# AGING MECHANISMS IN FIBERS AND POLYMER MATERIALS: IMPLICATIONS FOR LONG-TERM PERFORMANCE AND RELIABILITY

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# THE PRESENTER

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- Over 25 years of experience in R&D from technology conception to prototyping in the field of polymers and polymer composites
- Focus on energy industry and energy storage applications
- Collaborated nationally and internationally as university researcher and worked as private consultant
- Executive Member of Pressure Vessel and Piping Division of the American Society for Mechanical Engineers (ASME)
- Past President of the Canadian Association for Composite Structures and Materials (CACSMA)

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- A freely available online resource for composite materials engineering:

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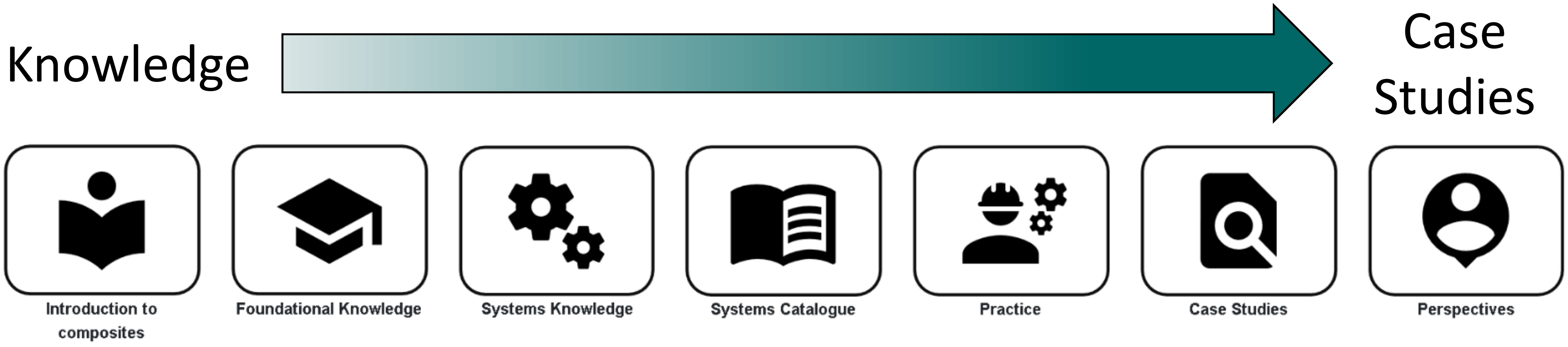
- Focus on practice, guided by foundational knowledge and a systems-based approach to thinking about composites manufacturing



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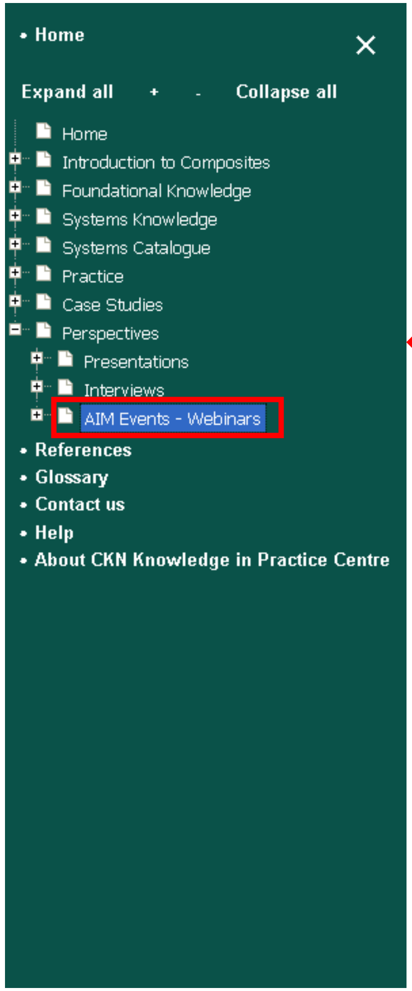



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Today's Webinar will be posted at:
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## TODAY'S TOPIC:

# *Aging Mechanisms in Fibers and Polymer Materials: Implications for Long-Term Performance and Reliability*

# OUTLINE

- **Aging Mechanisms in Polymers and Fibers**
  Why material aging matters; main aging mechanism in polymers and fibers
- **Influence of Aging on Material Properties**
  Aging effects on polymers; aging effect on fibers; coupled aging effects
- **Experimental Characterization and Design Integration**
  Characterization strategy; mechanical testing; thermal and viscoelastic characterization; microscopy and spectroscopy; accelerated aging; lifetime prediction; design integration; validation; standards and long-term monitoring
- **Hydrothermal Aging Case Studies and take-home messages**
  Fibers: E-glass, carbon; thermoplastics: PA6 and PVDF case comparison

# *Aging Mechanisms in Fibers and Polymer Materials*

# WHY MATERIAL AGING OF FIBER AND POLYMER MATTERS

**COMPOSITE MATERIAL**

**POLYMER MATRIX**

**FIBER REINFORCEMENT**

**Studying the constituents separately has advantages over examining fiber-polymer composites directly:**

- Create knowledgebase for guiding design decisions
- Understand severity and time-scale for aging effects
- Become aware of ‘worst-case scenario’ situations

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# WHY MATERIAL AGING OF FIBER AND POLYMER MATTERS

**MECHANISMS (WHAT MATERIALS EXPERIENCE)**

- TIME
- HEAT
- MOISTURE
- CHEMICALS
- UV/SUNLIGHT
- MECHANICAL LOADING

**POLYMER AND FIBER MATERIALS AND THEIR COMPOSITES**

**CONSEQUENCES (WHAT HAPPENS)**

- STRENGTH LOSS
- STIFFNESS CHANGE
- EMBRITTLEMENT
- MICROCRACKING
- DIMENSIONAL INSTABILITY
- REDUCED SERVICE LIFE

# DEFINING AGING MECHANISMS

**MAIN AGING MECHANISMS**

**1. THERMAL AGING**

**EXPOSURE**

Elevated temperature

**2. MOISTURE AND FLUID ABSORPTION**

**EXPOSURE**

Water, humidity, other fluids

**3. CHEMICAL DEGRADATION**

**EXPOSURE**

Oxidizing agents, (UV) radiation, ozone, chemicals

**4. MECHANICAL LOADING AND PHYSICAL AGING**

**EXPOSURE**

Sustained load, cyclic loading, vibration

**Various aging mechanisms may occur separately, consecutively, or concurrently**

# THERMAL AGING

## Polymer Thermal Aging

| | |
|---|---|
| Increased chain mobility → | Residual stress reduction, change in crystallinity |
| Chain scission → | Reduced molecular weight and mechanical properties |
| Oxidation → | Formation of carbonyls, radicals, etc. |
| Crosslinking → | New bonds form between chains |
| Shrinkage → | Free volume change, warpage, embrittlement |
| Softening near Tg → | Increase in volume and drop in stiffness |
| Reduced strength → | Lower load-bearing capacity and stiffness |

## Fiber Thermal Aging

- Surface oxidation
- Interfacial deterioration
- Embrittlement
- Microcrack formation
- Strength reduction

# MOISTURE AND FLUID ABSORPTION

## Environment

**Water (liquid)**

**Humidity (vapor)**

**Solvents / Oils**

## Effects in Polymers

**Swelling**
Volume increase, free volume rise

**Plasticization**
Chain mobility increases, Tg decreases

**Hydrolysis**
Polymer chain scission or matrix degradation

**Additive leaching**
Loss of stabilizers, plasticizers, fillers

**Reduced stiffness**
Lower modulus and higher creep

## Effects in Fibers

**Surface attack**
Reaction with surface functional groups

**Hydrolysis**
Breakdown of sizing or fiber constituents

**Dissolution / weakening**
Loss of mass and strength

**Increased roughness**
Surface erosion and fibrillation

## Consequences

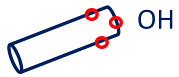
**Reduced mechanical performance**
Stiffness, strength

**Dimensional change**
Swelling, warping, shrinkage

# CHEMICAL AND UV DEGRADATION

## Oxidation

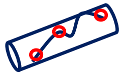

**Polymers**
Free-radical attack




**Fibers**
Surface chemistry change

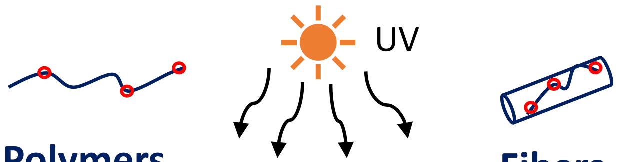
## Aggressive Chemicals

**Polymers**
Free-radical attack and plasticization



**Fibers**
Surface chemistry change

## UV / Photo-oxidation




**Polymers**
Photo-generated free radicals

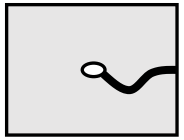
**Fibers**
Surface chemistry change

## Consequences

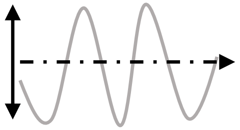
| Polymers | Fibers |
| --- | --- |
| Chain scission or crosslinking | Pitting |
| Yellowing | Leaching |
| Chalking | Loss of interfacial strength |
| Surface cracking | Microcracking |
| Environmental stress cracking | |

# MECHANICAL LOADING AND PHYSICAL AGING

**Crack initiation**
Localized damage originating at flaws

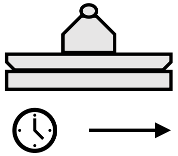


**Fatigue**
Damage accumulation

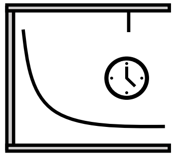


**Crazing**
Localized plastic yielding

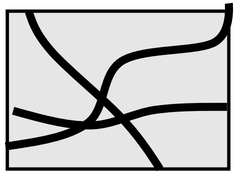
**Creep**
Time-dependent deformation



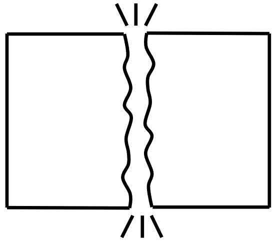
**Stress relaxation**
Stress decays under constant strain



**Microcrack propagation**
Cracks grow and link



**Eventual failure**
Loss of function



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# *Influence of Aging on Material Properties*

# AGING EFFECTS ON POLYMER PROPERTIES

**Mechanical properties**

- Strength ↓
- Modulus change
- Ductility often ↓
- Creep resistance ↓

**Thermal / viscoelastic**

- Tg can ↓
- Changes in storage modulus, damping behavior

**Physical / dimensional**

- Swelling or shrinkage
- Warping / distortion
- Mass change due to uptake or loss
- Free volume changes

**Surface / chemical signs**

- Yellowing or discoloration
- Chalking / roughness
- Oxidation / hydrolysis
- Surface cracking

**General polymer aging pathway**

1. **Exposure** heat, water, UV, chemicals
2. **Molecular change** chain scission, oxidation, plasticization
3. **Microstructural change** morphology, swelling, microcracks
4. **Property loss** stiffness, strength, toughness, durability

Key message: In polymers, aging often starts at the molecular level and then propagates into dimensional change, surface damage, and loss of mechanical performance

# AGING EFFECTS ON FIBER PROPERTIES

**Surface condition**

- Etching / roughness can increase
- Pitting or microdefects may form
- Surface chemistry can change
- Protective sizing may degrade

**Mechanical performance**

- Tensile strength can decrease
- Fatigue life becomes shorter
- Brittleness can increase
- Residual load capacity is reduced

**Hydrothermal / chemical**

- Moisture can weaken surfaces
- Leaching or hydrolysis may occur
- Chemical media can attack flaws
- Environmental damage accelerates crack growth

**Visible / practical signs**

- Surface whitening or discoloration
- Roughened or eroded surface
- Fraying or fibrillation in some fibers
- Greater scatter in measured strength

**General fiber aging pathway**

1. **Exposure** — heat, moisture, chemicals, UV, cyclic load
2. **Surface change** — roughness, etching, sizing degradation, flaw growth
3. **Damage evolution** — microcrack initiation, embrittlement, crack propagation
4. **Property loss** — tensile strength ↓, fatigue life ↓, reliability ↓

Key message: Fibers are highly sensitive to surface condition and flaw growth. Because fiber strength is typically flaw-controlled, relatively small environmental damage can lead to substantial loss in tensile strength and reduction in service life.

# POLYMERS VS FIBERS: MAIN PROPERTY CHANGES

| | Polymers | Fibers |
|---|---|---|
| **Most sensitive** | moisture / fluids, temperature near Tg, UV / oxidation | surface attack, flaw growth, hydrothermal damage, fatigue |
| **Typical mechanism** | chain scission, plasticization, oxidation, free-volume change | etching, hydrolysis, oxidation, crack initiation |
| **Most visible outcome** | swelling, softening, discoloration, cracking | roughness, pitting, surface flaws, embrittlement |
| **Main property loss** | stiffness, strength, toughness, creep resistance | tensile strength, fatigue life, reliability |

## How to interpret

- Polymers usually age through molecular and viscoelastic changes first
- Fibers usually show property loss through surface-damage and flaw-sensitive failure.
- Moisture can plasticize polymers, while in fibers it often promotes surface weakening or flaw growth
- Temperature affects both, but the governing mechanisms are different for polymers and fibers

# *Experimental Characterization and Design Integration*

# CHARACTERIZATION STRATEGY

| Mechanical testing | Thermal / viscoelastic analysis | Microscopy + spectroscopy | Accelerated aging + prediction |
|---|---|---|---|
| Quantify residual strength, modulus, fatigue and creep response | Track Tg, decomposition, storage modulus / loss modulus / damping | Associate property changes with cracks, surface damage and chemical degradation | Use heat, humidity, UV or fluids to generate lifetime-prediction data |

**Experimental workflow**

**Define environment temperature, fluids, UV, loading** → **Expose material real-time or accelerated aging** → **Measure changes in mechanical, thermal, chemical, morphology** → **Interpret damage mechanism-property link** → **Screen, select, validate**

Main message: Aging evaluation is strongest when property measurements are paired with chemical and morphological evidence, then used to support design decisions under realistic service conditions

# ACCELERATED AGING: REPRODUCING LONG-TERM EXPOSURE IN THE LAB

Accelerated tests generate practical data for durability evaluation when real-time aging is too slow

### Thermal aging

air oven, elevated temperature, no load

Image source: Materials Processing Institute

### Hydrothermal aging

immersion, humidity, hot water, saturation

Image source: LIB

### UV / oxidative exposure

UV chamber, oxygen-rich or outdoor-like exposure

Image source: ChiuVention

### Chemical immersion

acids, bases, solvents, fuels, service fluids

Image source: MICOM INC.

### Stress-assisted aging

mechanical load plus environment

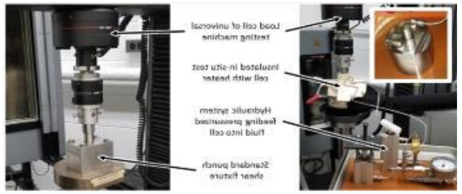

Image source: Materials 2022, 15(7), 2690. https://doi.org/10.3390/ma15072690

### Accelerated test planning

**Variables**
temperature • time • humidity • fluid • UV dose • stress

**Measured response**
mass uptake • strength retention • Tg • modulus • crack density

**Risk**
over-acceleration can introduce non-service mechanisms

**Goal**
identify damage pathway, not only speed up testing

Accelerated aging should preserve the relevant mechanism while shortening the time required to observe measurable degradation

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# MECHANICAL TESTING: RESIDUAL PERFORMANCE AFTER AGING

Use mechanical response to quantify how aging changes load-bearing capability

### Tensile

- Strength, modulus, strain-to-failure
- Best first indicator of aging-driven embrittlement or softening

### Flexural

- Bending stiffness and damage sensitivity
- Useful for materials where surface damage dominates

### Creep

- Time-dependent deformation
- Critical for sustained-load applications

### Fatigue

- Life under repeated loading
- Reveals crack initiation and cumulative damage

### Impact / fracture

- Toughness and crack resistance
- Sensitive to microcracking and brittle transition


Universal testing machine with AE monitoring

**Data interpretation logic**

Aged specimen → Mechanical data → Property retention → Damage mechanism → Design allowables

# THERMAL AND VISCOELASTIC CHARACTERIZATION

Thermal techniques reveal molecular and viscoelastic changes that may not be visible from strength data alone

## DSC

- Glass transition (Tg)
- Melting, crystallization
- Enthalpic relaxation
- Crystallinity changes

Image source: MELTER TOLEDO

## TGA

- Mass loss vs temp.
- Decomposition onset
- Thermal stability
- Oxidative degradation

Image source: MELTER TOLEDO

## DMA

- Storage modulus
- Loss modulus
- Damping factor
- Frequency / temperature sweep

Image source: NETZSCH

## How these outputs support aging interpretation

**Tg shift**
plasticization, physical aging, restricted mobility

**Modulus / damping shift**
changed stiffness, relaxation, vibration response

**Early decomposition**
weakened molecular bonds or oxidative damage

**Crystallinity change**
morphology change affecting strength and ductility

Thermal characterization links aging to transition behavior, thermal stability, and viscoelastic performance

# MICROSCOPY AND SPECTROSCOPY: LINKING MECHANISMS TO EVIDENCE

Use morphology and chemistry to explain why properties changed after aging

## Findings of property loss should be supported by physical evidence

### Optical microscopy

- surface discoloration
- crazing or visible cracks
- surface roughening

Image source: OPTI TECH SCIENTIFIC

### SEM

- microcrack morphology
- voids or cavities
- surface erosion / fracture features

Image source: JEOL

### TEM / AFM

- nanoscale structure
- local topography
- local stiffness variation

Image source: JEOL

### FTIR / Raman

- oxidation markers
- hydrolysis signatures
- chemical bond changes

Image source: Anton Paar

## Evidence chain

**Aging exposure**
heat / moisture / UV / chemicals

**Morphological evidence**
cracks, voids, roughness

**Chemical evidence**
oxidation, hydrolysis, bond changes

**Property evidence**
strength, stiffness, ductility, fatigue

Microscopy shows where damage occurs while spectroscopy helps identify the chemical pathway that caused it

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# LIFETIME PREDICTION: FROM ACCELERATED DATA TO SERVICE CONDITIONS

Use degradation-rate trends to estimate long-term behavior under realistic environments

**Aging data**
retention vs time at multiple temperatures

→

**Rate extraction**
fit degradation response or rate constants

→

**Temperature relation**
Arrhenius / TTS shift factors

→

**Master curve**
collapse data to reference condition

→

**Service estimate**
predict time to retention threshold

**Example of lifetime prediction using Arrhenius model**

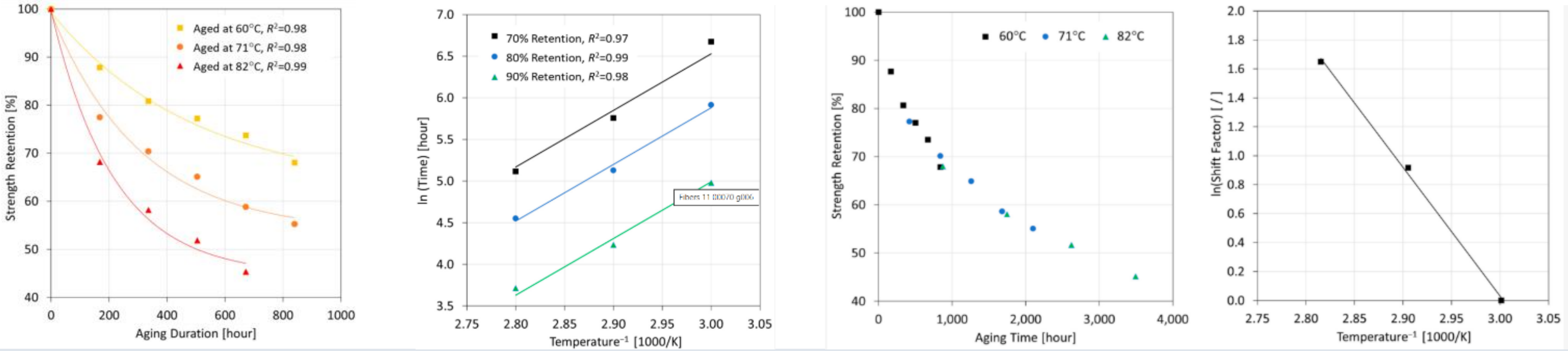


Image source: Fibers 2023, 11(8), 70.
https://doi.org/10.3390/fib11080070

- Do not extrapolate beyond a mechanism that is experimentally supported
- Confirm that accelerated conditions do not introduce unrealistic damage
- Use uncertainty ranges, not a single deterministic lifetime value
- Validate predictions with lower-temperature or longer-duration data when possible

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# DESIGN INTEGRATION: USING AGING DATA FOR MATERIAL SELECTION

Characterization data should feed directly into pre-screening, validation and design decisions

## Material-selection procedure

**Service requirements**
temperature, moisture, chemicals, load, lifetime

**Candidate materials**
polymer and fiber options

**Screening tests**
short-term exposure + key properties

**Accelerated validation**
mechanism-relevant exposure

**Design allowable**
property retention + uncertainty factor

## Design integration checklist

**1. Define exposure envelope**
max. temperature, humidity, fluid chemistry and loading

**2. Select response metrics**
strength retention, modulus, Tg, mass uptake, crack density

**3. Compare candidates**
rank by retention, variability, sensitivity, failure mode

**4. Account for uncertainty**
replicates, scatter, safety factors, model confidence

**5. Document validation path**
standards, protocols, inspection, monitoring plan

Aging characterization reduces uncertainty in material selection and supports safer long-term performance

# VALIDATION, STANDARDS AND LONG-TERM MONITORING

Make characterization reproducible and connect lab data to in-service reliability

## Standardized testing

- consistent specimen preparation
- repeatable aging conditions
- benchmarkable mechanical and thermal data
- traceable protocols for comparison

## Design under uncertainty

- use replicate testing
- report scatter and retention ranges
- combine accelerated and lower-severity data
- avoid unsupported extrapolation

## In-service monitoring

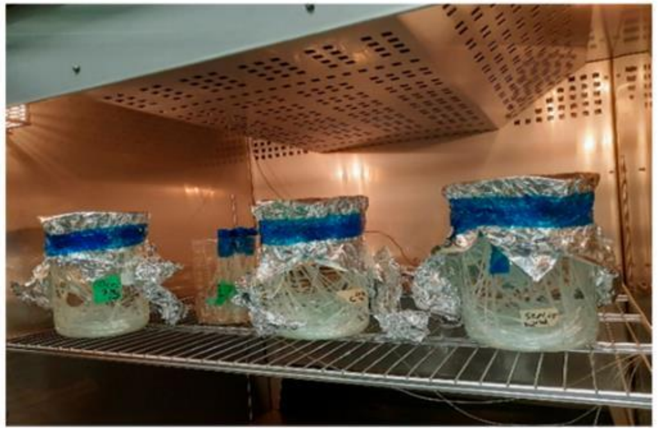
- acoustic emission (AE)
- embedded sensors
- periodic inspection
- link lab damage modes to field signals

# *Hydrothermal Aging Case Studies and Take-home Messages*

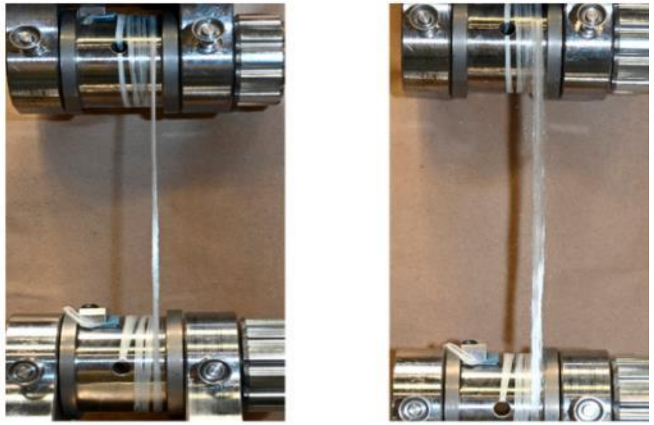
# GLASS FIBERS EXPOSED TO WATER AND ELEVATED TEMPERATURE

Hydrothermal exposure combines moisture and elevated temperature, accelerating constituent-level degradation

## Experimental setup

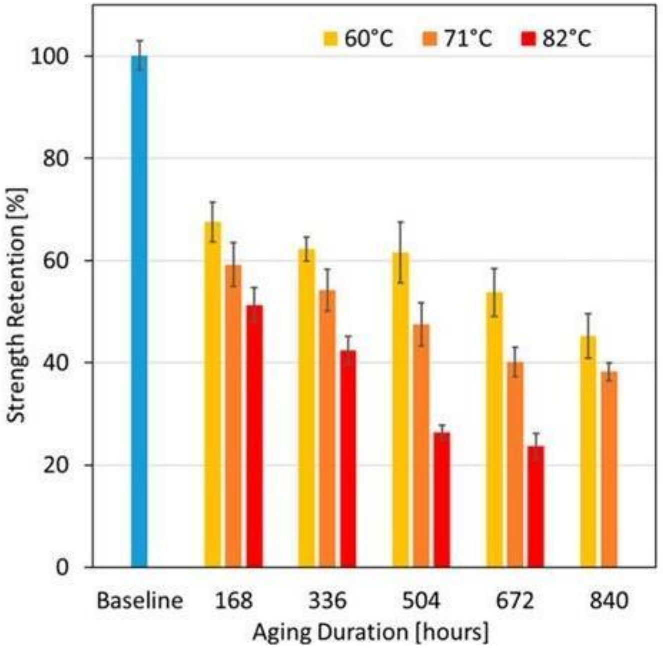


Aging oven / immersion beakers

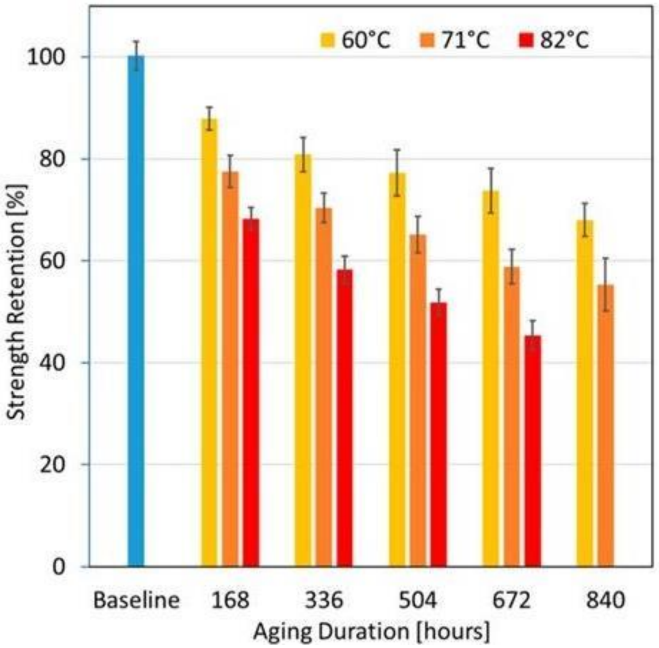


Capstan grip testing

Wet conditions




Dry conditions

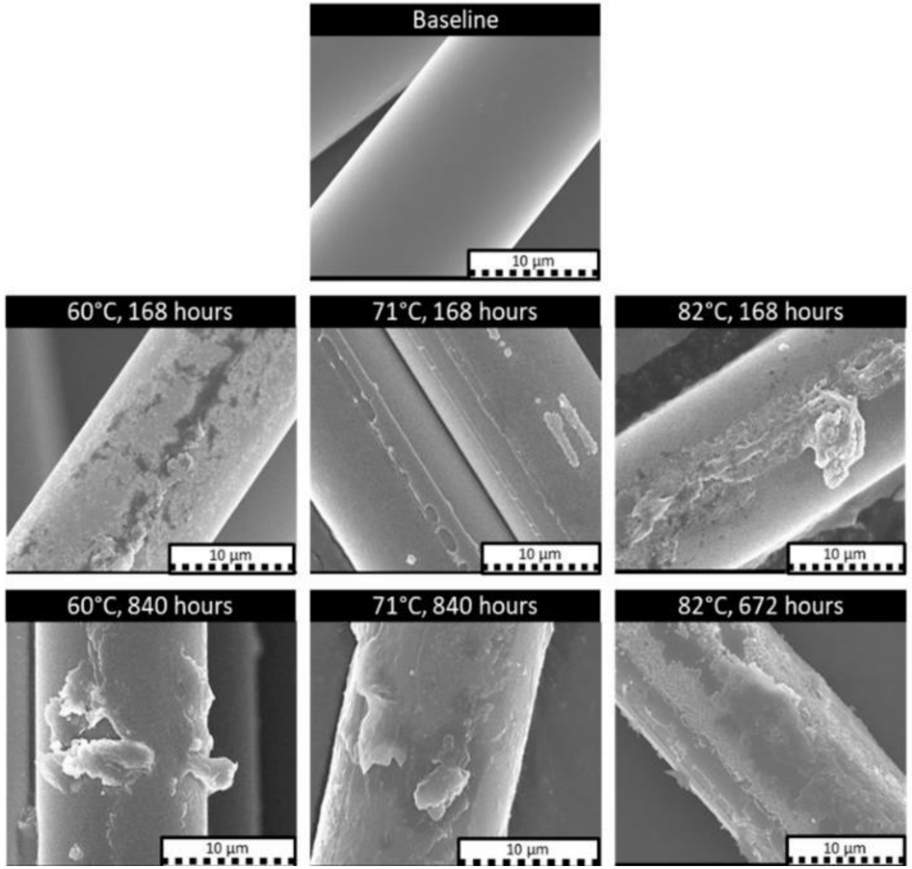



## E-glass fiber case study

- Strength retention decreases with increasing temperature and duration
- Wet-tested fibers show lower apparent strength than dried fibers
- Surface dissolution, hydroxyl attack, pitting, microcracking drive strength loss

# GLASS FIBERS EXPOSED TO WATER AND ELEVATED TEMPERATURE

## SEM: Surface morphology




## Interpretation for service life

- Water between filaments can reduce load sharing during testing
- Drying can partially restore frictional load sharing, but chemical surface damage remains
- Arrhenius-type acceleration can support lifetime estimation

**Mechanism chain**

**Water exposure** › **Leaching / hydrolysis** › **Surface pitting** › **Strength loss**

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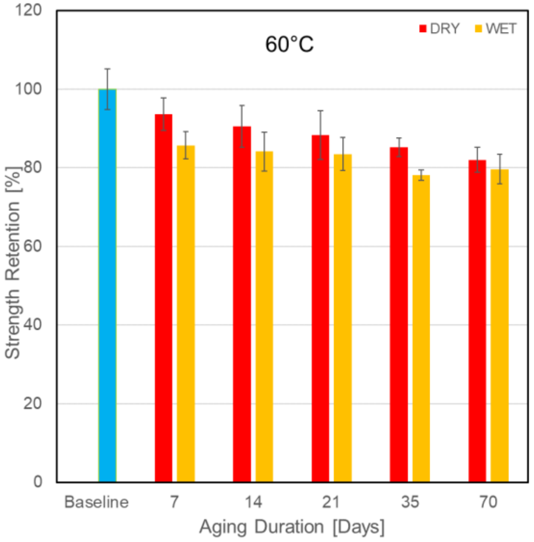
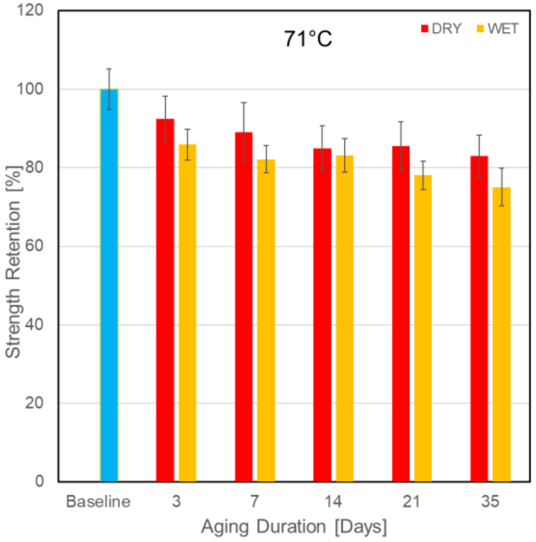
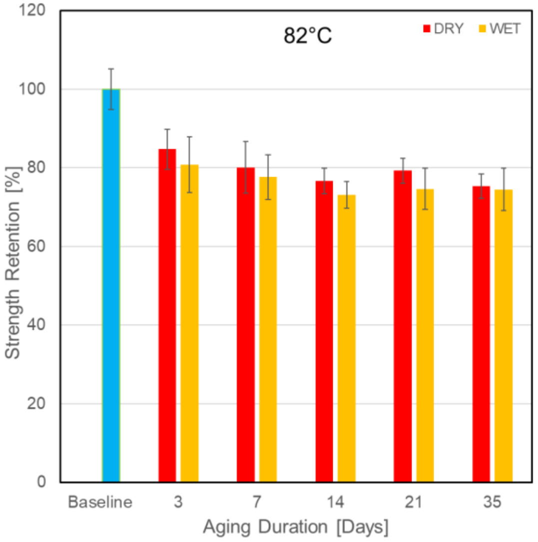
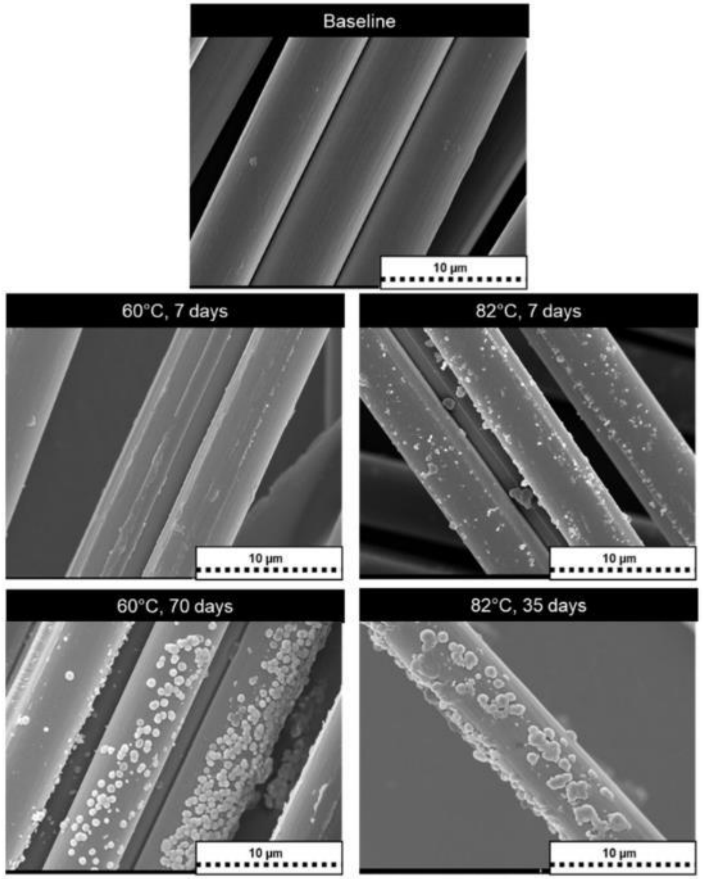
# CARBON FIBERS EXPOSED TO WATER AND ELEVATED TEMPERATURE




## SEM: carbon surface




- Higher retention compared with glass under similar conditions
- Possible degradation of sizing and surface flaws, but lower water sensitivity

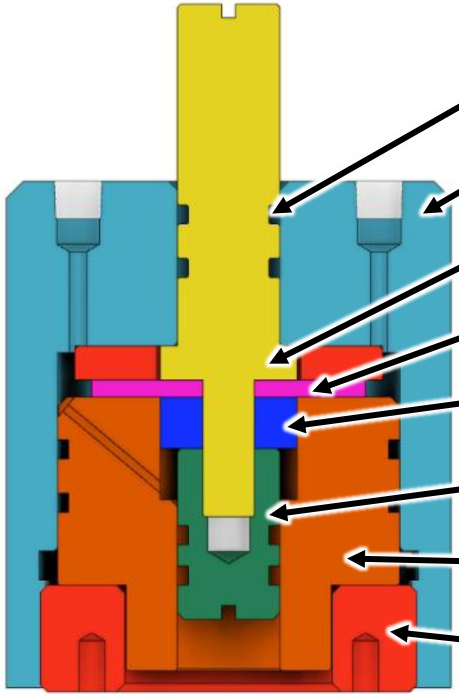
# THERMOPLASTICS EXPOSED TO WATER AND ELEVATED TEMPERATURE

## Punch-shear testing setup with in-situ test capabilities

Load cell of universal testing machine

Insulated in-situ test cell with heater

Hydraulic system feeding pressurized fluid into cell



O-ring seals

Test cell body

Punch rod with shear ring

Test coupon

Punch guide cylinder

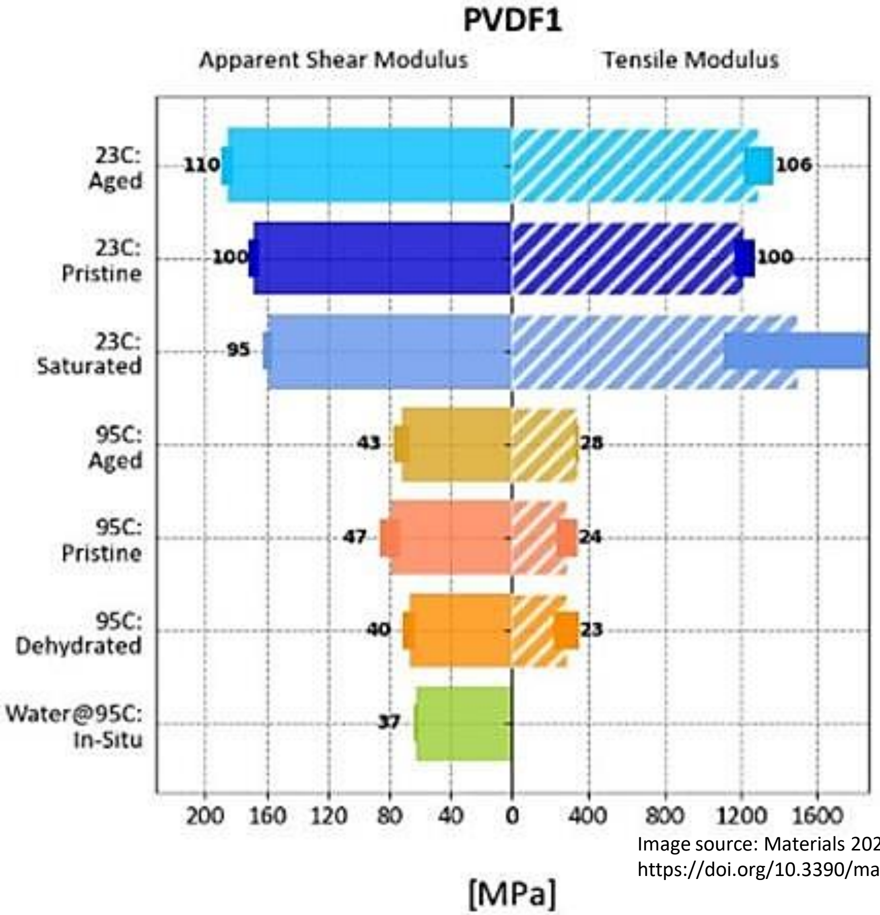
Punch bottom seal cylinder

Shear support and outer seal

Locking ring

# THERMOPLASTICS EXPOSED TO WATER AND ELEVATED TEMPERATURE

Plots compare PVDF1 under pristine, aged, saturated, dehydrated, and in-situ water conditions at 23 °C and 95 °C



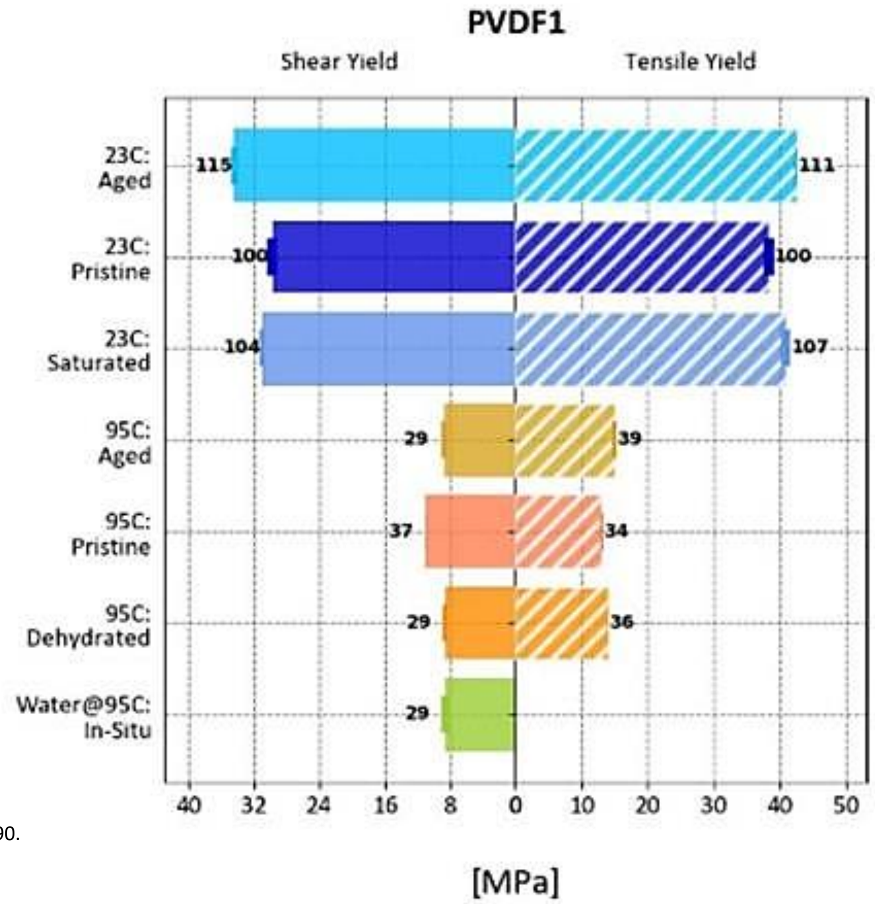




Image source: Materials 2022, 15(7), 2690.
https://doi.org/10.3390/ma15072690

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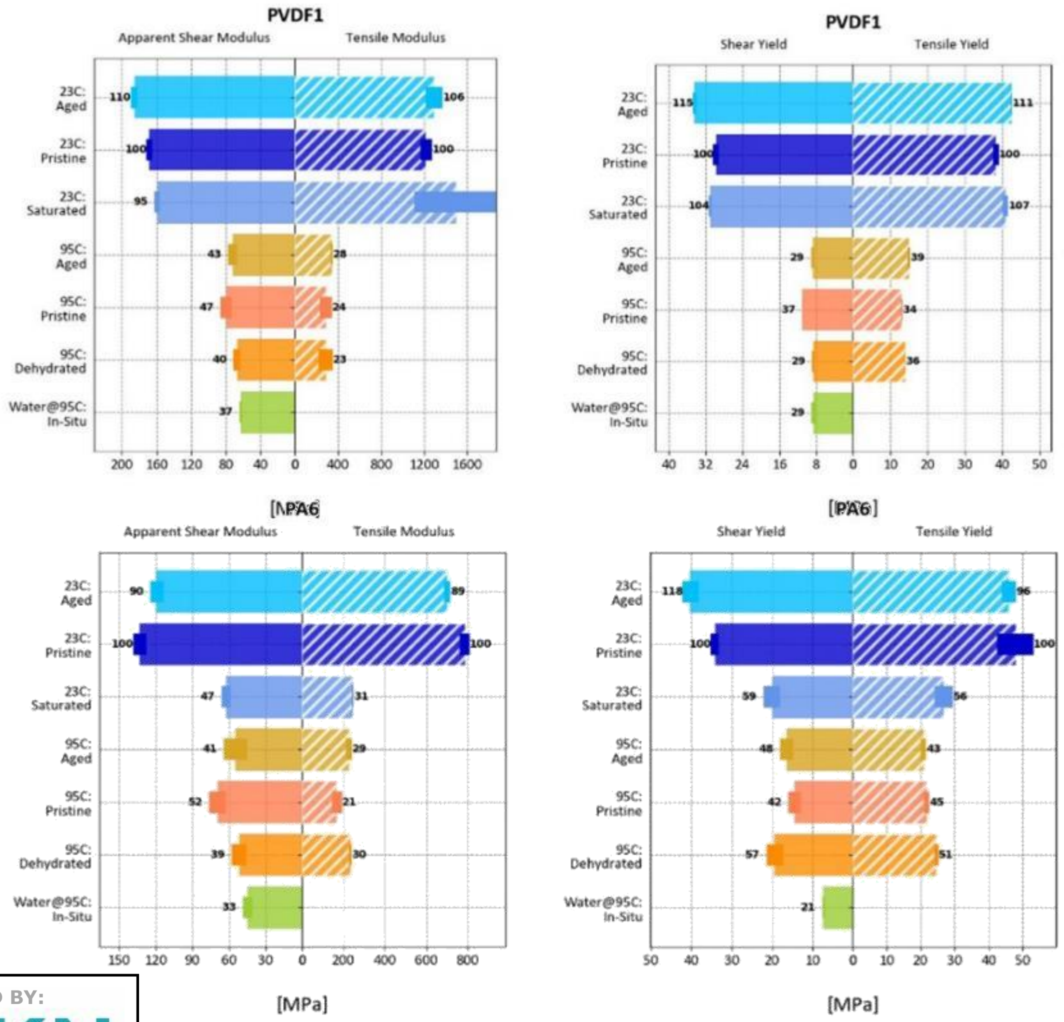
# THERMOPLASTICS EXPOSED TO WATER AND ELEVATED TEMPERATURE

PVDF and PA6 responses under hydrothermal conditioning




## Main observations

- PA6 exhibits stronger reduction in modulus, yield-related properties after hydrothermal conditioning
- PVDF1 retains mechanical performance more effectively than PA6 under same exposure conditions
- Saturated and in-situ water conditions highlight the plasticization effect of moisture on thermoplastics

## Interpretation

- The higher moisture sensitivity of PA6 is consistent with its more polar chemistry and greater water uptake
- The comparatively stable response of PVDF1 reflects stronger hydrothermal resistance expected for less hydrophilic thermoplastics

## Design takeaway

- For hydrothermal environments, matrix selection should prioritize low water affinity and better retention of modulus and yield behavior

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*Effect of cure on fracture properties of a composite: Part 3*
*Hosted by Dr. Casey Keulen*
*July 29, 2026*
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