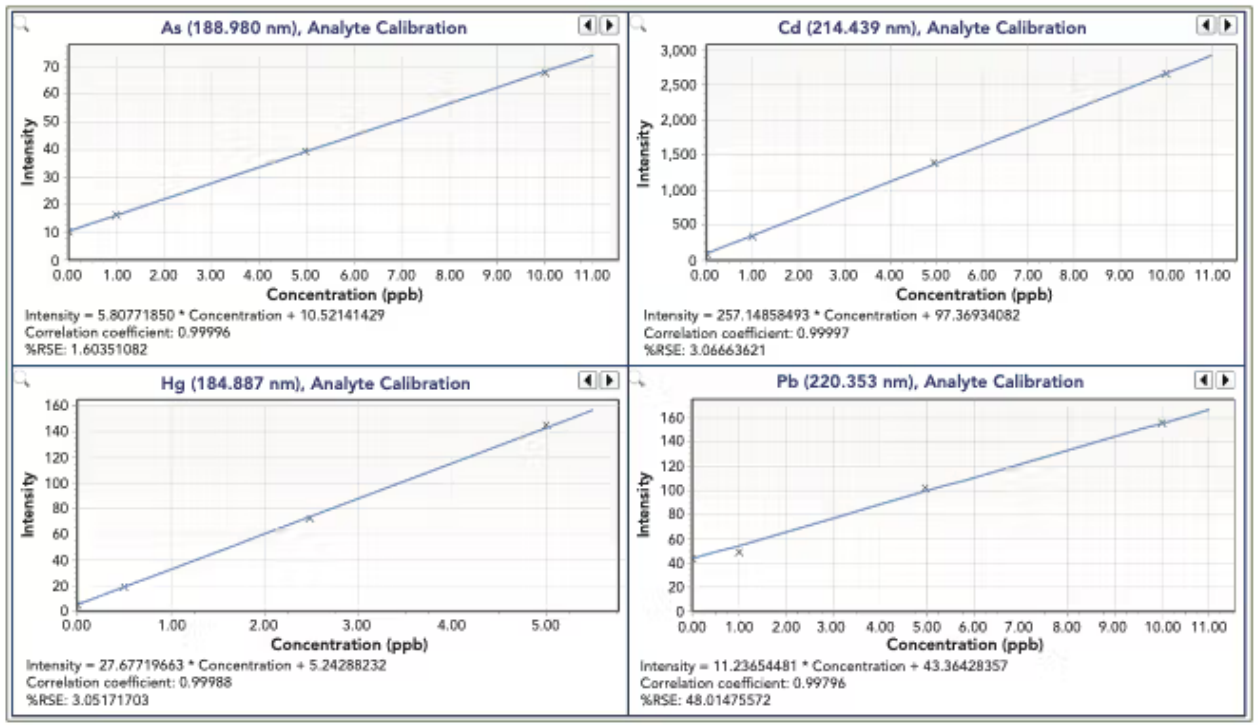
Coating additives

- Elements associated to inorganic fillers and pigments (concentration)
  e.g. calcium carbonate (Ca), Talc (Mg, Si), Kaolin (Al, Si), Barium sulfate (Ba, S), Wollastonite (Ca, Si)
- Pigment composition – no halogens
  e.g. TiO_2, iron oxide red, chromium oxide green, zinc oxide, ultramarine (Na, Al, Si, S)
- Elemental fingerprints for quality control and recycling studies
- Flame-retardant additives
  e.g. aluminum hydroxide, magnesium hydroxide, zinc borate, phosphorous, brominated retardants

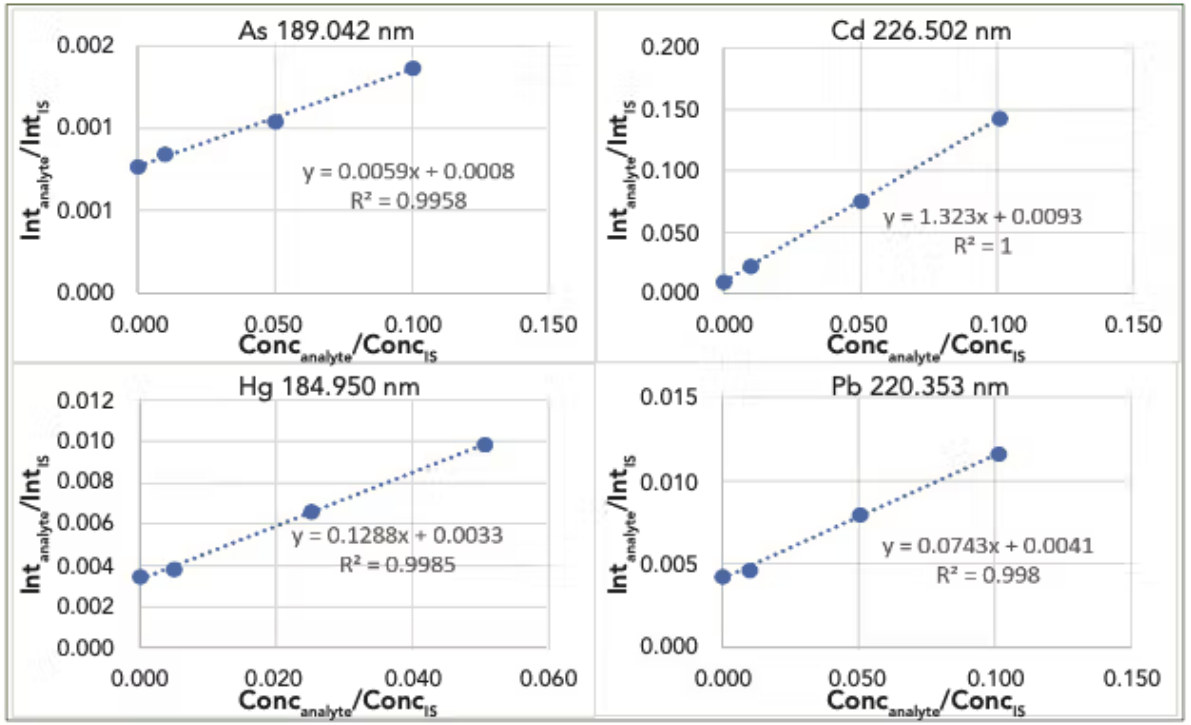
Compared with XRF, ICP-OES is generally much more sensitive and accurate for trace-element analysis

ICP-OES / ICP-MS

EXAMPLE: IDENTIFICATION OF TOXIC TRACE ELEMENTS



System 1



System 2

Matrix matched calibration curves carried out on two different ICP-OES systems. Elements analyzed for each system include (clockwise from upper right): arsenic, cadmium, mercury, and lead.

innovation forward

https://www.spectroscopyonline.com/view/icp-oes-as-a-viable-alternative-to-icp-ms-for-trace-analysis-meeting-the-detection-limits-challenge

DLS - Zetapotential

DYNAMIC LIGHT SCATTERING - PARTICLE SIZE DISTRIBUTION

Coating binder

- Surface charge and colloidal stability of binder particles (latexes)
  - e.g. waterborne coatings, latex binders, acrylic dispersions, styrene-acrylic emulsions, polyurethane dispersions (PUD), bio-based binder dispersions
- Dispersion stability, storage stability
- Binder-additive compatibility
- Effectiveness of dispersants and surfactants
- Sensitivity to pH
- Coagulation and film formation
- Aging and degradation
  - e.g. changes in zeta potential over time can indicate surfactant loss, binder degradation, microbial effects, changes in particle surface chemistry

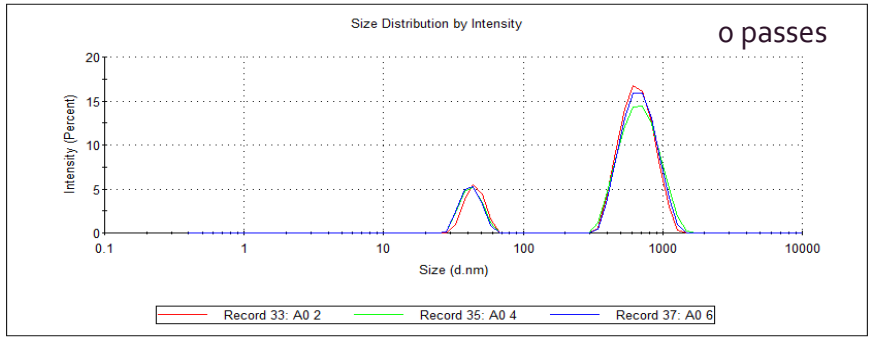
Coating additives

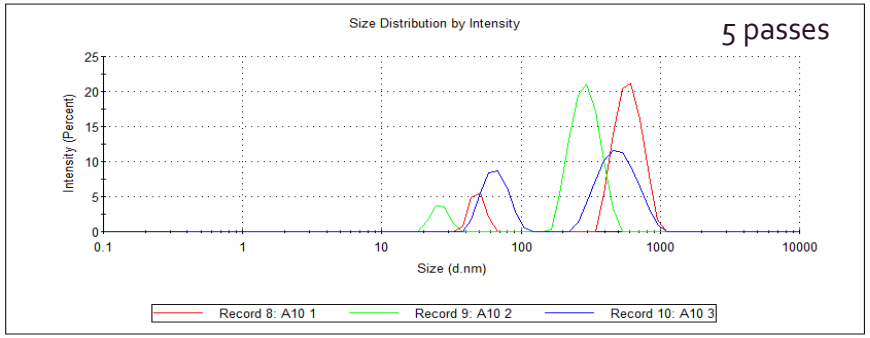
- Mean and average particle size
- Particle size distribution
  - e.g. particle size strongly influences gloss, opacity, color strength, surface smoothness, sedimentation rate
- Homogeneity of particle size
- Compatibility of surface modification
- Dispersion quality
- Particle stability
  - e.g. agglomeration, settling, flocculation, sedimentation, viscosity drift
- Surface charges
- Effectiveness/concentration of dipsersants
  - e.g. a good dispersant causes higher absolute zeta potential, greater particle repulsion, reduced flocculation
- Nano- versus microscale particles

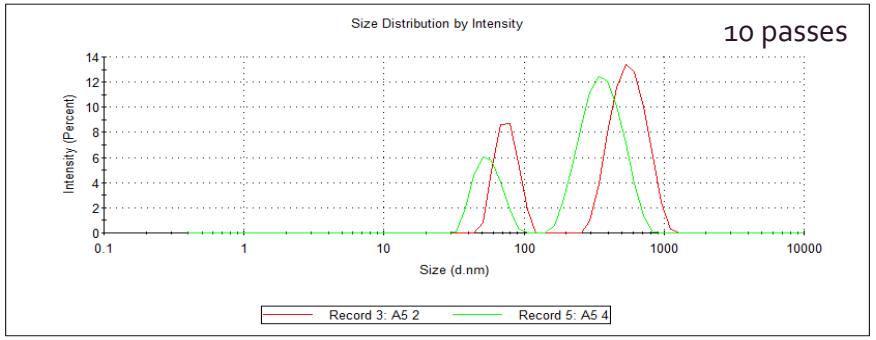
DLS - Zetapotential

EXAMPLE: HOMOGENIZATION OF AQUEOUS WAX DISPERSION FOR COATING APPLICATION









	Peak 1	Peak 2
A0	43.5 nm	700 nm
A5	65.7 nm	474 nm
A10	47.1 nm	467 nm

- High polydispersity with initial nm size fraction
- Instabilities and coalescence after processing

innovation forward

Samyn et al., non-published data

BET Surface analysis

BRUNAUER-EMMETT-TELLER THEORY

Coating binder

BET analysis is generally much less informative for the polymer binder than for solid additives.

BET is primarily a powder characterization technique that measures specific surface area and porosity through gas adsorption.

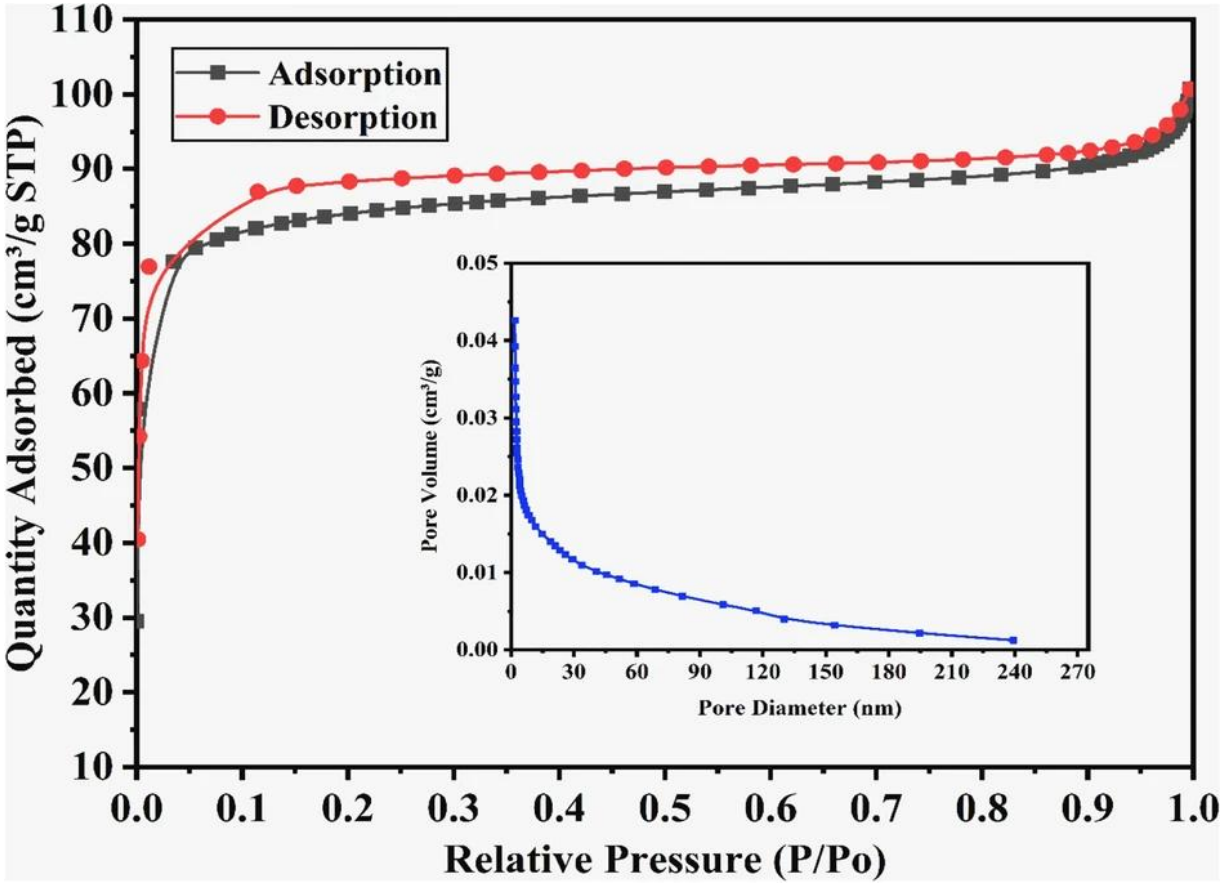
e.g. dried latex and binder particles
e.g. porosity of the binder
e.g. binder accessibility (water, solvents, additives)

Coating additives

- Specific surface area (m2/g)
- Porosity: pore volume and pore size distribution
  e.g. meso- versus nanoscale porosity
- Absorption capacity
  e.g. for water, solvents, binder components, functional molecules
- Surface treatment efficiency
  e.g. silane-treated silica, coated $CaCO_3$, fnctionalized nanoclay
- Nano-additive characteristics
  e.g. for approximately spherical particles, the small particles have a high BET, the large particles have a low BET

BET Surface analysis

EXAMPLE: EVALUATION OF BIOCHAR ADDITIVES



The WAS-BC adsorbent N2 adsorption–desorption isotherms and the pore diameter (inset) are presented in Fig. 1. The WAS-BC sample exhibits the type I adsorption isotherm curve, which suggests the formation of meso and macropores in the adsorbent.

The hysteresis loop of H4 showing non-limiting adsorption at high relative pressure imply the uniform narrow slit-shaped porosity of WAS-BC31,62,63.

The pore diameter and pore volume distributions of WAS-BC (Fig. 2 inset) show that the pores are mostly mesoporous because they fall into the range of 2–50 nm with an average pore diameter size of 4.09 nm. In addition, the total pore volume of WAS-BC was 0.042 (cm3/g).

https://www.nature.com/articles/s41598-021-82277-2

Contact angles

Coating binder

- Surface energy
- Binder film formation
- Adhesion potential
- Surface chemical changes during aging
- Surface segregation of binder components
- Compatibility with additives
- Anti-Fouling, Repellent and Easy-Clean Performance
  e.g. dirt release, water repellence, easy-clean performance

Coating additives

- Surface activity, surface energy modification
  e.g. silicone additives, fluorinated additives, waxes, surface-active agents
- Wettability
- Additive-binder compatibility
- Surface enrichment, surface coverage efficiency and migration
- Hydrophobicity
- Effectiveness of Surfactants
- Adhesion potential
- Aging and additive loss
  e.g. additive depletion, surface oxidation, surface contamination

Nanoindentation - Hardness

Coating binder

- Local mechanical properties (basic property)
  e.g. hardness (H), stiffness / elastic modulus (E)
- Crosslinking degree (degree of cure)
- Plasticization
- Gradients in mechanical properties or curing
- Aging/degradation effects and gradients
- Surface versus bulk properties
- Surface durability, scratch and wear resistance

Coating additives

- Reinforcement efficiency
  e.g. silica NP nanoclay, graphene, cellulose nanofibers, talc, TiO_2
- Additive-binder interface interactions
  e.g. binder-rich regions, filler-rich regions, interfacial regions
- Effects of surface treatment on compatibility
- Dispersion quality and uniformity
  e.g. additive agglomeration and dispersion
- Local adhesion and stress transfer near interface
  e.g. load transfer, property drop near particles
- Additive migration (property gradients surface versus bulk, surface curing)

Nanoindentation - Hardness

EXAMPLE: MECHANICAL REINFORCEMENT OF NANOCELLULOSE ADDITIVES IN BIO-EPOXY MATRIX

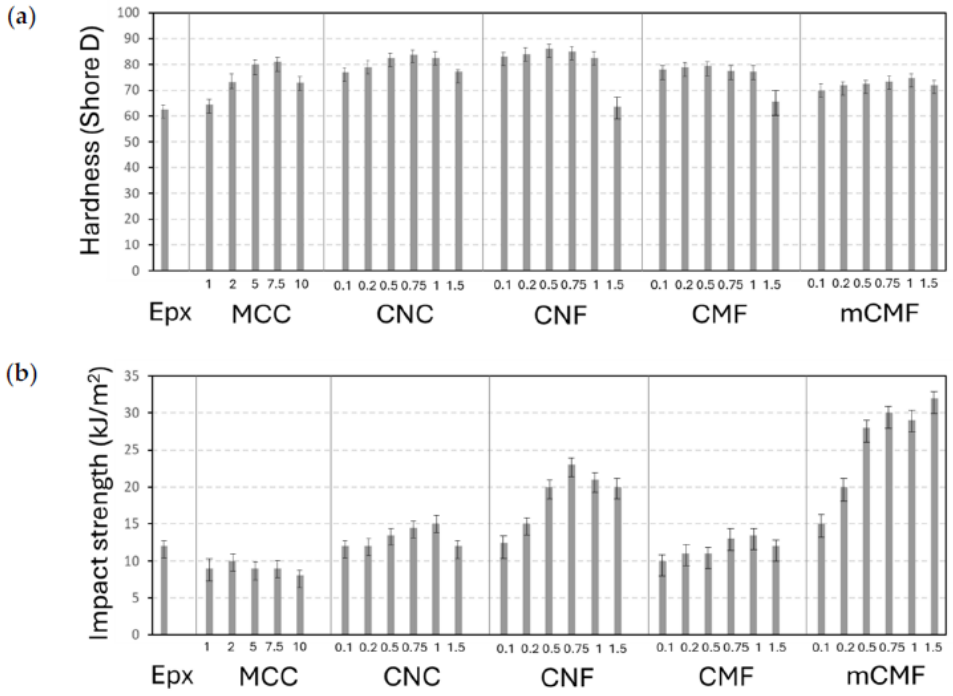


Figure 7. Mechanical testing results of epoxy coatings with different micro- and nanocellulose additives at various concentrations (numbers in X-bar represent wt.%), including (a) hardness and (b) impact strength.

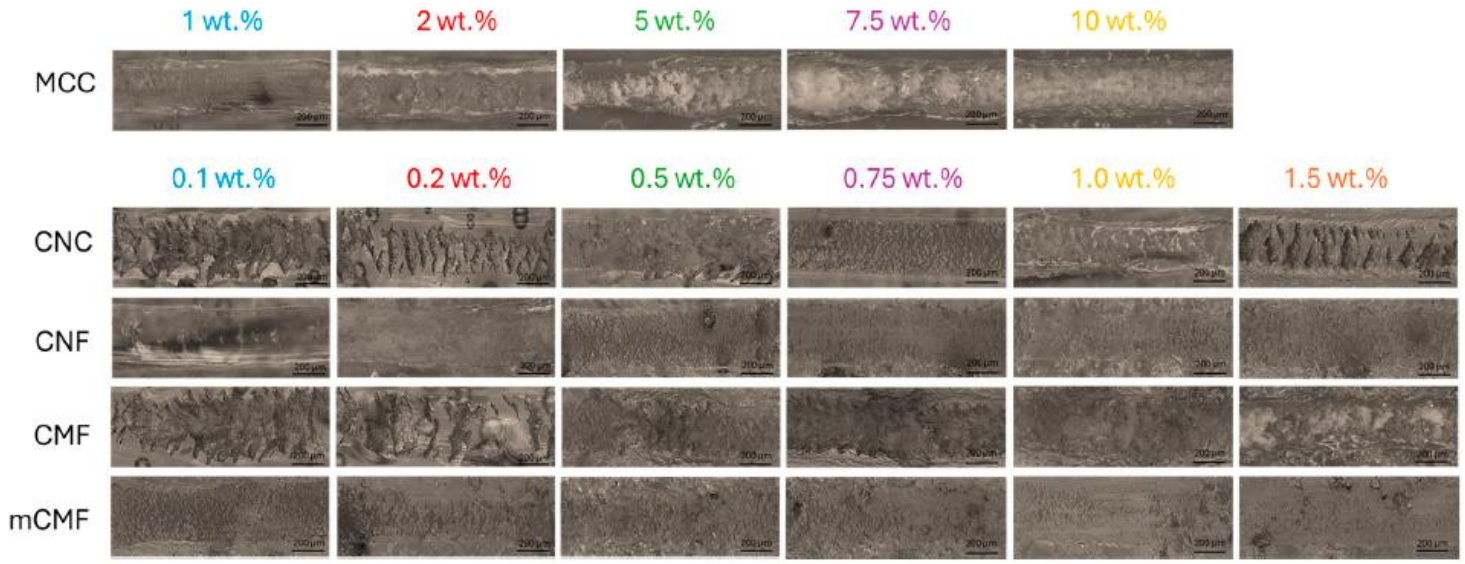


Figure 8. Scratching results of epoxy coatings with different micro- and nanocellulose additives at various concentrations, as observed through optical microscopy of the scratching track.

Raman spectroscopy – chemical mapping

COMPLEMENTARY SPECTROSCOPIC TECHNIQUE

Coating binder

FTIR detects vibrations that involve a change in dipole moment, making it particularly sensitive to polar functional groups such as: carbonyls (C=O), hydroxyls (O–H), amines (N–H), esters and ethers.

This makes FTIR excellent for identifying binder chemistries such as alkyds, acrylics, polyurethanes, epoxies, and degradation products formed during ageing.

Raman spectroscopy detects vibrations associated with a change in polarizability. It is particularly sensitive to C=C bonds, aromatic rings, polymer backbone structures, symmetric molecular vibrations.

As a result, Raman often provides information that is weak or absent in FTIR spectra.

Alkyd resins: FTIR clearly identifies ester carbonyl bands and oxidation products, while Raman provides information on unsaturated fatty acid chains and aromatic phthalate structures.

Acrylic binders: FTIR is highly effective for differentiating acrylate ester functionalities; Raman can help distinguish polymer backbone structures and copolymer composition.

Epoxy coatings: FTIR follows epoxy ring consumption and curing reactions, whereas Raman is useful for monitoring aromatic epoxy networks and degree of cure.

Information	FTIR strength	Raman strength
Functional groups (C=O, O–H, N–H)	Excellent	Moderate
Polymer backbone identification	Good	Excellent
Aromatic content	Moderate	Excellent
Pigment identification	Limited in many cases	Often excellent
Water-containing samples	Problematic due to strong water absorption	Usually less affected
Spatial resolution in microscopy	Moderate	Higher (typically ~1 µm)

Raman spectroscopy – chemical mapping

COMPLEMENTARY SPECTROSCOPIC TECHNIQUE

Coating additives

- Additive identity (both organic, inorganic)

  e.g., pigments (TiO_2, iron oxides, phthalocyanines, carbon black, etc.), mineral fillers ($CaCO_3$, $BaSO_4$, talc, silica), wax additives, polymer modifiers, some dispersants and processing aids, certain flame retardants and stabilizers, corrosion inhibitors and anticorrosive pigments

- Additive (semi-)quantification

  e.g., relative pigment concentration, binder to additive ratio, release properties

- Spatial distribution (Raman mapping)

  e.g. uniformly dispersion, Agglomeration of pigments or fillers, migration of additives toward the surface, layer-by-layer composition in multilayer coatings, coating surface coverage (%)

- Carbon content

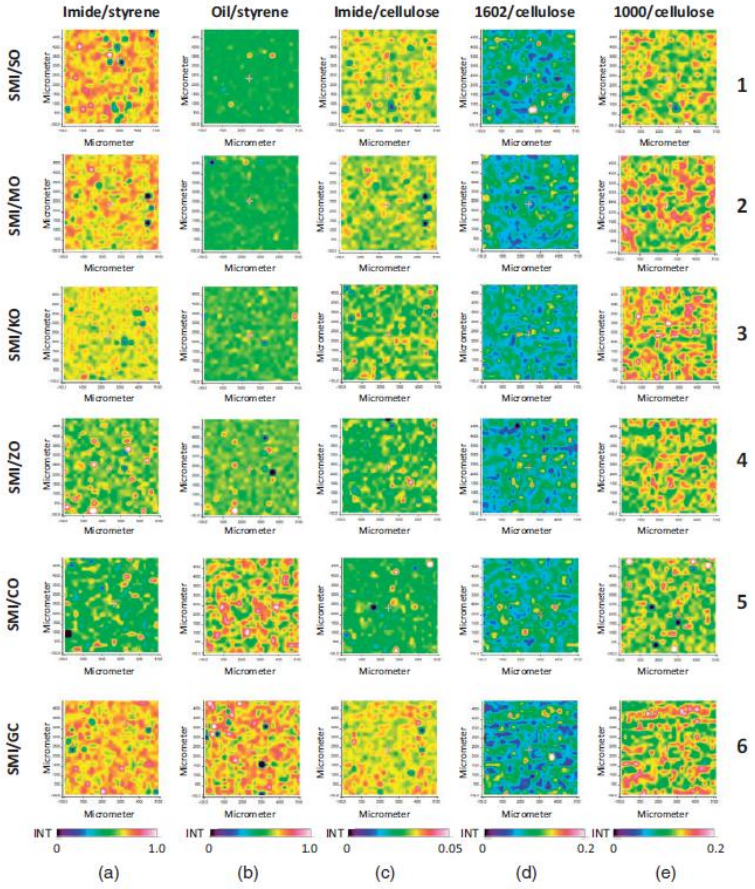
  e.g. carbon black, ashes, biochar,

Common limitations include:

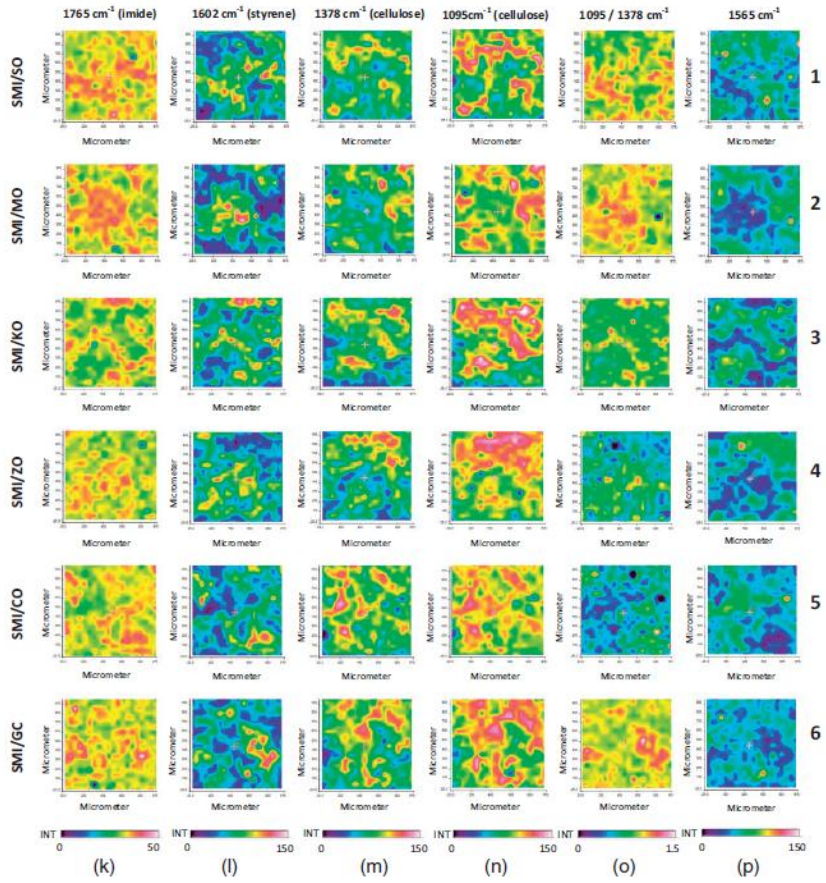
- very low additive concentrations (<0.1–1 wt%)
- strong fluorescence from organic binders or pigments
- additives with weak Raman scattering
- complex mixtures with overlapping spectra
- distinguishing chemically similar additives without reference spectra

Raman spectroscopy – chemical mapping

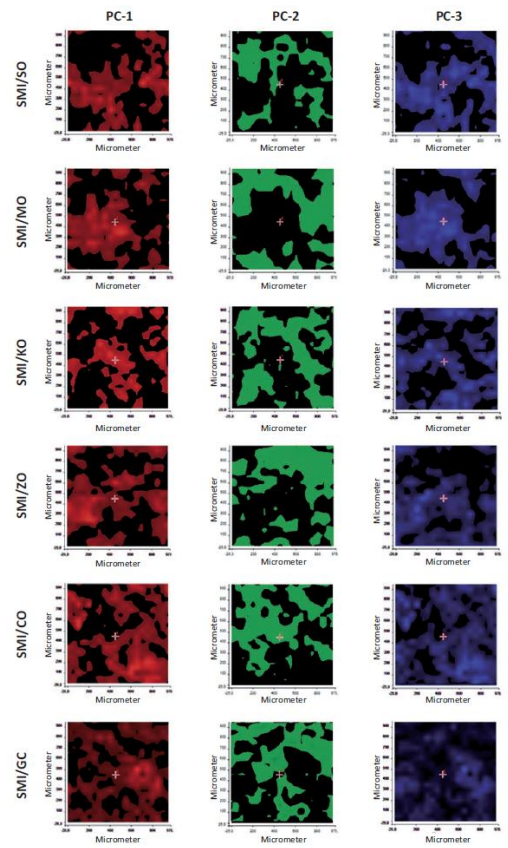
EXAMPLE: SURFACE MAPPING OF PAPER COATINGS WITH BIOBASED OIL-FILLED NANOCAPSULES, THERMAL RELEASE OF OIL AT SURFACE



Raman maps of SMI–oil coated paper (5x5mm²) with band intensity ratios of imide, oil, styrene, and cellulose.



Raman maps of SMI–oil coated paper (11mm2) with band intensity ratios of imide, oil, styrene, and cellulose



Principal component analysis of chemical maps for SMI–oil coated papers representing surface coverage of principal components PC-1, PC-2, and PC-3.

innovation forward

P. Samyn et al. Surface chemistry of oil-filled organic nanoparticle coated papers analyzed by micro-Raman mapping, Applied Spectroscopy 73 (2019), 67-77.

ToF-SIMS – chemical mapping

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROSCOPY

Coating binder

- Binder chemistry identification
  e.g., the mass spectrum contains characteristic ion fragments that act as a molecular fingerprint of the polymer: acrylics, polyurethane, epoxy, alkyd, polyester, fluoropolymers, silicones
- Surface enrichment and phase segregation
  e.g., silicone migration, fluoropolymer enrichment, wax blooming, surface-active resin components, phase separation between binder components
- Binder composition through the coating thickness (sputtering)
  e.g., using sputter depth profiling, ToF-SIMS can determine how binder chemistry changes with depth.This can reveal surface skin formation, multilayer coating structures, interdiffusion between primer and topcoat, binder gradients created during curing, resin-rich vs filler-rich regions
- Binder degradation and aging (fragmentation)

Based on experience with industrial coatings, Raman is often the better tool for pigments and fillers, while ToF-SIMS is usually the better tool for understanding the binder, surface chemistry, additive migration, and coating failures. The two techniques are highly complementary.

However, both techniques represent already highly advanced characterization

Question	Raman	ToF-SIMS
Identify binder type	Good	Excellent
Detect low-level surface species	Limited	Excellent
Surface chemistry (top nm)	Poor	Excellent
Additive migration	Moderate	Excellent
Depth profile through coating	Moderate	Excellent
Binder degradation products	Moderate	Excellent
Pigment identification	Excellent	Good
Quantification	Moderate	Difficult

ToF-SIMS – chemical mapping

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROSCOPY

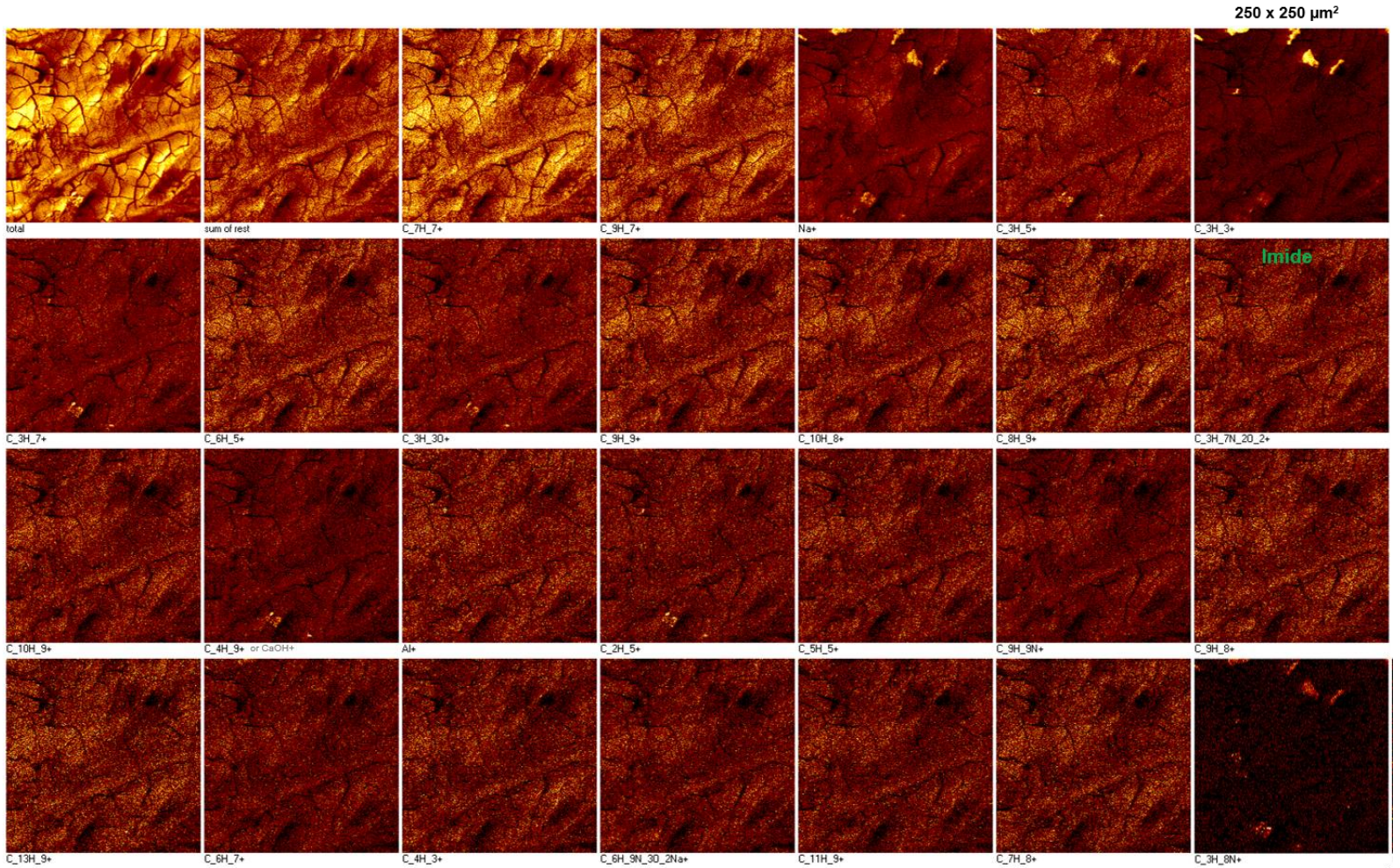
Coating additives

- Identify additives at very low concentrations
  e.g., silicone additives, fluorinated additives, wax additives, dispersants, flow and leveling agents, UV stabilizers, HALS stabilizers, plasticizers, corrosion inhibitors, surfactants and defoamers
- Additive migration and separation
  e.g., additive-rich domains, agglomerates, surface defects, craters and fisheyes, pigment-additive interactions, heterogeneous dispersion
- Additive distribution maps
  e.g., surface enrichment of silicone additives, depletion zones below the surface, migration toward interfaces, additive concentration gradients, differences between topcoat and primer
- Elemental analysis
- Additive depth profiles
- Additive-binder compatibility
- Contaminants versus intentional additives

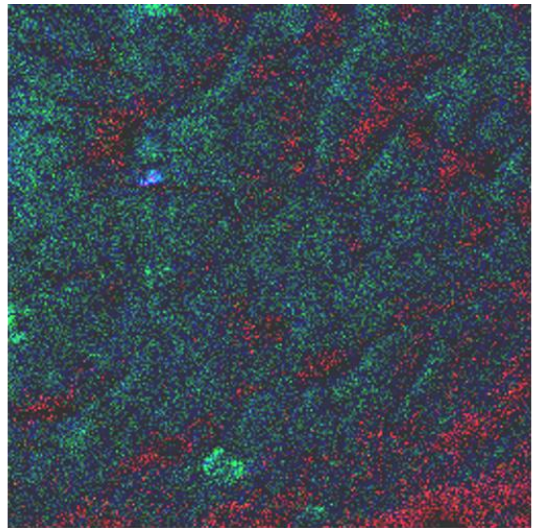
The ability to determine the **spatial distribution** of additives is one of the strongest advantages of Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Unlike bulk analytical methods that provide only an average composition, ToF-SIMS reveals where additives are located within a coating—on the surface, around pigments, at interfaces, or throughout the coating thickness. It combines chemical specificity with high spatial resolution and can generate both 2D and 3D chemical maps.

ToF-SIMS – chemical mapping

SPATIAL DISTRIBUTION OF ADDITIVES BY CHEMICAL MAPPING OF MOLECULAR FRAGMENTS

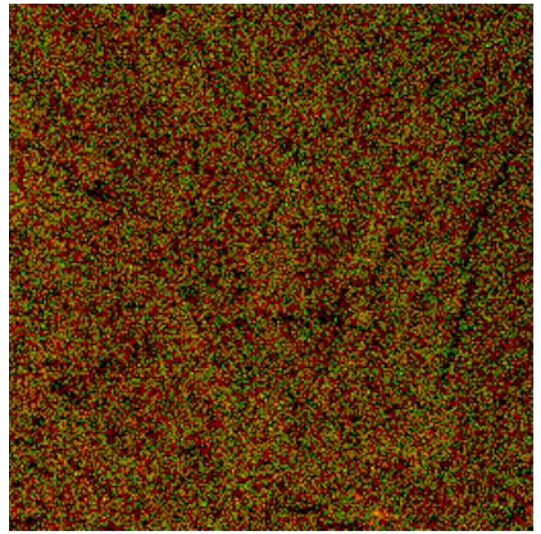


Distribution of coating over paper



Red : C^- Green : $CHNO^-$ Blue : OH^-

Distribution of oil and fillers in coating



Red : $C_{20}H_{15}^-$ Green : $CaOH^-$

innovation forward

P. Samyn et al. Advanced chemical surface characterization of coated papers using ToF-SIMS spectral analysis and imaging, PTS Symposium 2014.

Contact

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