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Review

Vitrimerization Routes for Waste PET Upcycling

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ABSTRACT: The accumulation of massive post-consumer poly(ethylene terephthalate) (PET) waste poses severe ecological hazards. Conventional mechanical recycling induces irreversible chain scission and severe property depreciation, while chemical depolymerization consumes excessive energy and toxic solvents, creating a performance-cost downcycling bottleneck limiting high-value PET reuse. This comprehensive critical review highlights vitrimer chemistry based on associative dynamic exchange as a transformative upcycling solution. The field is organized around two fabrication routes—depolymerization-reconstruction and in-situ/direct network construction while preserving the PET backbone—together with a cross-cutting transesterification catalytic dimension covering externally catalyzed, self-catalytic, and metal-free, no-added-catalyst (including residual-catalyst-assisted), and fully catalyst-free designs. Solvolysis-derived oligomers afford vitrimers with tunable glass transition temperature (T_g) (38~240 °C) and tensile strength up to 117 MPa; solvent-free extrusion fits continuous industrial lines, and metal-free designs may reduce heavy-metal contamination. Several optimized systems retain over 80% mechanical performance after cyclic reprocessing, although significant variations exist; for example, the bis(2-hydroxyethyl) terephthalate (BHET)/pyromellitic dianhydride (PMDA)/trimethylolpropane (TMP) vitrimer decreases from approximately 30 MPa to 16 MPa after two compression-molding cycles. These technologies show potential for closed-loop recycling and reprocessability, may reduce virgin resin demand, and may reduce carbon footprints, pending full life-cycle assessment. Major industrial barriers include insufficient creep resistance, incomplete monomer recovery, and non-uniform testing standards. This work delivers integrated theoretical and engineering guidance for scalable PET vitrimer circular-material development.

Keywords: Vitrimer; Post-consumer PET waste; Dynamic covalent network; Circular upcycling; Reactive extrusion

1. Introduction

Modern industrial civilization relies extensively on synthetic polymers, among which poly(ethylene terephthalate) (PET) stands as one of the most widely used commodity polyesters, with annual production surpassing 82 million metric tons [1]. Benefiting from outstanding barrier performance, superior

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mechanical strength, and robust chemical inertness, PET has been massively deployed in food packaging, beverage containers, engineering plastics, and textile fibers. Nevertheless, the rigid aromatic backbones and stable ester linkages of PET render the polymer highly recalcitrant to biodegradation under ambient natural conditions [2–4]. Under the synergistic effects of ultraviolet irradiation, thermo-mechanical weathering, and mild microbial erosion, accumulated waste PET gradually fragments into microplastics and nanoplastics [5,6]. These fine plastic particles possess ultra-large specific surface areas and readily adsorb toxic persistent organic pollutants (POPs) from surrounding media. Subsequent bioaccumulation along aquatic and terrestrial food chains poses well-documented threats to ecological balance and human physiological health [7–12].

1.1. Existing Problems in PET Recycling

Mechanical recycling currently dominates commercial waste PET treatment [2,13,14]; however, this technique represents a typical downcycling pathway with fundamental thermodynamic and kinetic drawbacks [3,12]. During repeated high-temperature melt reprocessing combined with moisture-induced hydrolysis and thermo-oxidative aging, random irreversible scission occurs along PET's ester backbone [14]. This chain cleavage drastically reduces intrinsic viscosity and weight-average molecular weight (M_w) [14,15]. Macroscopically, recycled PET (rPET) suffers severe deterioration in tensile strength, impact toughness, elongation at break, and melt strength. Poor melt processability disqualifies rPET from demanding forming technologies such as blow molding and film casting, restricting its applications to low-value commodities including staple fibers, packing fillers, and carpet backing, and failing to meet performance criteria for high-strength structural components and premium food-contact packaging [16–18]. With only 20~30% of the original value retained and energy costs per cycle reaching 40~60% of virgin production, this reprocessing pathway yields progressively inferior material properties [19,20]. The compounded loss, worsened by yellowing and haze, restricts rPET to a mere 2~3 cycles before it is consigned to landfill. These constraints thus highlight the critical need for upcycling to break the cycle of value degradation rather than merely postponing disposal.

To overcome the fundamental bottlenecks of mechanical downcycling, the concept of polymer upcycling has emerged as a paradigm shift in waste valorization. The core logic of upcycling lies in converting low-value plastic waste into high-value advanced polymers or fine chemicals through precise chemical restructuring [16,18]. Covalent adaptable networks (CANs), particularly vitrimers, deliver a revolutionary solution for the high-value upcycling of waste PET [21–26]. The vitrimer concept was first proposed by Leibler's group in 2011 [27]. As a subclass of crosslinked polymeric networks, vitrimers rely on associative dynamic covalent exchange reactions [24]. Unlike dissociative dynamic networks that suffer fluctuating crosslink density during bond rearrangement, associative exchange maintains constant crosslink density throughout simultaneous bond cleavage and reformation.

Conventional thermoplastics exhibit a sharp viscosity drop above their glass transition temperature (T_g) due to full chain disentanglement. In contrast, vitrimers undergo gradual topological rearrangement once heated beyond the topology freezing transition temperature (T_v) [28,29], and their viscosity decreases following Arrhenius-type temperature dependence, a unique silica-like rheological signature [27,30–32]. At service temperatures where dynamic exchange is kinetically suppressed, vitrimers exhibit solvent resistance, excellent dimensional stability, and high-temperature creep resistance comparable to conventional thermosetting resins [33]. Transforming linear waste PET into vitrimers aligns perfectly with the vision of a closed-loop circular plastic economy [34–37].

1.2. The Core Route for PET Recycling and Upgrading

Catalytic depolymerization and vitrimerization pursue different objectives and are better regarded as complementary branches of PET upcycling than as competing options. Catalytic routes—hydrolysis, glycolysis, methanolysis, aminolysis, hydrogenolysis and, more recently, electro- and photocatalytic conversion—cleave the ester backbone to recover monomers such as terephthalic acid, bis(2-hydroxyethyl) terephthalate (BHET), dimethyl terephthalate and ethylene glycol, or to convert PET into value-added chemicals and polymer building blocks [11,18,38,39]. Their figure of merit is monomer yield and selectivity, and the recovered products must be re-polymerized before re-entering the materials stream. Vitrimerization is instead a polymer-to-polymer strategy: it retains the aromatic ester backbone, and hence the polymerization energy already embodied in the material, while introducing dynamic covalent crosslinks that turn a thermoplastic into a reprocessable thermoset. Its figure of merit is therefore not monomer yield but the retention of molecular weight together with an expanded property space—creep resistance, solvent resistance, weldability, self-healing, foamability and printability—none of which is accessible through mechanical recycling or monomer recovery alone. The two families are moreover sequential rather than mutually exclusive: depolymerization-reconstruction vitrimers begin with solvolysis, and vitrimer networks can themselves be chemically depolymerized at end-of-life. Vitrimerization thus occupies the middle ground between mechanical downcycling and complete chemical depolymerization.

Reflecting this division, existing review articles on PET recycling predominantly focus on catalytic depolymerization for monomer recovery or on simple physical blending [2,38,39]. Comprehensive reviews covering the full vitrimerization transformation of waste PET, together with corresponding molecular design principles, remain scarce. This review fills this research gap by examining two fabrication routes for waste PET vitrimerization: (i) depolymerization into low-molecular-weight oligomers followed by re-crosslinking with small-molecule crosslinkers, and (ii) *in-situ*/direct network construction that preserves the PET backbone via reactive melt processing. Transesterification catalytic regulation, rather than a standalone fabrication route, is a cross-cutting molecular-design dimension applicable to both routes; it is therefore presented as a separate section to facilitate systematic comparison of catalytic strategies. By dissecting each route in terms of reaction pathways, thermodynamic/kinetic constraints, industrial processing compatibility, and microscopic anti-creep mechanisms, this review provides both theoretical depth and practical processing guidance for polymer scientists and materials engineers [2,38,39].

To the best of our knowledge, this is among the first comprehensive critical reviews to integrate the two fabrication routes for waste PET vitrimerization with the cross-cutting transesterification catalytic dimension, and to compare their molecular design principles, processing compatibility, and sustainability trade-offs. By placing vitrimerization explicitly alongside catalytic monomer-recovery routes, we further intend this review to bridge the polymer-materials and catalysis/reaction-engineering communities, and to be accessible to readers interested in plastic upcycling beyond the vitrimer field.

1.3. Data Comparison Criteria and Terminology

This review is a comprehensive critical review based on peer-reviewed literature. The standards used in the cited studies were not consistently available in the source information compiled for this review. Accordingly, each table in this review carries a note stating that the compiled values were obtained under different sample preparation and measurement protocols, so that cross-study comparison requires verification of the original methods. A specific ASTM or ISO standard is named only where it was explicitly reported in the source; representative relevant standards include ASTM D638 [40] or ISO 527 [41] for tensile properties and ASTM D3418 [42] or ISO 11358 [43] for thermal analysis, but these are not attributed to a study unless explicitly reported therein. Comparisons of tensile strength, Tg, gel fraction, and stress-relaxation behavior should therefore be interpreted with reference to the conditions reported in the original studies.

In this review, catalyst source, metal content, and self-catalytic behavior are treated as separate descriptors. "Externally catalyzed" means that a catalyst is deliberately added, irrespective of whether it is metal-based or organic. "Self-catalytic" means that catalytic moieties are covalently embedded in the crosslinker or network; it does not by itself specify whether metal residues are present. "Metal-free" means that no metal catalyst or metal-containing residue is intentionally present or reported. In the systems reviewed here, TGDDM and BIS-TRIS are both self-catalytic and metal-free, but these terms are not treated as synonyms. "No-added-catalyst" is the parent category for systems in which no additional catalyst is introduced. "Residual-catalyst-assisted" is a subcategory of no-added-catalyst in which residual catalyst already present in commercial PET, such as Sb_2O_3, demonstrably contributes to exchange. "Fully catalyst-free" is reserved for systems with neither an added catalyst nor evidence of a catalytically active residual species, where exchange is driven solely by intrinsic molecular reactivity.

2. Vitrimer Fabrication Routes and Catalytic Evolution for Waste PET Upcycling

This section is organized around two fabrication routes: (i) depolymerization-reconstruction with small-molecule crosslinkers and (ii) *in-situ*/direct network construction while preserving the PET backbone. Transesterification catalytic regulation is discussed separately in Section 2.3 for convenience, but it is a cross-cutting mechanistic dimension applicable to both routes and is not a third fabrication route.

2.1. Vitrimer Fabrication via Depolymerization-Reconstruction with Small-Molecule Crosslinkers

Following the dynamic exchange mechanism depicted in Figure 1, the depolymerization-reconstruction strategy consists of two sequential stages: controlled solvolytic depolymerization of bulk PET into low-molecular-weight oligomers, followed by re-crosslinking with multifunctional small-molecule crosslinkers to construct dynamic covalent networks [44]. Two mainstream solvolysis chemistries have been established: glycolysis and aminolysis, which generate oligomers with distinct terminal functional groups that dictate the type of dynamic bonds in the final networks [27,45]. Glycolysis yields hydroxyl-terminated precursors suitable for transesterification vitrimers with activation energies (E_a) ranging from 70 to 130 kJ·mol^{-1}. By contrast, as shown in Table 1, aminolysis produces amine-terminated oligomers that form imine-based vitrimers with lower exchange activation energies (40–90 kJ·mol^{-1}), enabling reprocessing without an added catalyst under mild thermal conditions [35,36]. Both solvolytic pathways drastically reduce the molecular weight of raw PET from 20,000~40,000 Da to oligomers with molecular weights of several hundred to several thousand Daltons, accompanied by the loss of native polymer chain entanglements—a defining limitation of this two-step route [35,36,44,46].

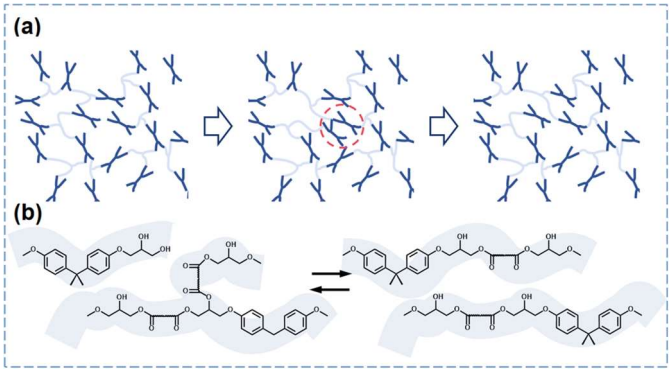


Figure 1. Schematic illustration of the vitrimer exchange mechanism. (**a**) Topological rearrangement via associative exchange reactions that preserve the total number of linkages and the average crosslink functionality. The middle panel emphasizes that the exchange does not proceed through a depolymerization intermediate. (**b**) Associative transesterification mechanism in hydroxy-ester vitrimer networks. The red circle highlights the dynamic covalent bond undergoing associative exchange. Adapted from Montarnal et al. [27].

Table 1. Depolymerization Conditions for PET Vitrimer Precursors. Abbreviations: BHET, bis(2-hydroxyethyl) terephthalate; DETA, diethylenetriamine; EDA, ethylenediamine; DP, degree of polymerization; Mw, molecular weight.

Parameter	Glycolysis	Aminolysis
Typical reagents	Ethylene glycol, glycerol	DETA, EDA
Temperature (°C)	190~250	115~150
Time (h)	2~8	0.5~3
Catalyst	$Zn(OAc)_2$, $Ti(OBu)_4$	None required
Products	OH-terminated oligomers, BHET	NH_2-terminated oligomers
Mw of Oligomer (Da)	500~4000	336~2200
DP range	1~11	1~5
Subsequent chemistry	Transesterification	Imine condensation (Schiff-base)
References	[44,46,47]	[35,36,48]

Note: Values compiled across studies were obtained under different sample preparation and measurement protocols (e.g., thermal analysis conditions, tensile testing rates, and gel fraction extraction). Direct cross-study comparison therefore requires verification of the original methods, including the relevant testing standards where reported (e.g., ASTM D638, ISO 527, ASTM D3418, or ISO 11358). All data presented in this table were reported in the respective original studies, which did not employ a unified, standardized depolymerization protocol.

2.1.1. Polyol-Mediated Transesterification Vitrimer Networks

Glycolysis represents the most extensively investigated depolymerization pathway for PET vitrimerization. Under 190~250 °C with transesterification metal catalysts, PET reacts with ethylene glycol to produce bis(2-hydroxyethyl) terephthalate (BHET) and hydroxyl-terminated oligomeric polyols [44,47]. The degree of depolymerization can be precisely tuned by adjusting the glycol-to-PET molar ratio, reaction temperature, and holding duration, allowing customizable molecular weights and terminal functionalities for subsequent crosslinking [35,36]. Continuous-flow glycolysis technologies have been developed to shorten reaction durations while retaining high depolymerization efficiency, marking critical progress toward industrial translation. Glycolysis-derived polyols constitute the dominant precursor for vitrimer construction, as abundant hydroxyl groups are generated while native PET ester backbones are preserved [46,47]. Upon thermal activation, associative transesterification occurs between hydroxyl and ester moieties without altering overall crosslink density, endowing the resulting materials with characteristic vitrimer behaviors, including reprocessability, weldability, and intrinsic self-healing, free of small-molecule byproducts or irreversible structural degradation [46]. Table 2 compares the thermomechanical properties of three polyol-based vitrimers from depolymerized PET.

Table 2. Thermomechanical Properties of Polyol-Based Vitrimers from Depolymerized PET. Abbreviations: BHET, bis(2-hydroxyethyl) terephthalate; PMDA, pyromellitic dianhydride; TMP, trimethylolpropane; T_g, glass transition temperature.

Property	BHET/PMDA/TMP	Glycerol:rPET 1:1	BHET/Sebacic/Citric
Gel content (%)	90.8	~95	Not reported
T_g (°C)	120	106.4	38~68
Storage modulus at 30 °C (MPa)	1994	~1060 (Young's)	Not reported
Tensile strength (MPa)	30	47.3 ± 4.0	~15
Elongation at break (%)	~20	~5	~150
Reprocessing method	Compression molding	Compression molding	Solution casting
Reprocessability	2 cycles (30→25→16 MPa)	4 cycles (stable)	Not reported
Activation energy E_a (kJ/mol)	173	Not reported	Not reported
References	[47]	[44]	[49]

Note: property values and activation energies (E_a) are obtained under different measurement and fitting protocols across the cited studies (e.g., DSC/DMA conditions, tensile testing rates, gel fraction extraction, and stress-relaxation-based E_a determination); the E_a of 173 kJ/mol for the Gupta et al. system is as reported in the original study [47]. All data presented in this table were reported in the respective original studies, which did not employ a unified, standardized depolymerization protocol.

The thermomechanical properties of these polyol-based vitrimers can be systematically tailored through precursor stoichiometry, crosslink density, and network topology. Gupta et al. [47] fabricated thermoset-like CANs by crosslinking waste PET-derived BHET with pyromellitic dianhydride (PMDA) and trimethylolpropane (TMP). The resultant BHET/PMDA/TMP network achieved a gel fraction of 90.8%, a T_g of 120 °C, and a storage modulus of 1994 MPa at 30 °C, with a tensile strength of 30 MPa. Efficient stress relaxation was observed at 155~170 °C, consistent with Arrhenius-dependent topological rearrangement. After two compression-molding recycling cycles, tensile strength declined from 30 MPa to 16 MPa, demonstrating feasible reprocessing.

Ng et al. [44] implemented glycerol-mediated controlled glycolysis to generate branched oligomeric polyols from waste PET, which were directly converted into vitrimers via solvent-free melt processing (Figure 2). The optimized vitrimer exhibited a T_g of 106.4 °C and tensile strength of 47.3 ± 4.0 MPa, with mechanical properties remaining stable across four compression-molding cycles. Notably, this polyol-mediated strategy is compatible with heterogeneous mixed plastic waste streams, where *in-situ* formed macromolecular polyols simultaneously act as compatibilizers and crosslinkers, alleviating strict pre-sorting requirements for conventional mechanical recycling.

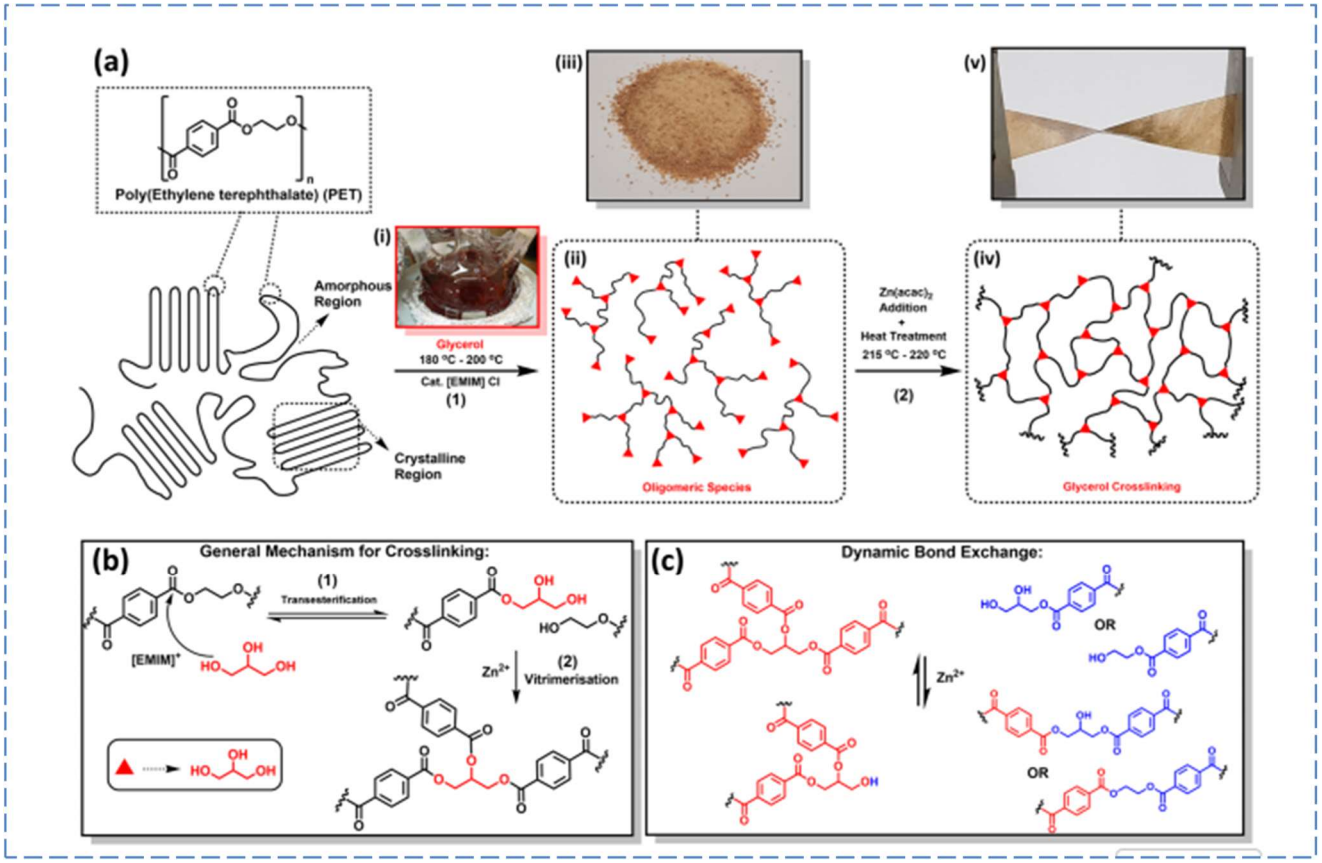


Figure 2. Schematic illustration of the concept and reaction scheme for poly(ethylene terephthalate) (PET) depolymerization. (**a**) Experimental scheme where (1) PET chain scission by glycerol in the presence of a catalytic amount of 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), in N-methyl-2-pyrrolidone (NMP) as a solvent, to form a dark red reaction mixture (i), to produce glycerol grafted polyol oligomers (ii), which are precipitated (iii) and isolated as recovered poly(ethylene terephthalate) (RPET). (2) Through the addition of a zinc catalyst followed by heat treatment, a crosslinked network (iv) is formed from RPET and can be processed into a film (v). (**b**) Scheme showing (1) Carbonyl exchange (transesterification) with glycerol degrades the bulk PET into branched oligomeric PET. (2) Catalytic addition of a Zn-containing species into RPET encourages glycerol insertion, which contributes to the crosslinking of the material. (**c**) Mechanism for dynamic bond exchanges via further transesterification for processibility after crosslinking. Reproduced from Ng et al. [44].

Bio-derived polycarboxylic acids such as citric acid have been introduced as eco-friendly small-molecule crosslinkers to expand the structural diversity of polyol vitrimers. Park et al. [49] synthesized fully recycled dynamic polyesters via melt polycondensation of BHET, sebacic acid, and citric acid. Trifunctional citric acid established rigid three-dimensional scaffolds while supplying additional hydroxyl sites to activate transesterification. When compounded with carbon nanofiller hybrid electrodes for supercapacitors, reprocessed vitrimer devices retained 93.93% of initial capacitance over 1000 charge-discharge cycles.

In summary, polyol-based vitrimerization leverages PET's inherent ester backbones to fabricate tunable, reprocessable dynamic networks governed by transesterification [46,47,49]. However, most transesterification systems require elevated temperatures and external metal catalysts to achieve practical bond-exchange kinetics [24,34]. Polyamine-mediated imine vitrimers are a complementary alternative with milder reprocessing conditions [34], whereas the universal drawbacks of the depolymerization-reconstruction workflow [high energy consumption, complex purification, and residual catalyst contamination] are elaborated in the next Section [50].

2.1.2. Polyamine-Mediated Imine Vitrimer Networks

As illustrated in Figure 3, aminolysis employs multifunctional amines (diethylenetriamine (DETA), ethylenediamine (EDA)) to cleave PET ester bonds, generating amide-amine oligomers terminated with primary and secondary amine groups. Owing to the higher nucleophilicity of amine reagents, aminolysis proceeds at lower temperatures (115~150 °C) compared with glycolysis. The obtained amine-terminated oligomers undergo imine condensation with multi-aldehyde crosslinkers to form Schiff-base dynamic networks [35,36]. Amide linkages generated during aminolysis introduce additional hydrogen-bonding interactions and thermal stability, while residual amine groups support transamidation chain extension during thermal processing [35]. Microwave-assisted aminolysis further accelerates depolymerization to yield well-defined terephthalate diamine monomers for high-performance polyimine fabrication [48].

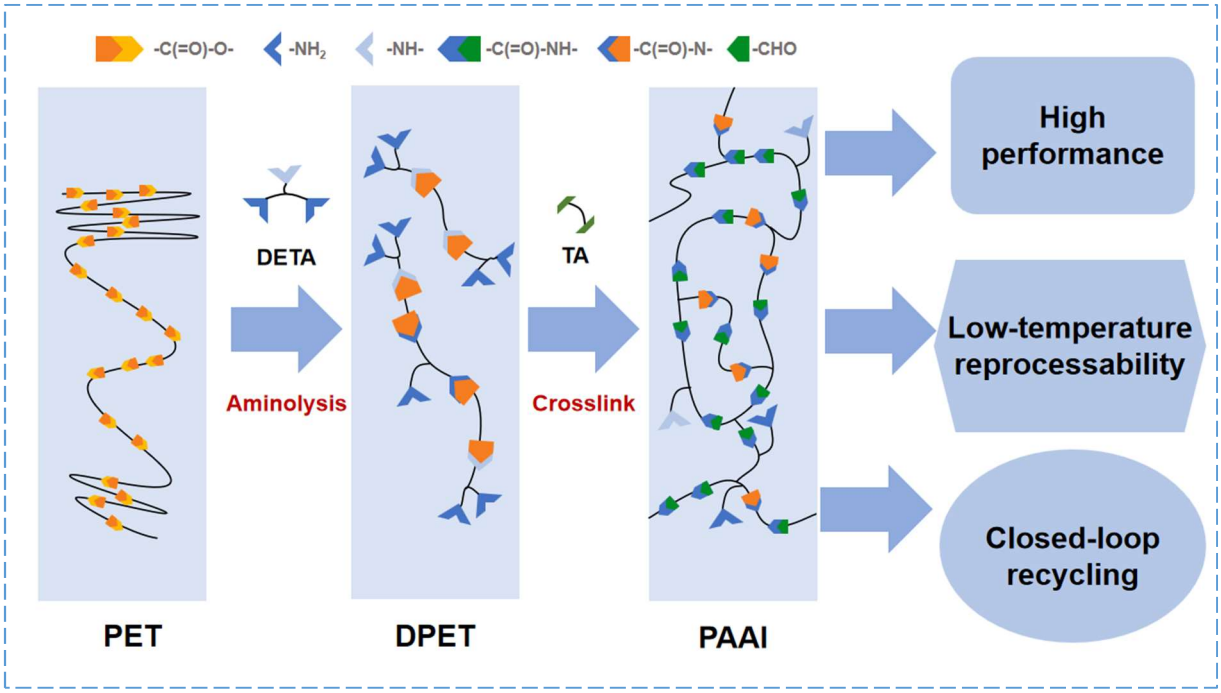


Figure 3. Schematic illustration of the upcycling of waste PET into a poly(amide-amine-imine) (PAAI) vitrimer via diethylenetriamine (DETA)-mediated aminolysis followed by crosslinking with terephthalaldehyde (TA). The resulting dynamic network exhibits high performance, methanol-assisted low-temperature reprocessability, and chemical closed-loop recycling as reported in ref. [36]. Redrawn by the authors based on the reaction scheme reported in ref. [36].

Imine exchange proceeds via an associative transimination pathway: incoming amine nucleophiles attack electrophilic imine carbon atoms to form aminal intermediates, followed by elimination of the original amine without altering crosslink density or releasing volatile byproducts [35,36]. A core advantage of imine vitrimers lies in their much lower exchange activation energy of 40~90 kJ·mol^{-1} (70~130 kJ·mol^{-1} for polyol-based transesterification), enabling rapid stress relaxation and reprocessing under mild thermal conditions [27,45]. Within the framework of PET upcycling, aminolysis yields amine-terminated PET oligomers, serving as versatile precursors to construct imine dynamic networks. The amine species adopted for solvolysis drastically modulate the functionality and topological structure of oligomeric intermediates, thereby dictating the thermomechanical performances of the resultant vitrimers.

The molecular structure of the amine used during PET aminolysis strongly influences the functionality and molecular architecture of the resulting oligomeric precursors and, consequently, the thermomechanical properties of the final vitrimer network, as shown in Table 3. Du et al. [35] systematically compared diethylenetriamine (DETA) and ethylenediamine (EDA) as aminolysis reagents for post-consumer PET. Optimized DETA-mediated aminolysis (150 °C, 30 min) produced oligomers with a weight-average molecular weight of 2118 Da, whereas EDA treatment yielded shorter-chain precursors after 3 h reaction at 115 °C. Intramolecular transamidation occurred during vacuum distillation of DETA-derived oligomers, converting tertiary amides into reactive primary amines (44 mol% of total amide linkages). Crosslinking with vanillin-functional cyclophosphazene afforded recyclable thermosets with gel fractions exceeding 98%. The DETA-based network delivered a T_g of 240 °C and tensile strength of 105 MPa, superior to the EDA counterpart (T_g = 169 °C). Both materials achieved UL-94 V-0 flame retardancy with limiting oxygen index (LOI) values of 35.7% and 31.2%, respectively, and only 0.1% creep strain under 5 MPa loading at 230 °C. Near-quantitative closed-loop recycling was realized with 99% retention of mechanical performance.

Table 3. High-Performance Polyamine-Based Vitrimers from Aminolyzed PET. Abbreviations: DPET, depolymerized PET; DETA, diethylenetriamine; EDA, ethylenediamine; PAAI, poly(amide-amine-imine). RTP and BDV are sample codes used in the cited studies.

Property	DPET-DETA-RTP	DPET-EDA-RTP	PAAI	BDV
Aminolysis agent	DETA	EDA	DETA	DETA
Crosslinker	Vanillin-cyclophosphazene	Vanillin-cyclophosphazene	Terephthalaldehyde	Terephthalaldehyde
Gel content (%)	>98	>98	98.4	>95
T_g (°C)	240	169	217	~180
Tensile strength (MPa)	105	~60	117	~80
LOI (%)	35.7	31.2	—	—
UL-94 rating	V-0	V-0	—	—
Creep at 230 °C, 5 MPa (%)	0.1	—	<0.1 at 200 °C	—
Closed-loop recycling	Yes (99% retention)	Yes	Yes (Amberlyst)	Yes
References	[35]	[35]	[36]	[51]

Note: Values compiled across studies were obtained under different sample preparation and measurement protocols (e.g., thermal analysis conditions, tensile testing rates, and gel fraction extraction). Direct cross-study comparison therefore requires verification of the original methods, including the relevant testing standards where reported (e.g., ASTM D638, ISO 527, ASTM D3418, or ISO 11358). All data presented in this table were reported in the respective original studies, which did not employ a unified, standardized depolymerization protocol.

In further work, Du et al. [36] constructed poly(amide-amine-imine) (PAAI) vitrimers by crosslinking DETA-aminolyzed PET with terephthalaldehyde at a 1:1 NH_2/CHO stoichiometric ratio. The hybrid network integrated amide, secondary amine, and imine functional groups. Controlled vacuum distillation (150 °C, 6 h) was critical to eliminate impurities without inducing over-crosslinking insolubility. The optimized PAAI vitrimer possessed a T_g of 217 °C and maximum tensile strength of 117 MPa. Methanol

plasticization enabled reprocessing at only 100 °C, with post-reprocessing tensile strength maintained at 99 MPa and a T_g of 234 °C. Complete chemical closed-loop recycling was achieved using basic anion-exchange resin adsorbents. The generality of this approach has been independently validated by Das et al., who reported upcycling of waste PET into recyclable crosslinked polyimine networks through aminolysis followed by imine condensation [51]. This confirmed the broad applicability of the polyamine-based depolymerization-reconstruction strategy.

Despite outstanding low-temperature reprocessability and ultrahigh mechanical rigidity, polyamine-based imine vitrimers present notable limitations: higher raw material costs, moisture sensitivity of imine bonds, reduced ductility at elevated crosslink densities, and inferior long-term thermo-oxidative stability relative to transesterification polyester vitrimers.

2.1.3. Inherent Limitations of the Depolymerization-Reconstruction Route

Diverse dynamic network architectures can be obtained from polyol- and polyamine-mediated solvolysis; nevertheless, this two-step depolymerization-reconstruction workflow exhibits inherent drawbacks that hinder large-scale industrial deployment, stemming mainly from irreversible backbone cleavage of PET upon solvolysis [44,50].

The most fundamental defect is severe molecular weight degradation during glycolysis or aminolysis, generating oligomers with degrees of polymerization (DP) of only 1~11, whereas aminolysis products are typically shorter (DP 1–5) [35,46]. Typical entanglement molecular weights for polyesters exceed several thousand Daltons; depolymerized precursors fall far below this threshold, eliminating native physical entanglement as a stress-dissipation and creep-suppression mechanism. Although covalent crosslinks partially compensate for lost entanglements, they cannot fully replicate the energy-dissipation behavior of high-molecular-weight entangled PET, resulting in compromised creep resistance under sustained thermal loads [27,50]. Additionally, shortened oligomeric segments generate heterogeneous network topologies with broad strand length distributions and abundant structural defects [35,36].

A fundamental performance trade-off arises between reprocessability and high-temperature dimensional stability. Dynamic bond exchange, which enables reshaping, is thermally activated and proceeds continuously at service temperatures above ambient [27]. Low-Ea imine networks offer facile low-temperature reprocessing but suffer severe creep under moderate thermal loads. High-Ea transesterification polyester vitrimers exhibit superior anti-creep performance yet demand higher processing temperatures and external catalytic additives [35,36,45]. While ultrahigh crosslink densities can mitigate creep deformation for imine vitrimers, this strategy simultaneously sacrifices material ductility and fracture toughness.

From a manufacturing perspective, depolymerization-reconstruction requires discrete batch unit operations: solvolysis (3~8 h) [44,46], vacuum distillation purification, stoichiometric crosslinker blending, and thermal curing. Each stage increases time, energy, and capital costs while introducing risks of incomplete conversion and feedstock contamination. Excess diol or diamine reagents demand high-vacuum separation at 150 °C (1~30 mbar) [35,36], an energy-intensive step difficult to integrate into continuous production lines. Low melt flow and limited solubility of oligomeric intermediates further complicate downstream melt processing. Glycolysis requires 190~250 °C with metal transesterification catalysts, whereas aminolysis, despite milder reaction temperatures, still relies on lengthy vacuum purification. Residual catalyst or amine contaminants disrupt long-term dynamic exchange kinetics and accelerate thermo-oxidative degradation over multiple recycling cycles [50].

Most reported depolymerization-reconstruction vitrimers are fabricated via discontinuous batch synthesis [35,36,44,46]. Precise stoichiometric control, moisture/oxygen sensitivity, and rheological fluctuations near gelation impede integration into continuous reactive extrusion or injection molding workflows. Overall economic viability depends heavily on crosslinker pricing, recycling-loop energy

consumption, and end-product market value, requiring coordinated advances in catalyst engineering and continuous process design for industrial adoption [32,34,44].

2.2. In-Situ Dynamic Network Construction via Macromolecular Reactive Modifiers

Distinct from the two-step depolymerization-reconstruction paradigm, the *in-situ* crosslinking strategy directly incorporates functional macromolecular modifiers during PET melt processing without separate solvolysis pretreatment. Multifunctional epoxy-, anhydride-, or polyester-based modifiers react with PET terminal –OH/–COOH groups in twin-screw extruders to form dynamic covalent networks in minutes. This one-step workflow eliminates oligomer purification and retains native PET high molecular weight and chain entanglements, fully compatible with existing continuous industrial recycling lines. Four major modifier categories are reviewed herein: epoxy-polyol synergistic systems, anhydride-mediated chain extension/crosslinking, reactive polyester blending, and unified reactive extrusion manufacturing platforms.

2.2.1. Epoxy-Mediated *In-Situ* Vitrimerization

Epoxy-functional modifiers represent the most widely studied *in-situ* crosslinking agents for PET vitrimers, owing to the high reactivity of oxirane rings toward PET carboxyl and hydroxyl termini, alongside rich molecular tunability of multi-functional epoxy architectures.

Incarnato et al. [52] pioneered reactive extrusion modification of recycled PET using pyromellitic dianhydride (PMDA) as a linear chain extender, validating the feasibility of one-step melt reactive modification under continuous processing conditions, though early work focused solely on molecular weight elevation rather than full crosslinked vitrimer networks.

Building upon this foundation, Qiu et al. [28] fabricated continuously reprocessable PET vitrimers via twin-screw reactive extrusion incorporating diglycidyl ether of bisphenol A (DGEBA) and tris(hydroxymethyl)aminomethane derivative (BIS-TRIS), a polyol bearing intrinsic tertiary amine groups, as shown in Figure 4. BIS-TRIS serves three integrated functions: supplying hydroxyl transesterification sites, autocatalyzing dynamic exchange via hydrogen-bonded tertiary amines, and defining network spatial topology. DGEBA epoxy rings couple discrete PET chains to construct percolating dynamic networks. The resulting vitrimers exhibited creep resistance improved by three orders of magnitude relative to neat PET and were compatible with compression molding, extrusion, and injection molding recycling workflows.

Targeting low-quality post-consumer food-tray rPET, Fabrizio et al. [53] implemented melt extrusion with DGEBA crosslinker and zinc acetylacetonate ($Zn(acac)_2$) transesterification catalyst. Optimized stoichiometry delivered a crosslinking degree of 75%, accompanied by three orders-of-magnitude enhancement in melt strength and doubled room-temperature tensile strength (55 MPa), with stable dimensional stability up to 260 °C. This work confirmed the efficacy of epoxy *in-situ* crosslinking for low-viscosity, contaminated waste PET unsuitable for conventional mechanical recycling.

Wu et al. [29] further advanced self-catalytic, metal-free epoxy vitrimerization by adopting N,N′-tetraglycidyl-diaminodiphenylmethane (TGDDM), a tetrafunctional epoxy crosslinker with covalently embedded tertiary amine catalytic moieties. By regulating TGDDM loading (0.7~2.0 wt%), material architectures were tuned from lightly branched polymers to fully crosslinked vitrimers with variable gel fractions (Figure 5). The intrinsic autocatalytic mechanism eliminates exogenous metal additives, balancing thermal resistance, anti-creep performance, and reprocessability. Notably, the intrinsic autocatalytic feature of TGDDM bridges in-situ crosslinking chemistry and the emerging self-catalytic and metal-free vitrimer paradigm.

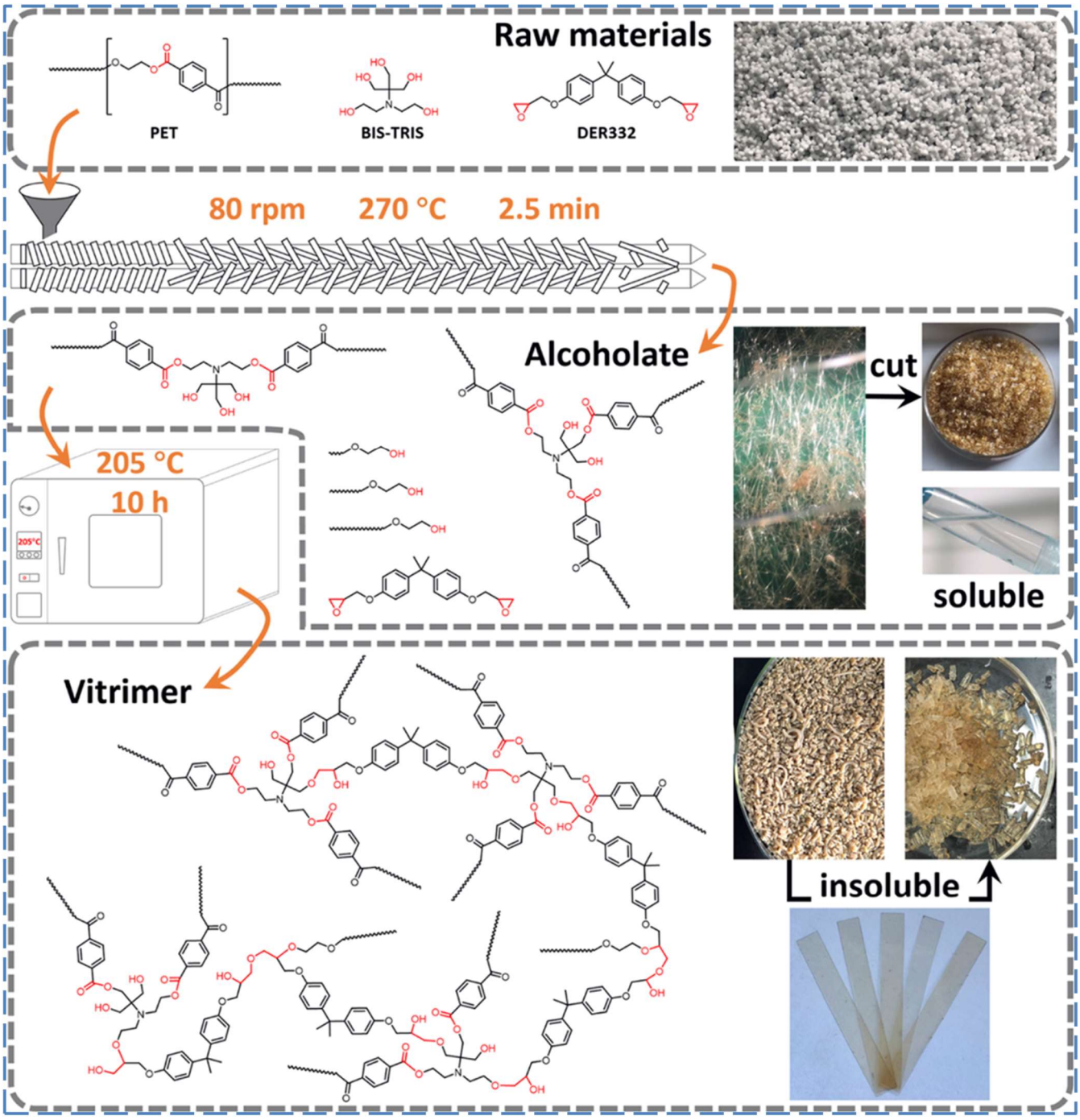


Figure 4. Schematic illustration of the reactive extrusion upcycling of waste PET into continuously reprocessable vitrimers using tris(hydroxymethyl)aminomethane derivative (BIS-TRIS) and diglycidyl ether of bisphenol A (DGEBA). BIS-TRIS serves three coordinated functions: its three hydroxyl groups provide transesterification sites for network formation, its tertiary amine autocatalyzes the transesterification reaction, and its spatial geometry defines the network architecture. DGEBA supplies two epoxy groups that couple PET chains into the developing dynamic covalent network. Reproduced from Qiu et al. [28].

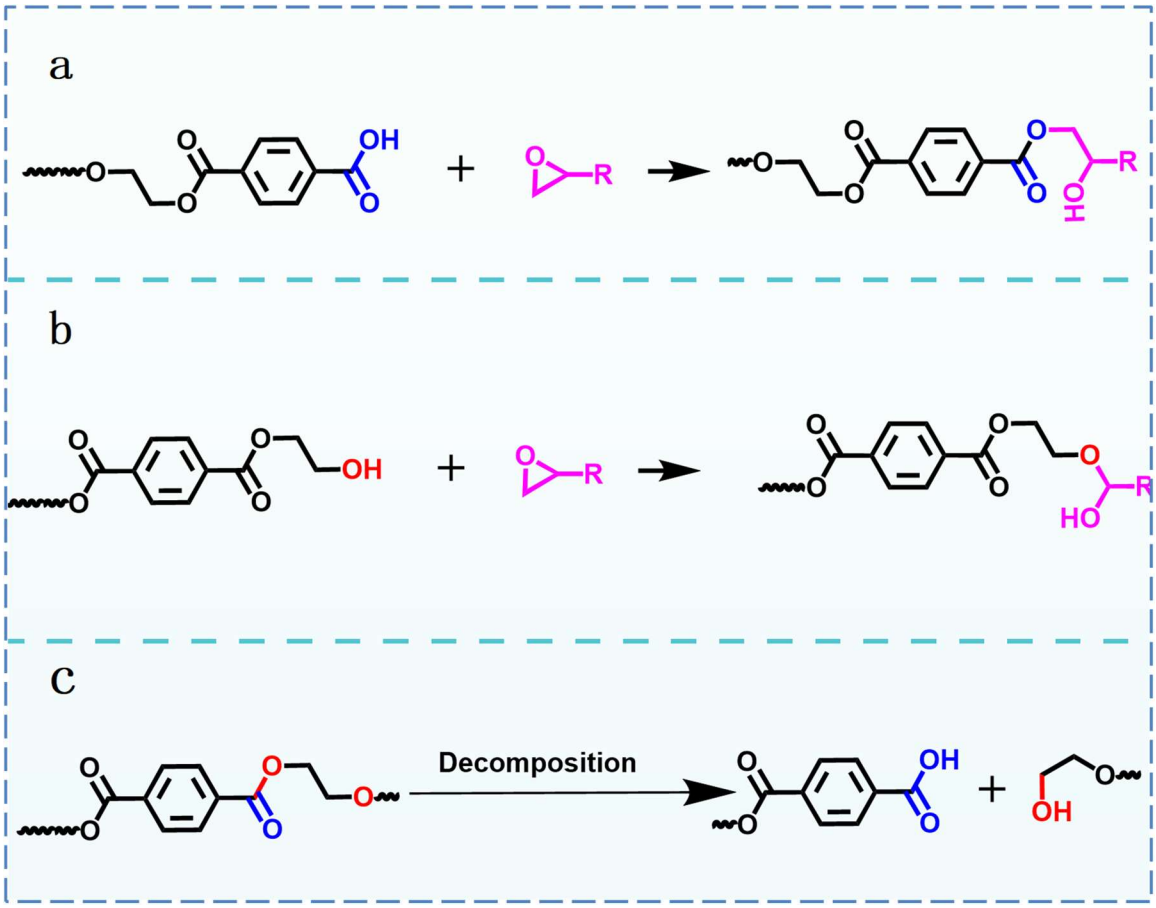


Figure 5. Schematic illustration of the self-catalytic, metal-free upcycling of waste PET into vitrimers using N,N′-tetraglycidyl-diaminodiphenylmethane [TGDDM]. (**a**) TGDDM molecular structure and reactive sites; (**b**) resulting crosslinked PET network topology; (**c**) dynamic transesterification exchange pathway that enables reprocessability. Adapted from Wu et al. [29].

2.2.2. Anhydride-Mediated *In-Situ* Chain Extension and Crosslinking

Anhydride-functional modifiers deliver an alternative *in-situ* vitrimerization pathway, acting simultaneously as chain extenders and latent catalytic agents via *in-situ* generated neighboring carboxylic acid groups.

Ge et al. [54] combined PMDA and triglycidyl isocyanurate (TGIC) to introduce long-chain branching into recycled PET during reactive extrusion, drastically enhancing melt foamability. Although this research did not target full vitrimer network formation, it established optimized extrusion temperature-shear processing windows for anhydride-epoxy co-modified rPET.

Li et al. [55] reported a one-pot green *in-situ* strategy using PMDA and BIS-TRIS to construct PET covalent adaptable networks. PMDA reacts with PET hydroxyl termini via anhydride ring-opening to generate ortho-carboxylic acid groups capable of neighboring-group participation (NGP) transesterification catalysis, while BIS-TRIS supplements additional hydroxyl sites and tertiary amine co-catalysis, as shown in Figure 6. The complete crosslinking reaction finished within only 5.5 min at 270 °C, representing one of the fastest reported *in-situ* vitrimer synthesis protocols. However, elevated processing temperatures risk hydrolytic and acidolytic PET backbone cleavage triggered by excess *in-situ* carboxylic acid, potentially reducing final crosslink density.

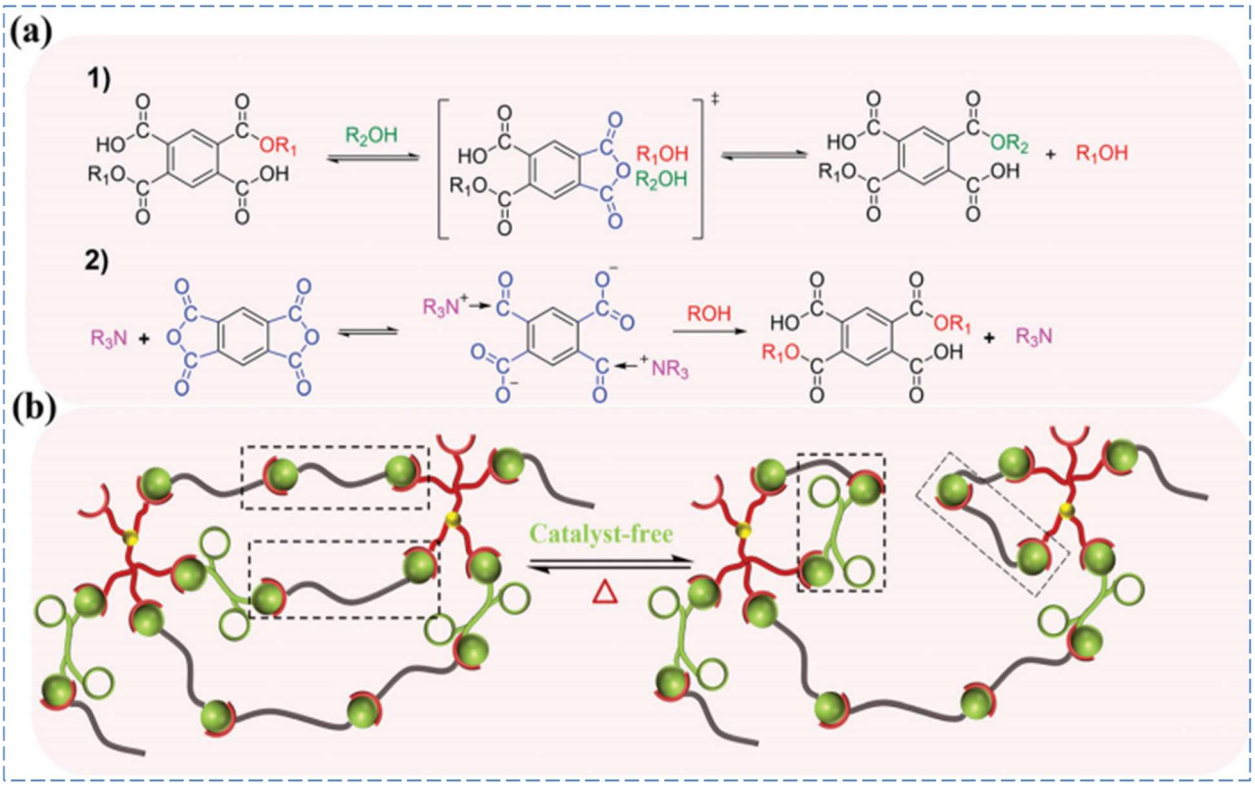


Figure 6. (**a**) Catalytic effect of tris(hydroxymethyl)aminomethane derivative (BIS-TRIS) and pyromellitic dianhydride (PMDA): (1) neighboring-group participation (NGP) of PMDA for transesterification; (2) BIS-TRIS catalyzes reactions between hydroxyl groups and acid anhydrides. (**b**) Schematic illustration of the exchange reaction for the topology network structure. Reproduced from Li et al. [55]. The dashed box marks the local catalytic environment in which the hydroxyl and anhydride groups participate in transesterification.

2.2.3. Reactive Melt Blending with Polymeric Modifiers

Beyond small-molecule epoxy/anhydride additives, melt reactive blending with foreign polyesters constitutes a versatile *in-situ* strategy capable of valorizing mixed heterogeneous polyester waste streams.

Leung et al. [56] systematically investigated catalytic melt transesterification blending of PET and polycaprolactone (PCL) using tetrabutyl titanate ($Ti(OBu)_4$) catalyst. *In-situ* transesterification initially formed block copolymers, gradually evolving into statistical poly(ethylene terephthalate-co-caprolactone) copolyesters analogous to commercial PBAT biodegradable polyesters [57]. The feedstock mass ratio governed PET block length and resultant thermomechanical performance, and post-blending chain extension was proposed to improve ductility at high PET loadings. Comprehensive follow-up reviews summarized polyester melt transesterification mechanisms and applications for mixed waste polyester recycling [58].

Fang et al. [59] developed a catalyst- and solvent-free upcycling protocol utilizing hydrogenated dimer acid (HDA) as a macromolecular dicarboxylic modifier. Intrinsic residual antimony trioxide (Sb_2O_3) from virgin PET manufacturing catalyzed melt transesterification without exogenous additives, producing biodegradable poly(ethylene hydrogenated dimerate-co-terephthalate) (PEHT) copolyesters with tensile strength exceeding 30 MPa. The copolyesters exhibited a 40% higher melt flow index than neat PET and achieved >95% depolymerization within 60 weeks under industrial composting conditions, with stoichiometric terephthalic acid monomer recovery. Additional studies explored reactive blending of rPET with PBT using Joncryl chain extenders, as well as compounding recycled epoxy vitrimers as toughening modifiers for PET matrices, enabling simultaneous dual waste valorization of epoxy and polyester plastic feedstocks [60,61].

Separate research efforts have exploited recycled epoxy vitrimers as macromolecular tougheners for PET matrices. Chen et al. [62] verified that blending PET with recycled epoxy vitrimers remarkably boosts the material's toughness without compromising tensile rigidity, which also delivers a dual waste valorization route to simultaneously upcycle discarded PET and epoxy vitrimer feedstocks.

2.2.4. Reactive Extrusion Manufacturing Platform

All aforementioned *in-situ* crosslinking chemistries rely on twin-screw reactive extrusion as the core continuous manufacturing platform, enabling precise control over residence time, shear rate, and temperature gradients compatible with standard industrial recycling infrastructure.

Sabeeh et al. [37] directly fabricated reprocessable vitrimer filaments via one-step reactive extrusion for fused deposition modeling (FDM) 3D printing, delivering high-strength, thermally resistant, repairable printed components and validating a complete end-to-end waste PET-to-functional-product workflow. Zhang et al. [63] quantitatively correlated crosslink density and network homogeneity with linear/nonlinear viscoelastic behavior of PET vitrimers, establishing a quantitative framework to select modifier chemistry and extrusion parameters for targeted rheological specifications.

Collectively, *in-situ* reactive crosslinking via melt extrusion eliminates energy-intensive separate depolymerization, supports continuous production, and tolerates moderately contaminated mixed waste PET feedstocks. Primary limitations include strict thermal stability requirements for modifiers under 260~280 °C melt temperatures, alongside statistical random transesterification reactions that limit precise molecular control over network topology, relative to the depolymerization-reconstruction route. Table 4 summarizes representative *in-situ* vitrimerization systems for comparative reference.

Table 4. *In-situ* Crosslinking Strategies for PET Vitrimers. Abbreviations: PMDA, pyromellitic dianhydride; DGEBA, diglycidyl ether of bisphenol A; BIS-TRIS, tris(hydroxymethyl)aminomethane derivative; TGDDM, N,N′-tetraglycidyl-diaminodiphenylmethane.

System	PMDA	BIS-TRIS/DGEBA	DGEBA	TGDDM	PMDA/BIS-TRIS
Modifier	PMDA	BIS-TRIS, DGEBA	DGEBA	TGDDM	BIS-TRIS, PMDA
Catalyst	Neighboring COOH	Tertiary amine (intrinsic)	$Zn(acac)_2$	Tertiary amine (intrinsic)	Neighboring COOH
Gel content (%)	—	>90	75	60~95	93
Crosslinking route/time	Reactive extrusion	Reactive extrusion	Melt extrusion	Melt mixing injection	Internal mixer, 5.5 min
T_g (°C)	—	80~90	~85	82~120	~80
Tensile (MPa)	—	~40	55	35~50	~40
Key feature	Increase M_w only	Creep resistance × 1000	Food tray waste	Self-catalytic, metal-free (reported example), tuneable	Fastest synthesis
References	[52]	[28]	[53]	[29]	[55]

Note: Values compiled across studies were obtained under different sample preparation and measurement protocols (e.g., thermal analysis conditions, tensile testing rates, and gel fraction extraction). Direct cross-study comparison therefore requires verification of the original methods, including the relevant testing standards where reported (e.g., ASTM D638, ISO 527, ASTM D3418, or ISO 11358). All data presented in this table were reported in the respective original studies, which did not employ a unified, standardized reactive-extrusion protocol.

2.3. Evolution of Transesterification Catalysis

Transesterification constitutes the core dynamic exchange reaction enabling vitrimer reprocessability, and catalyst selection dominates network formation kinetics, processing temperature, material purity, and environmental sustainability. This section systematically categorizes catalytic strategies along an evolutionary spectrum: conventional metal Lewis acid catalysts, self-catalytic tertiary amine catalysis,

neighboring-group intrinsic activation, residual-catalyst-assisted systems, and fully catalyst-free molecular architectures. Comparative analysis of activation energy, processing temperature, and practical trade-offs is provided for each category, as summarized in Table 5.

Table 5. Catalytic Strategies for PET Vitrimer Transesterification. Abbreviations: IL, ionic liquid; Ea, activation energy; Mw, molecular weight; τ*, characteristic relaxation time obtained from stress-relaxation measurements or fits reported in the original studies.

Category	Externally Catalyzed (Zn)	Externally Catalyzed (Ti)	Externally Catalyzed (Metal IL)	Self-Catalytic, Metal-Free	Neighboring Group	No-Added-Catalyst (Residual-Assisted Subcase)	Fully Catalyst-Free
Catalyst type	Zn[II]	Ti[IV]	Zn-containing IL	Tertiary amine	Carboxylic acid	Sb_2O_3	Dissociative
Example	$Zn[acac]_2$, $Zn[OAc]_2$	$Ti[OBu]_4$	$[C_{12}mim]_2$, $[ZnCl_4]$	TGDDM, BIS-TRIS	PMDA-derived COOH	Sb_2O_3 in rPET; high/low-Mw PET blend (residual Sb_2O_3 status not reported)	Intrinsically reactive polyester networks
E_a [kJ/mol]	70~130	—	—	80~120	~100	—	>200
Processing T [°C]	160~260	270~300	200~260	180~200	270	260~290	>200
Relaxation time [τ*/s]	5~300	—	—	10~100	~300 s	—	10~1000
Advantages	High activity	High activity for PET-PCL	Reduced leaching	No metal, uniform	*In-situ* generated	Zero added cost	No additives
Limitations	Toxicity, leaching	Moisture sensitive	Still contains metal	Higher T needed	High T required	Variable Sb content	Very high T
References	[53,64]	[56]	[65]	[28,29]	[55]	[59,66,67]	[68–70]

Note: Values compiled across studies were obtained under different sample preparation and measurement protocols (e.g., thermal analysis conditions, tensile testing rates, and gel fraction extraction). Direct cross-study comparison therefore requires verification of the original methods, including the relevant testing standards where reported (e.g., ASTM D638, ISO 527, ASTM D3418, or ISO 11358). All data presented in this table were reported in the respective original studies, which did not employ a unified, standardized catalytic or kinetic protocol.

2.3.1. Metal-Based Lewis Acid Catalysts

Zinc(II), titanium(IV), and tin(II) complexes represent the most widely adopted transesterification catalysts for polyester vitrimers, including zinc acetate ($Zn(OAc)_2$), zinc acetylacetonate ($Zn(acac)_2$), tetrabutyl titanate ($Ti(OBu)_4$), and tin(II) 2-ethylhexanoate($Sn(Oct)_2$). As Lewis acids, metal centers coordinate with ester carbonyl oxygen atoms to enhance carbonyl electrophilicity, accelerating nucleophilic attack by hydroxyl groups. Typical catalyst loadings range from 0.5 to 5 mol% relative to reactive chain ends, enabling efficient stress relaxation at 160~200 °C.

The catalytic activity of different metal centers follows established trends. Zn(II) catalysts strike an optimal balance between transesterification activity and suppression of unwanted thermo-oxidative degradation, emerging as the most prevalent choice in PET vitrimer research. $Zn(acac)_2$ enabled 75% crosslinking for food-tray rPET vitrimers at 260 °C [53], while $Ti(OBu)_4$ delivered superior catalytic activity for PET/PCL melt transesterification. Novel metal-containing ionic liquid catalysts have been developed to mitigate metal leaching risks while retaining high exchange kinetics [65]. Demongeot et al. [64] established the foundational concept of Zn[II]-catalyzed epoxy-vitrimer formation via reactive extrusion, using poly(butylene terephthalate) (PBT) as a model polyester substrate.

Nevertheless, metal-catalyzed systems face three interconnected practical drawbacks: residual metal ions continuously catalyze hydrolytic and thermo-oxidative degradation during long-term service and

multiple recycling cycles; EU RoHS and REACH regulations impose strict limits on heavy metal residues in consumer plastics; complete separation of metal catalysts from crosslinked vitrimer matrices is economically unfeasible within circular manufacturing loops.

2.3.2. Covalently Bonded Self-Catalytic Tertiary Amine Architectures

A promising metal-free strategy embeds tertiary amine catalytic moieties directly within crosslinker molecular skeletons, eliminating exogenous metal additives entirely. Tertiary amine nitrogen lone pairs form hydrogen bonds with hydroxyl protons to increase hydroxyl nucleophilicity, lowering transesterification activation energy without free catalyst migration.

TGDDM and BIS-TRIS are two representative self-catalytic crosslinkers with integrated tertiary amine functionality. TGDDM's four epoxy groups drive PET chain coupling, while internal tertiary amines simultaneously catalyze dynamic transesterification without extra metal salts [29]. As mentioned in the previous part, this system belongs to the *in-situ* crosslinking route; it is self-catalytic because the tertiary amine is covalently embedded, and it is metal-free in the reported formulation; the present section focuses specifically on its catalytic mechanism. BIS-TRIS combines three hydroxyl crosslinking sites and a central tertiary amine to create localized hydrogen-bond catalytic microenvironments during melt extrusion. Systematic comparative studies confirm covalently tethered tertiary amines deliver far superior uniform catalytic performance compared to physically blended amine additives, avoiding catalyst leaching during repeated thermal reprocessing [28].

Beyond the identity of the catalytic group, its local structural environment also governs performance. Su and coworkers [71] systematically probed the correlation between tertiary amine molecular architectures and transesterification catalytic performance. They fabricated a series of epoxy vitrimers functionalized with aliphatic, aromatic, and cyclic tertiary amine moieties, and further contrasted the catalytic disparities between covalently tethered amine catalysts and physically blended amine additives. Covalently integrated tertiary amines delivered markedly superior catalytic activity, attributed to their homogeneous molecular-scale dispersion and suppressed catalyst leaching upon repeated thermal reprocessing. As an early precedent supporting this design strategy, Altuna et al. [72] validated that tertiary amines covalently embedded within epoxy backbones efficiently facilitate transesterification reactions at temperatures exceeding 150 °C, affording stress relaxation kinetics comparable to conventional metal-catalyzed vitrimer systems.

2.3.3. Neighboring-Group and Residual-Catalyst-Assisted Systems

Two distinct additive-minimized catalytic pathways avoid external catalyst loading: neighboring-group carboxylic acid activation and utilization of residual antimony catalyst from virgin PET polymerization. For PMDA-modified *in-situ* vitrimers, anhydride ring-opening generates ortho-carboxylic acid groups spatially adjacent to ester backbones. These carboxylic acids stabilize six-membered-ring transesterification transition states via neighboring-group participation, lowering the reaction activation energy without external catalysts, though reaction temperatures are elevated to 270 °C to achieve practical exchange rates [55].

The residual-catalyst-assisted antimony strategy leverages inherent catalyst (Sb_2O_3) (50~300 ppm) retained in commercial PET feedstocks, eliminating additional catalyst costs. However, catalytic activity varies drastically across waste PET batches due to inconsistent antimony content, and residual antimony poses chronic toxicity risks alongside progressive catalytic deactivation over sequential recycling cycles [59]. This represents a no-added-catalyst strategy, but it fundamentally relies on endogenous metal-mediated catalysis. Zhang et al. [66] extended this mechanism to solid-state PET upcycling using antibacterial functional monomers. Nevertheless, the residual antimony catalytic route suffers critical

drawbacks: inconsistent Sb concentrations across waste feedstocks, inherent toxicological risks, and gradual catalytic deactivation after successive thermal recycling cycles.

2.3.4. No-Added-Catalyst and Fully Catalyst-Free Designs

This subsection distinguishes fully catalyst-free molecular networks from no-added-catalyst systems, which do not introduce an additional catalyst but may retain residual catalyst such as Sb_2O_3. Within this review, residual-catalyst-assisted systems are treated as a subcategory of the broader no-added-catalyst family. The high/low-molecular-weight PET blend discussed below is therefore classified as no-added-catalyst rather than fully catalyst-free because its residual Sb_2O_3 content was not reported.

The ultimate green vitrimer target eliminates all external catalytic additives by engineering intrinsic molecular reactivity to drive ester exchange at elevated temperatures.

One representative design blends high- and low-molecular-weight PET fractions: low-M_w PET chains possess concentrated terminal hydroxyl/carboxyl groups that act as intrinsic exchange promoters for high-M_w PET backbones, yielding a no-added-catalyst vitrimer with enhanced creep resistance, reprocessability and foaming performance [67]. Because the residual Sb_2O_3 content of the PET feedstock was not specified, this system is classified herein as no-added-catalyst rather than fully catalyst-free. Mechanistic studies identified dissociative transesterification as the dominant exchange pathway for fully catalyst-free polyesters, distinct from the associative mechanism that prevails in metal-catalyzed vitrimers [68]. Dissociative cleavage-recombination of ester bonds proceeds without coordinated metal mediation, requiring processing temperatures exceeding 200 °C to achieve measurable stress relaxation [68]. Recent literature reports high-toughness, flame-retardant, fully catalyst-free polyester vitrimers with full closed-loop chemical recyclability, as well as fully catalyst-free epoxy-polyester powder coating formulations with intrinsic self-healing functionality.

Ye et al. [69] fabricated fully catalyst-free transesterification vitrimers combining high strength, superior toughness, intrinsic flame retardancy, and closed-loop recyclability. The precisely balanced rigid aromatic and flexible aliphatic segments within the molecular architecture enable efficient transesterification without sacrificing mechanical robustness. Zhao et al. [70] further expanded this fully catalyst-free design to polyester–epoxy powder coatings, whose intrinsic reactivity facilitates dynamic covalent exchange upon thermal treatment.

2.3.5. Comparing Catalytic Strategies and Future Directions

Metal catalysts deliver fast exchange kinetics and low processing temperatures but introduce toxic residual metals incompatible with food and medical contact applications. The catalytic strategies reviewed in this work span a spectrum from conventional metal catalysis to fully catalyst-free systems, as summarized in Table 5 and Figure 7. Covalently tethered tertiary amine self-catalysis achieves metal-free operation with moderate processing windows [180~200 °C], ideal for premium eco-friendly plastic goods. Neighboring-group and residual antimony catalysis minimize additive costs yet suffer from narrow processing windows and compositional variability. Fully catalyst-free architectures represent the most sustainable option but demand high forming temperatures and elevated energy consumption.

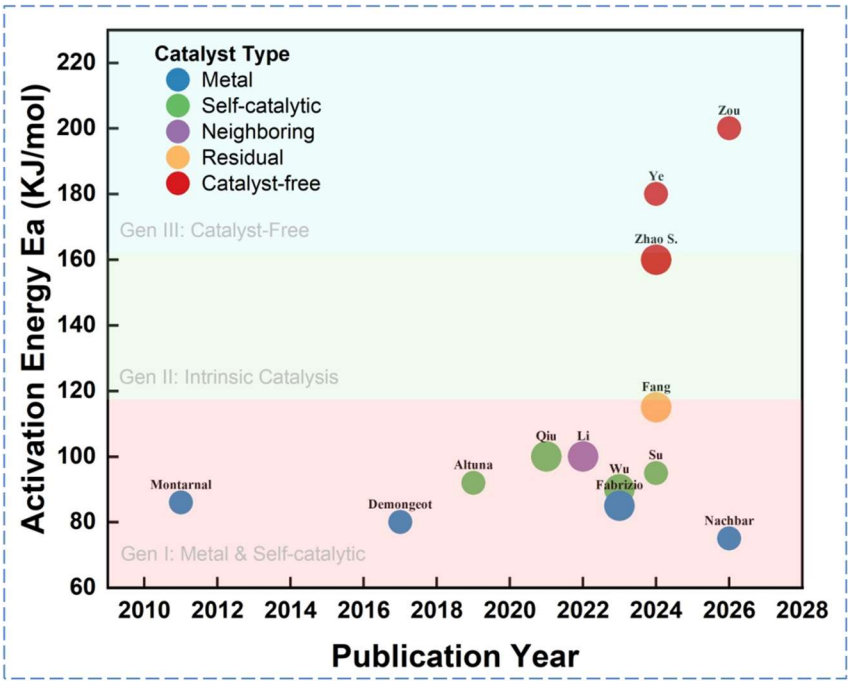


Figure 7. Evolution of catalytic strategies for transesterification in PET vitrimers. The trajectory spans from conventional metal catalysts (Zn(acac)2, Ti(OBu)4, Sn(Oct)2) through self-catalytic, metal-free tertiary-amine crosslinkers (BIS-TRIS and TGDDM), neighboring-group and no-added-catalyst systems, including residual-catalyst-assisted cases (PMDA and Sb2O3), to fully catalyst-free molecular designs. Following Section 1.3, "self-catalytic" and "metal-free" are separate descriptors, and "residual-catalyst-assisted" is treated as a subcase of "no-added-catalyst". The vertical axis denotes activation energy (Ea) and the horizontal axis denotes publication year. Circle size is used only as a schematic category marker and does not encode a separate quantitative variable.

Practical catalyst selection depends strongly on target application requirements: food-contact and biomedical vitrimers prioritize tertiary amine self-catalytic or fully catalyst-free designs. Bulk commodity recycled plastics may utilize residual-catalyst-assisted antimony catalysis to cut formulation costs. High-throughput industrial structural components can adopt low-dose zinc catalyst systems to balance production efficiency and environmental compliance.

3. Outlook and Perspective

This review discusses two fabrication routes for waste PET vitrimerization—depolymerization-reconstruction and *in-situ*/direct network construction—together with a cross-cutting transesterification catalytic dimension. Then the review compares the two routes and the catalytic design space in terms of energy consumption, catalyst toxicity, and processing continuity, providing an engineering reference for the industrial recycling of post-consumer PET waste. Despite remarkable advances at the laboratory scale, several pivotal bottlenecks remain to be addressed for large-scale industrial deployment of PET vitrimer recycling technologies.

3.1. Continuous Process Integration Challenges

The depolymerization-reconstruction workflow delivers exceptional molecular tunability, affording vitrimers with T_g spanning 38~240 °C and tensile strengths up to 117 MPa. However, multi-batch solvolysis, purification and curing steps contrast sharply with the single-pass continuous reactive extrusion of *in-situ* crosslinking. Key engineering priorities include developing integrated continuous solvolysis-extrusion hybrid lines that combine the molecular design flexibility of two-step routes with the low-cost continuous manufacturing of melt reactive extrusion.

3.2. Long-Term Service Durability Data Gaps

Thermally activated dynamic exchange, which enables reprocessing, simultaneously renders vitrimers susceptible to creep deformation under sustained high-temperature loading. While imine-based vitrimers have demonstrated ultra-low creep strain (<0.1% at 200~230 °C), systematic standardized evaluations of fatigue resistance, hydrolytic stability, and UV weathering remain scarce across the vitrimer literature. Establishing unified accelerated aging testing protocols for dynamic covalent networks will enable quantitative cross-study performance comparison and accelerate material qualification for structural industrial applications.

3.3. Standardized Closed-Loop Recycling Benchmarks

Recent reports have demonstrated near-quantitative chemical closed-loop recovery for imine vitrimers and fully depolymerizable biodegradable polyester vitrimers. Nevertheless, comprehensive techno-economic and life-cycle carbon footprint benchmarks comparing vitrimer recycling against conventional mechanical or chemical PET recovery are absent. Unified performance thresholds should be established as universal industrial evaluation criteria.

3.4. Green Catalysis: Balancing Energy Efficiency and Sustainability

The field's catalytic evolution from heavy metal Lewis acids toward self-catalytic amines, neighboring-group activation, and fully catalyst-free architectures reflects growing emphasis on circular green chemistry. Fully catalyst-free vitrimers eliminate all additive contamination yet require excessively high processing temperatures. Hybrid molecular designs integrating low-dose benign catalysts with intrinsic self-catalytic functional groups represent a promising compromise between low forming energy and zero toxic residues.

3.5. Need for Full Life-Cycle Assessment (LCA)

Compelling laboratory results for PET-derived vitrimers have been widely reported; nevertheless, systematic LCA studies remain largely under-explored for most vitrimerization strategies. Most existing publications prioritize material-level thermomechanical characterization, while neglecting quantitative evaluation of cradle-to-grave environmental burdens, including energy consumption, greenhouse-gas emissions, solvent usage, and waste generation across the full recycling loop. For instance, the high-energy-intensive purification steps of the depolymerization-reconstruction route and the environmental footprint of various crosslinkers and catalysts have rarely been quantified side-by-side. Future LCA work should benchmark vitrimer upcycling against conventional mechanical and chemical PET recycling, as well as virgin PET production. Such quantitative environmental metrics will help identify trade-offs between performance improvement and environmental cost, guide the selection of green modifiers and catalytic systems, and accelerate the industrial translation of promising vitrimer technologies toward a true circular plastics economy.

3.6. Tolerance to Industrial Mixed Waste Feedstocks

Existing research has validated vitrimerization compatibility with PET/PBT and PET/PCL mixed polyester waste streams without rigorous pre-sorting. Systematic investigations into the influence of real-world contaminants [printing inks, pigment fillers, PVC fragments, polyolefin impurities] on dynamic network formation and multi-cycle stability remain underexplored, a critical prerequisite for deploying vitrimer technology within commercial mixed plastic recycling facilities.

3.7. Unified Standardized Characterization Protocols

Inconsistent measurement methodologies for key vitrimer parameters (activation energy, topology freezing temperature, stress relaxation half-time, gel fraction) hinder quantitative cross-literature comparison. Establishing community-wide standardized testing frameworks analogous to unified vitrimer characterization guidelines will accelerate knowledge translation from fundamental lab research to industrial recycling lines.

In summary, waste PET vitrimerization has matured from conceptual laboratory demonstrations into a diversified multi-pathway technology ecosystem. The synergistic integration of solvolysis chemistry, reactive melt processing, and green catalytic molecular design creates a robust technical foundation for realizing fully circular plastic manufacturing. Cross-disciplinary collaboration between polymer synthetic chemists, processing engineers, and sustainability analysts will be essential to address unresolved bottlenecks and unlock large-scale industrial deployment of high-value vitrimer upcycling for post-consumer PET waste.

Statement of the Use of Generative AI and AI-Assisted Technologies in the Writing Process

During the preparation of this manuscript, the author(s) only used DeepSeek V4 in order to polish the language. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Author Contributions

Conceptualization, R.D. and W.L.; Methodology, R.D.; Investigation, S.Q., N.L., S.H., H.L., M.H. and W.X.; Validation, N.L., S.H. and H.L.; Visualization, S.Q., N.L. and W.X.; Writing—original draft, S.Q.; Writing—review and editing, S.Q., R.D. and W.L.; Resources, S.H., M.H. and C.Z.; Supervision, R.D., W.L. and C.Z.; Project administration, W.L. and C.Z.; Funding acquisition, W.L. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement

Not applicable.

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No new data were created or analyzed in this study. Data sharing is not applicable to this review article. All data discussed are available in the cited publications.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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