LECTURE 3

Components of Polymer Composite Materials (Binders) and Their Types

Resin Chemistry, Curing Kinetics, Crosslinking Architectures, and Matrix Performance

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Lecture Overview: Plan, Aim & Key Tasks

Lecture Plan

1. Role of Binders: Matrix functions & wettability

2. Thermosets: Epoxy, phenolic, polyester & vinyl ester

3. Thermoplastics: Commodity & high-temperature resins

4. Curing & Kinetics: Gelation, vitrification & crosslinking

5. Bio-Binders: Bio-resins & industrial additives

Lecture Aim

To investigate the chemical synthesis, reaction kinetics, rheological behavior, and structural classification of polymer binders (matrices), evaluating their pivotal contribution to mechanical load distribution and environmental stability.

Key Learning Tasks

Differentiate: Thermosetting vs. thermoplastic binders

Analyze: Epoxide ring opening & curing agents

Construct: TTT (Time-Temperature-Transformation) diagrams

Assess: Bio-based matrix replacement viability

Core Definition: Binders (polymer matrices) bind reinforcing fibers together, transfer shear stress, determine operating temperature limits, and protect fibers against environmental chemical attack.

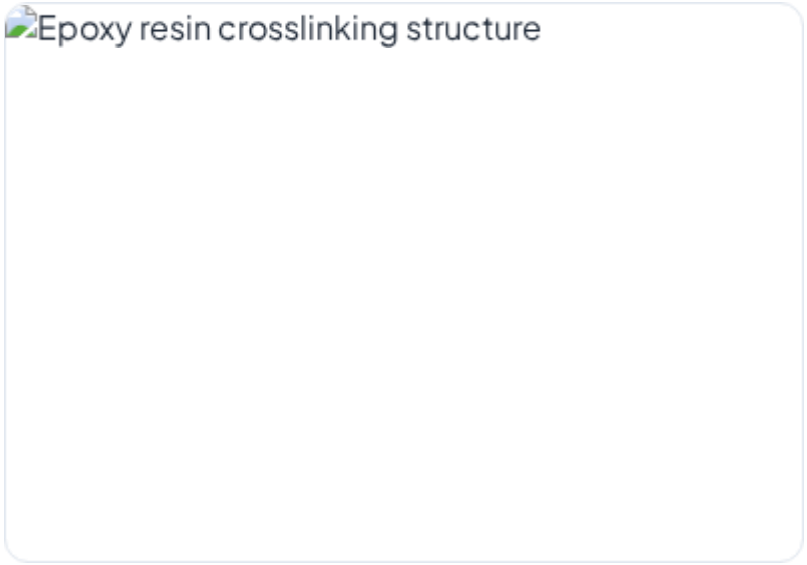
Essential Roles of Polymer Binders

The polymer binder acts as the continuous phase that unifies discrete structural fibers into a functional solid component.

Shear Load Transfer
Distributes externally applied forces evenly across billions of individual fibers via interfacial shear stress.

Surface Protection
Shields delicate ceramic or carbon fiber filaments from abrasive wear and chemical corrosion.

Structural Geometry Maintenance
Prevents fiber micro-buckling under compressive loading conditions.



Key Property Control: Transverse strength, interlaminar shear strength (ILSS), and max service temperature.

Taxonomy of Polymer Binders

Thermosetting Binders

Irreversible Covalent Networks

Low initial viscosity precursors that polymerize via chemical crosslinking into infusible 3D networks.

- Epoxy Resins (DGEBA, TGDDM)
- Unsaturated Polyesters (UPR)
- Vinyl Ester Resins (VER)
- Phenolic & Polyimide Resins

Thermoplastic Binders

Reversible Intermolecular Chains

High-molecular-weight linear or branched polymers that soften upon heating and solidify upon cooling.

- Amorphous: Polyetherimide (PEI), Polycarbonate
- Semi-Crystalline: PEEK, PPS, Polyamide (PA)
- Commodity: Polypropylene (PP), Polyethylene (PE)
- Bio-Polymers: PLA, PHA

Processing Distinction: Thermosets cure via heat/catalysts; thermoplastics process via melt rheology.

Epoxy Binders: Synthesis & Precursors

DGEBA & Tetrafunctional Epoxies

Diglycidyl Ether of Bisphenol A (DGEBA) is synthesized by reacting Bisphenol A with Epichlorohydrin. Contains strained three-membered oxirane (epoxide) rings.

> **Epoxide Equivalent Weight (EEW)**
> Weight of resin in grams containing one gram-equivalent of epoxide groups (typically 170–190 g/eq for DGEBA monomers).

Aerospace Grade: TGDDM (Tetraglycidyl Diaminodiphenylmethane) yields higher crosslink density and Tg > 200°C.

Epoxy Characteristics

- Low polymerization shrinkage (<2%)
- Excellent adhesion to carbon & glass
- Absence of volatile reaction byproducts

Key Parameter: Resin viscosity range (100 – 15,000 mPa·s at processing temperature).

Epoxy Hardener Systems & Crosslinking

Amine Hardeners

Aliphatic vs. Aromatic Amines

Aliphatic (TETA, DETA): Rapid room-temperature curing; lower thermal limit.

Aromatic (DDS, DDM): Requires elevated cure temperatures (150–180°C); delivers high Tg and solvent resistance.

Mechanism: Active hydrogen atoms on amine nucleophilically attack epoxide carbon.

Anhydride Hardeners

NMA, MTHPA System

Characteristics: Long pot-life, low exotherm, excellent dielectric properties.

Requirement: Tertiary amine accelerators required to initiate esterification.

Applications: Filament winding of high-voltage insulators and pressure vessels.

Stoichiometric Precision: Amine-to-epoxy ratio must equal 1:1 active hydrogen per oxirane group.

Unsaturated Polyester Resins (UPR)

Condensation Polymer Backbone

Synthesized by polycondensation of unsaturated dibasic acids (maleic anhydride) and saturated acids (phthalic anhydride) with glycols (propylene glycol).

Reactive Monomer Diluent: Styrene

Styrene (30–45 wt%) acts as solvent to reduce resin viscosity and copolymerizes with polyester double bonds during curing.

Polymerization Shrinkage

6% - 10%

Free-Radical Initiation: MEKP (Methyl Ethyl Ketone Peroxide) paired with cobalt naphthenate promoter.

Vinyl Ester Resins: Chemical Hybrid Synergy

Chemical Structure

Produced by reaction of methacrylic acid with epoxy resin backbone. Terminal double bonds provide rapid free-radical curing, while ester groups are shielded by methyl groups.

Terminal Unsaturation: High crosslinking efficiency.
Epoxy Backbone: Superior toughness & tensile strength.

Performance Profile

Hydrolytic Resistance: Steric hindrance protects ester linkages against acid/alkali attack.

Toughness: Higher elongation at break (4–6%) compared to unsaturated polyesters (2%).

Applications: Marine hulls, chemical storage tanks, scrubber stacks.

Comparative Advantage: Combines processing ease of polyesters with mechanical durability of epoxies.

High-Temperature Binders: Phenolics & Polyimides

Phenolic Resins (PF)

Char Yield: High carbon char formation (50–60%) provides ablation resistance in rocket nozzles.

Novolac & Resole Precursors

Reaction products of phenol and formaldehyde. Excellent fire, smoke, and toxicity (FST) performance.

Polyimide Resins (PI)

Thermal Ceiling: Continuous operation up to 250°C – 315°C in jet engine ducting.

Bismaleimides (BMI) & PMR-15

Synthesized via condensation of dianhydrides and diamines. Contains stable imide ring heterocycles.

Processing Challenge: Condensation polyimides release water/alcohol volatiles during cure, requiring high void-suppression pressures.

Commodity Thermoplastic Matrices

Polypropylene (PP)
Tm ≈ 165°C | Low Density

Widely used with glass fibers in automotive underbody shields and interior trim.

Polyamides (Nylon 6, 66)
Tm ≈ 220–260°C | Hydrogen Bonding

High tensile strength and wear resistance; prone to moisture absorption plasticization.

Polybutylene Terephthalate
PBT | Rapid Crystallization

Excellent dimensional stability and surface finish in electrical housing connectors.

Coupling Agent Requirement: Maleic Anhydride Grafted Polypropylene (MAH-g-PP) essential for covalent bonding with glass fiber silanols.

High-Performance Engineering Thermoplastics

Polyaryletherketones (PEEK / PEKK)

Semi-crystalline aromatic polymers linked by rigid ether and ketone moieties, offering extraordinary chemical solvent resistance and mechanical toughness.

Glass Transition (Tg)
143°C - 160°C

Melting Point (Tm)
343°C - 386°C

Key Technical Merits

- Fracture toughness GIC > 1000 J/m²
- Indefinite shelf life at room temperature
- Rapid stamp-forming processing cycles
- Low flame propagation & toxic gas release

Other High-Temp Resins: Polyetherimide (PEI, amorphous, Tg = 217°C) and Polyphenylene Sulfide (PPS, Tm = 285°C).

Rheological Behavior & Viscosity Windows

Viscosity Profile During Processing

As thermoset binders heat up, thermal energy reduces viscosity to a minimum (chemorheological trough) before polymerization crosslinking exponentially escalates viscosity towards gelation.

Impregnation Processing Window

Resin must maintain viscosity **η < 0.5 Pa·s** to achieve complete fiber wetting without entrapping dry void pockets.

Rheological Regimes by Method

Resin Transfer Molding (RTM): 0.05 – 0.3 Pa·s

Filament Winding: 0.3 – 1.0 Pa·s

Prepreg Impregnation: 10 – 100 Pa·s (tacky state)

Thermoplastic Melt Extrusion: 100 – 1,000 Pa·s

Shear Thinning: Non-Newtonian pseudoplastic flow behavior under high shear strain rates.

Curing Dynamics: Gelation & Vitrification

Gelation Point (Gelation)

Irreversible Liquid-to-Rubber Transition

- Formation of an infinite 3D macromolecular network grid.
- Resin flow completely ceases; storage modulus (G') equals loss modulus (G").
- Occurs at a specific critical conversion degree (αgel), independent of temperature.

Vitrification

Reversible Liquid/Rubber-to-Glass Transition

- Occurs when growing glass transition temperature (Tg) reaches cure temperature (Tcure).
- Reaction kinetics drop dramatically into a diffusion-controlled state.
- Post-curing at T > Tg is required to achieve 100% full chemical conversion.

Critical Process Rule: Pressure consolidation must be applied prior to reaching the gel point.

Time-Temperature-Transformation (TTT) Diagram

State Map of Thermoset Curing

The TTT diagram encapsulates material states (liquid, rubber, gelled glass, ungelled glass) as a function of isothermal cure temperature and log time.

Tg0 (Uncured Resin Tg)
Below Tg0, uncured resin remains trapped in a glassy unreacted state.

gelTg (Gel Point Tg)
Temperature where gelation and vitrification coincide simultaneously.

Analytical Method: Differential Scanning Calorimetry (DSC) measures heat flow (dH/dt) for kinetic modeling.

Binder Modifiers: Toughening Agents

Liquid Rubbers (CTBN/ATBN)

Reaction-Induced Phase Separation

Carboxyl-terminated butadiene acrylonitrile precipitates as 1–5 μm rubbery spheres, absorbing crack energy.

Thermoplastic Blends

PES / PEI Dissolution

Polyethersulfone added to epoxy increases fracture toughness without lowering overall Tg or modulus.

Pre-formed Core-Shell Rubber

CSR Nanoparticles

Crosslinked silicone/acrylic core with shell compatible with epoxy, guaranteeing uniform particle size.

Toughening Trade-Off: Rubber addition can slightly reduce compressive strength and elastic modulus.

Process Additives: Diluents & Catalysts

Reactive & Non-Reactive Diluents

Reactive Diluents: Mono-epoxides (glycidyl ethers) lower resin viscosity and participate in crosslinking.

Non-Reactive Diluents: Solvents/plasticizers reduce viscosity but can outgas, causing voids.

Accelerators & Promoters

Imidazoles & Lewis Acids (BF3-MEA): Catalyze homopolymerization and lower required curing temperature.

Latent Catalysts: Inactive at ambient temperature, triggering rapid curing only above 120°C.

Prepreg Formulation: Latent catalysts enable 6 to 12 months out-life storage at -18°C.

Functional Fillers & Rheology Modifiers

Thixotropic Rheology Control

Fumed silica (SiO_2) forms a temporary 3D hydrogen-bonded network in liquid resin, preventing resin sag and bleed-out on vertical mold surfaces during cure.

Flame Retardant Fillers

Aluminum Trihydrate (ATH) releases endothermic water vapor at >200°C to suppress combustion.

Particulate Addition: Calcium carbonate ($CaCO_3$) reduces raw material cost and volumetric shrinkage.

Sustainable Bio-Based Binders

Epoxidized Plant Oils (ESO/ELO)

Benefit: Improved matrix flexibility and reduced carbon footprint.

Epoxidized soybean and linseed oils supply bio-based aliphatic oxirane groups, substituting 20–50% of petro-chemical DGEBA resins.

Lignin & Furan Derivatives

Lignin Phenolics: Technical lignin replaces petroleum phenol in phenolic resole syntheses.

Polyfurfuryl Alcohol (PFA): Bio-resin derived from agricultural waste with high fire resistance.

Polylactic Acid (PLA): Bio-thermoplastic matrix for natural flax fiber composites.

Sustainability Index: Commercial bio-epoxies achieve up to **50% bio-based carbon content** (ASTM D6866).

Interlayer Resin Engineering & Prepreg Tack

Interleaf Particle Toughening

Thermoplastic particles (polyamide, 15–30 μm) concentrated exclusively in the resin-rich interlayer between carbon plies arrest mode-I and mode-II delamination cracks.

Prepreg Tack & Drapability

Controlled B-stage partial curing yields targeted surface adhesion (tack) allowing automated placement of plies onto complex curved tooling molds.

Manufacturing Control: Rheological storage modulus (G') at 25°C dictates tack life.

Binder Selection vs. Manufacturing Process

Autoclave Prepreg
High-Viscosity Epoxies / BMIs

Requires controlled flow under vacuum pressure to eliminate inter-ply void entrapment.

RTM & Infusion
Ultra-Low Viscosity Monomers

Resins must stay below 0.3 Pa·s for extended periods to wet dense fiber preforms.

Pultrusion
Rapid-Curing Polyesters / VER

Fast exotherm initiation required as composite profile is pulled through heated die (1–3 m/min).

Thermoplastic Alternative: In-situ polymerization of low-viscosity cyclic monomers (e.g., CBT, APA-6) inside RTM molds.

Chemical & Environmental Resistance

Hydrolytic Attack on Esters

Epoxy & PEEK binders exhibit superior hydrolytic stability.

Water and alkaline solutions cleave ester bonds (-COO-) in polyester matrices, causing mass loss, micro-cracking, and mechanical strength loss.

Solvent Swelling & ESC

Organic Solvents (Acetone, MEK): Penetrate low-crosslink domains, swelling chains.

Environmental Stress Cracking (ESC): Amorphous thermoplastics under tensile stress crack rapidly when exposed to aggressive solvents.

Crosslink Density Protection: High network density prevents solvent diffusion.

Design Factor: Aviation fluid compatibility testing (Skydrol hydraulic fluid resistance).

Analytical Characterization of Binders

DSC (Differential Scanning Calorimetry)

Measures total reaction enthalpy (ΔHtotal), residual heat of reaction, and glass transition temperature (Tg).

DMA (Dynamic Mechanical Analysis)

Determines storage modulus (E'), loss modulus (E''), and tan δ peak for viscoelastic relaxation spectra.

Rheometer Oscillatory Shear

Tracks gel time, minimum viscosity point, and vitrification kinetics under isothermal holds.

Degree of Cure Formula: $\alpha = (\Delta H_{total} - \Delta H_{residual}) / \Delta H_{total} \times 100\%$.

Summary: Matrix Selection Criteria

01

Thermal Operating Window

Select binder with dry and wet Tg at least 30°C above maximum service environmental temperature.

02

Processing Compatibility

Match resin pot-life, minimum viscosity profile, and cure kinetics to selected tooling and cycle time.

03

Interfacial Compatibility

Ensure matrix chemistry matches fiber sizing for high interfacial shear strength (IFSS).

Final Takeaway: The binder dictates composite environmental durability, fracture toughness, and manufacturing viability.

Thank You for Your Attention

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