

Long-Term Durability and Stabilization of Polyurea Protective Coatings: Degradation Mechanisms, Interfacial Engineering, and Lifetime Prediction

xue gao

Shenyang Ligong University

feng zhao

Scottzhao@sylu.edu.cn

Shenyang Ligong University

zhonghua du

Shenyang Ligong University

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Long-Term Durability and Stabilization of Polyurea Protective Coatings: Degradation Mechanisms, Interfacial Engineering, and Lifetime Prediction

Abstract

Polyurea protective coatings are widely used in anticorrosion, waterproofing, marine engineering, transportation infrastructure, and industrial protection because of their rapid curing, high toughness, strong adhesion, and resistance to aggressive media. However, their long-term reliability depends not only on initial mechanical performance, but also on barrier retention, coating/substrate interfacial stability, and resistance to environmental aging. This review examines the durability and stabilization of polyurea protective coatings from the perspective of organic coating degradation. The effects of molecular architecture, hydrogen-bonding networks, hard/soft segment microphase separation, curing behavior, and interfacial structure on coating stability are first discussed. Aging and failure mechanisms under ultraviolet irradiation, thermo-oxidative exposure, hygrothermal conditions, salt spray, marine environments, cyclic loading, and mechanically coupled service conditions are then reviewed, with emphasis on water and ion transport, hydrogen-bond disruption, microphase relaxation, crack evolution, adhesion loss, and barrier failure. Stabilization strategies involving molecular structure regulation, nanofiller-induced barrier enhancement, interfacial engineering, dynamic networks, self-healing systems, recyclable designs, and lifetime prediction are further evaluated. The available evidence shows that polyurea coating failure is rarely governed by a single degradation pathway; rather, it results from the coupled evolution of chemical aging, moisture and ion diffusion, microphase rearrangement, interfacial damage, and mechanical defects.

Future research should focus on standardized aging protocols, in situ characterization, structure-durability relationships, and data-driven lifetime prediction to guide the design of durable polyurea coatings for long-term protective applications.

Keywords: Polyurea protective coatings; Organic coatings; Corrosion resistance; Environmental aging; Interfacial degradation; Lifetime prediction

1. Introduction

1.1 Long-term service behavior and durability challenges of polyurea protective coatings

Polyurea (PUA) protective coatings are segmented polymer systems formed through the rapid reaction between isocyanates and amine-terminated compounds. Their microphase-separated architecture composed of hard and soft segments, together with a dense hydrogen-bonding network associated with urea linkages, provides high mechanical strength, toughness, energy dissipation capability, and resistance to aggressive media [1-7]. Owing to their rapid curing behavior, high solid content, low volatile organic compound (VOC) emissions, and combined resistance to water ingress, corrosion, and abrasion, polyurea protective coatings have been widely applied in building waterproofing, industrial corrosion protection, transportation infrastructure, marine engineering, and specialized protective systems [8-13]. Compared with conventional organic coatings such as polyurethanes and epoxy resins, the strong urea hydrogen bonding, physical crosslinking within hard segments, and pronounced hard/soft segment phase separation enable improved structural adaptability under dynamic loading, corrosive environments, and complex service conditions [14,15].

However, the engineering performance of polyurea protective coatings is not solely determined by their initial mechanical properties. Long-term barrier retention, interfacial stability, and structural integrity during service are equally critical. Under thermo-oxidative exposure, ultraviolet radiation, hygrothermal conditions, salt spray, cyclic mechanical fatigue, and irradiation, polyurea coatings may undergo soft-segment oxidation and chain scission, weakening of hydrogen-bonding networks, relaxation of microphase-separated structures, water and ion transport, coating/substrate interfacial debonding, and crack propagation. These processes ultimately lead to mechanical degradation, loss of adhesion, reduced barrier performance, and functional failure of the coating system [16-20]. Accordingly, research attention has gradually shifted from achieving high initial properties to maintaining structural stability and protective reliability during long-term service.

From a structural perspective, degradation and failure of polyurea coatings exhibit pronounced multiscale

characteristics. At the molecular level, isocyanate chemistry, soft-segment composition, chain extender structure, and hard-segment content govern chain stability, hydrogen-bond density, and oxidation susceptibility. At the supramolecular and microphase level, hydrogen-bonding networks, hard-domain aggregation, and hard/soft interfacial regions control water diffusion, ion migration, stress transfer, and crack evolution [21-23]. At the macroscopic scale, these coupled structural evolutions manifest as reductions in strength, toughness, adhesion, barrier performance, and overall service life [18,24]. Therefore, performance degradation of polyurea coatings under complex environments does not arise from a single chemical pathway, but from the coupled effects of chemical aging, physical relaxation, microphase reorganization, aggressive species penetration, interfacial degradation, and mechanical damage.

Although polyurea materials have been extensively applied in protective coating and structural protection fields, a systematic understanding of their long-term degradation behavior, interfacial failure mechanisms, and service-life attenuation remains limited. Existing reviews have mainly focused on synthesis strategies, structural regulation, or specific application scenarios. For instance, some studies emphasize optimization of polyurea synthesis routes [25], development of CO₂-based polyurethane/polyurea systems [26], or structural protection applications such as blast and impact resistance [27-29]. In contrast, a comprehensive perspective from the standpoint of organic coating durability remains insufficient, particularly regarding how coupled environmental factors—including thermo-oxidation, UV exposure, moisture, salt spray, mechanical loading, and irradiation—affect chain mobility, hydrogen-bond reconfiguration, microphase evolution, coating/substrate interface stability, barrier performance, and macroscopic failure behavior.

To address these issues, this review focuses on the long-term durability of polyurea protective coatings, with an emphasis on structural evolution, failure mechanisms, and lifetime extension strategies during service. Unlike previous reviews that mainly concentrate on synthesis routes, impact resistance, or isolated application scenarios, this work highlights degradation and failure processes in realistic service environments and attempts to correlate molecular structure, hydrogen-bonding networks, microphase morphology, aggressive species transport, interfacial evolution, and macroscopic performance deterioration. The discussion first summarizes the effects of hard/soft segment structure, reaction kinetics, hydrogen-bond assembly, and microphase separation on the initial stability of polyurea coatings. It then analyzes dominant degradation behaviors under thermo-oxidative, UV, hygrothermal, salt spray, mechanical fatigue, low-temperature, high-pressure, and irradiation environments. Subsequently, strategies for enhancing durability are discussed, including molecular design, nanoscale barrier reinforcement, interfacial engineering, dynamic networks, self-healing systems, non-isocyanate routes, and recyclable design

concepts. Finally, the application of in-situ characterization, multiscale simulation, machine learning, and digital twin approaches for lifetime prediction is introduced. This framework aims to provide a reference for the design and optimization of durable polyurea protective coatings under long-term service conditions.

1.2 Development History of Polyurea Materials

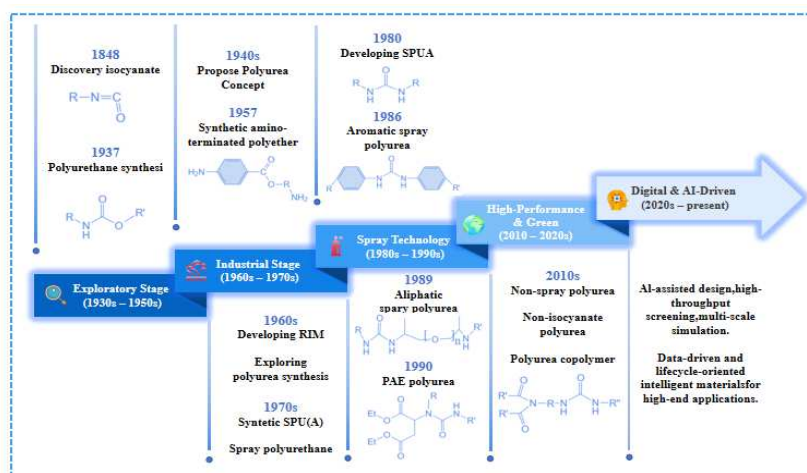


Fig. 1. Development history of polyurea.

Polyurea (PUA) development has evolved from fundamental chemical understanding, through process engineering of spray application, to current emphasis on long-term service stability design. With its expanding use in protective coatings, industrial corrosion protection, marine engineering, and structural shielding, degradation issues induced by thermo-oxidative exposure, ultraviolet radiation, hygrothermal conditions, salt spray, mechanical loading, and irradiation have received increasing attention. Accordingly, research on polyurea has gradually shifted from rapid film formation and improvement of initial properties toward degradation mechanisms, interfacial stability, barrier retention, and lifetime prediction. The overall development trajectory is illustrated in Fig. 1.

(1) The period from the 1930s to 1950s corresponds to the stage of fundamental chemical exploration. Otto Bayer established the theoretical basis of isocyanate addition polymerization, which promoted the development of polyurethane and polyurea chemistry. This work also laid the foundation for understanding urea linkages, hydrogen-bonding interactions, and the stability of segmented polymer architectures [30].

(2) The 1960s to 1970s represent the formation stage of industrial fundamentals. The development of key raw materials such as amine-terminated polyethers (ATPE), together with the introduction of reaction injection molding (RIM), enabled the engineering-scale fabrication of polyurea materials. Research during this period mainly focused on reaction kinetics, processing efficiency, and basic mechanical properties [27,31-34].

(3) The 1980s to 1990s mark the emergence of spray polyurea technology. With advances in high-pressure spraying and rapid mixing systems, spray polyurea (SPUA) was widely applied in waterproofing, corrosion

protection, wear resistance, and impact protection. However, the rapid curing process may also introduce structural heterogeneity, residual stress, porosity, and interfacial defects. These intrinsic features at the initial stage can significantly influence subsequent aging behavior, aggressive species transport, and long-term service stability of the coating system [35-37].

(4) Since around 2010, research on polyurea has progressively shifted from enhancing initial performance toward improving environmental durability, damage tolerance, and interfacial reliability. Strategies including nanofiller incorporation, dynamic network design, self-healing structures, and molecular architecture optimization have been employed to enhance resistance against aging, crack propagation, water/salt spray penetration, and interfacial degradation [38,39]. Meanwhile, developments in low-VOC systems, non-isocyanate routes, and recyclable formulations have linked durability-oriented design with green manufacturing and life-cycle considerations [40].

(5) In recent years, the development of multiscale simulation, machine learning, and data-driven design has driven polyurea research from empirical formulation optimization toward service-life-oriented engineering. By integrating experimental aging data, microstructural characterization, molecular simulations, and lifetime prediction models, it becomes possible to establish cross-scale relationships linking molecular structure, microphase morphology, interfacial state, and macroscopic coating degradation. Such a framework can support the long-term reliable application of polyurea protective coatings in marine engineering, transportation infrastructure, industrial corrosion protection, and specialized defense systems [41-44].

2. Fundamentals of Polyurea Structure and Stability

2.1 Molecular Structure of Polyurea and Degradation Sensitivity

Polyurea is a class of polymeric materials formed through a rapid, solvent-free step-growth reaction between isocyanates and amine compounds [45-47]. The outstanding performance of polyurea arises from its highly tunable molecular architecture, particularly the ordered arrangement of hard segments and soft segments and the resulting microphase-separated morphology. This cross-scale structural organization governs its stability under extreme environments, as well as its mechanical energy dissipation behavior and failure mechanisms.

2.1.1 Hard and soft segment structure

Polyurea is generally regarded as a segmented polymer network composed of alternating hard and soft domains. By adjusting the isocyanate component [48], amine species, chain extenders, and their stoichiometric

ratios, key structural parameters such as hard segment content, soft segment length, hydrogen-bond density, and degree of microphase separation can be precisely tuned. These structural variables directly determine the resulting mechanical properties, environmental adaptability, and long-term service stability [49-54]. The basic chemical composition of polyurea and its hard/soft segment microphase-separated morphology are illustrated in Fig. 2(a).

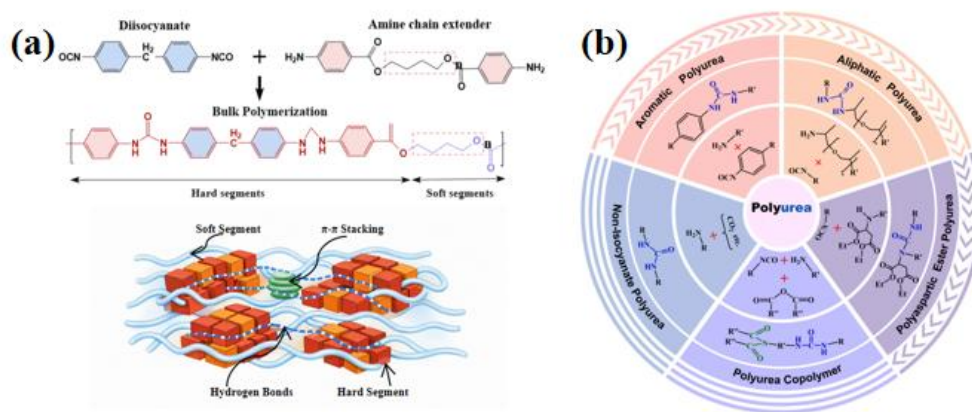


Fig. 2. (a) Chemical structure and microphase-separated morphology of polyurea (PU); (b) Classification of polyurea materials [59].

The hard segments of polyurea are primarily formed through the reaction between isocyanate components and low-molecular-weight amine chain extenders. These segments exhibit high polarity, strong urea-based hydrogen bonding, and relatively high glass transition temperatures (T_g). Within polyurea systems, hard segments tend to associate via hydrogen bonding to form nanoscale hard domains. In aromatic structures, additional π - π interactions between aromatic rings may also contribute to domain stabilization. These hard domains function as reversible physical crosslinking points, enhancing modulus, strength, thermal stability, and energy dissipation capacity. From a long-term service perspective, however, excessive hard-segment aggregation may increase local rigidity and stress concentration, thereby promoting embrittlement and microcrack propagation under thermo-oxidative aging, UV irradiation, or low-temperature conditions.

Soft segments are typically derived from long-chain polyethers, polyalkanes, or other flexible amine-terminated oligomers. They possess low T_g and high chain mobility, forming a continuous flexible phase within the microphase-separated structure [22,55]. Soft segments provide high elongation at break, elastic recovery, low-temperature flexibility, and fatigue resistance. Li et al. [21] investigated PUR1000 and reported that increasing the soft-segment fraction leads to a reduction in tensile strength, accompanied by a decrease in glass transition temperature (T_g).

The thermodynamic incompatibility between hard and soft segments is the primary driving force for

microphase separation in polyurea. When the service temperature is above the T_g of the soft phase but below that of the hard domains, the hard-segment aggregates provide structural rigidity, while the soft segments remain in a rubbery state with high chain mobility. This combination enables polyurea to simultaneously exhibit high strength and excellent elasticity [56,57]. Guo et al. [58] confirmed that the hard/soft segment ratio, loading rate, and temperature significantly influence the mechanical response of polyurea. From the perspective of degradation and stability, the resulting microphase-separated morphology also governs the transport pathways of water, oxygen, and chloride ions, as well as stress transfer and crack initiation behavior. Accordingly, the hard/soft interphase represents a key structural region for understanding long-term service stability.

Overall, polyurea is not a single-constituent material but a segmented network system in which mechanical performance and durability are governed by hard-segment chemistry, soft-segment flexibility, urea hydrogen bonding, and microphase-separated morphology. Representative polyurea systems include aromatic polyurea, aliphatic polyurea, polyaspartic ester (PAE) polyurea, polyurea copolymers, and non-isocyanate polyurea [59], as illustrated in Fig. 2(b). These systems differ in chain rigidity, hydrogen-bonding capability, phase organization, weathering resistance, and degradation sensitivity. Such differences provide the structural basis for subsequent discussions on aging mechanisms and stabilization strategies.

2.1.2 Comparison between Aromatic Polyureas and Aliphatic Polyureas

Polyurea materials are commonly classified into aromatic and aliphatic systems according to the chemical nature of the isocyanate-derived hard segments. Aromatic polyureas are typically based on MDI, TDI, and their modified aromatic diisocyanates as hard-segment precursors [60]. Zhao et al. [47] reported that, due to the higher conformational rigidity of aromatic rings and stronger intermolecular interactions, aromatic hard segments tend to form locally dense packing structures and develop relatively stable hard domains through urea-based hydrogen bonding. As a result, aromatic polyureas generally exhibit higher initial modulus, tensile strength, hardness, and thermal dimensional stability. These characteristics make them suitable for impact-resistant protective coatings, heavy-duty anticorrosion systems, and rapid spray-coating applications.

Structural-property studies and related reviews [61-63] consistently indicate that the intrinsic rigidity and strong aggregation tendency of aromatic hard segments provide the structural basis for their high load-bearing capacity and thermal stability. However, their limitations are also evident, particularly in terms of weatherability and ultraviolet resistance. Guo et al. [60] showed that aromatic rings are more sensitive to UV irradiation, leading to pronounced photo-oxidative degradation during long-term outdoor exposure. This process is often accompanied by yellowing, gloss loss, surface embrittlement, and the initiation of microcracks. Therefore, although aromatic

polyureas provide superior mechanical robustness, their long-term outdoor durability and photostability generally require further improvement through UV stabilizers, aliphatic topcoats, or nanostructured barrier architectures.

In contrast, aliphatic polyureas are typically constructed from aliphatic or cycloaliphatic diisocyanates such as HDI, IPDI, and HMDI. Owing to the absence of aromatic chromophores, these systems exhibit a significantly reduced tendency toward UV-induced yellowing and color fading, and therefore demonstrate better weather resistance, anti-yellowing performance, and long-term outdoor stability [64-67]. From a mechanical perspective, aliphatic hard segments are relatively more flexible, with higher chain mobility. This structural feature often results in improved ductility, low-temperature flexibility, and resistance to cyclic deformation, making them more suitable for outdoor protective coatings, flexible encapsulation systems, and applications requiring stable appearance retention [68].

It should be emphasized that aliphatic polyurea does not imply weakened hard-segment interactions. He Yong et al. [62] demonstrated that diisocyanate molecular symmetry, steric hindrance, and chain flexibility collectively influence hard-segment packing behavior, hydrogen-bonding network organization, and the characteristic length scale of microphase separation. Therefore, the differences between aromatic and aliphatic polyureas cannot be simply interpreted as a binary distinction of “stiffer versus softer”. Instead, they arise from systematic variations in hard-segment rigidity, polarity distribution, local packing motifs, and interfacial organization between phases.

Overall, the distinction between aromatic and aliphatic polyureas extends beyond stiffness differences and reflects a combined effect of hard-segment chemistry, UV sensitivity, hydrogen-bonding architecture, phase morphology, and environmental stability. Aromatic polyureas typically provide higher initial strength and thermal dimensional stability but are more prone to UV-induced discoloration and photo-oxidative surface degradation. Aliphatic polyureas, on the other hand, generally exhibit superior weatherability and long-term outdoor durability, although their modulus and load-bearing capacity may be relatively lower. Consequently, the selection of hard-segment chemistry in polyurea protective coatings should be guided by the specific service environment, balancing mechanical performance, thermal stability, photo-oxidative resistance, barrier performance, and long-term durability.

2.1.3 Polyaspartic Ester Polyurea

Conventional spray-applied polyurea coatings are formed through the rapid addition reaction between primary amines and isocyanates, with gelation and curing completed within seconds. This ultrafast reaction is advantageous for rapid film formation and on-site application. However, excessive reaction rates may also lead to insufficient mixing, inadequate wetting of the substrate, locally heterogeneous crosslinking, residual stress

accumulation, and interfacial defects. From a long-term service perspective, these initial defects can act as preferential pathways for water, oxygen, and chloride ion transport, thereby accelerating interfacial degradation, crack initiation, and deterioration of protective performance. Accordingly, in polyurea protective coatings, the reaction kinetics and curing process govern not only application efficiency but also the initial structural quality, coating/substrate interface integrity, and long-term durability.

Polyaspartic ester (PAE) polyurea systems regulate amine reactivity through secondary amine structures and steric hindrance effects, thereby extending the application window and improving flow leveling, substrate wetting, and interfacial film formation. The bulky dialkyl succinate structure in PAE monomers further reduces reaction rates, while reactivity can also be tuned by adjusting ester group size, amine structure, and maleate composition [69,70]. As a result, PAE-based systems provide an effective strategy for controlling gel time, curing kinetics, and coating/interfacial quality in polyurea protective coatings. Liu et al. [71] synthesized polyaspartic esters via Michael addition between dialkyl maleates and bis(4-aminocyclohexyl)methane (PACM). The resulting coatings exhibited good chemical resistance, adhesion performance, and UV aging resistance.

Natour et al. [72] reported that PAE-based polyurea coatings show favorable adhesion, weather resistance, water resistance, and chloride ion resistance. These properties are closely associated with the controllable curing process, improved substrate wetting, and the aliphatic nature of the hard segments. However, PAE systems are not universally superior to conventional spray polyurea under all service conditions. The relatively slower curing kinetics may limit their applicability in scenarios requiring extremely rapid film formation and immediate service. In addition, the incorporation of ester groups may introduce hydrolysis susceptibility under hygrothermal exposure, potentially affecting long-term stability [73]. Therefore, the value of PAE polyurea lies not in replacing conventional spray polyurea, but in providing a tunable reaction kinetics strategy to balance application window, interfacial quality, chloride barrier performance, and long-term durability.

2.1.4 Copolymerized Polyureas and Non-Isocyanate Polyureas

Beyond aromatic, aliphatic, and polyaspartic ester-based polyureas, structural expansion of polyurea systems mainly follows two routes: copolymerization design and non-isocyanate construction. Copolymerization strategies involve introducing additional flexible, rigid, or functional segments into the conventional soft-segment/hard-segment (urea-based) network. These segments are incorporated through copolymerization, grafting, or block architectures, allowing regulation of hard-segment aggregation, soft-hard segment compatibility, hydrogen-bonding distribution, and overall network topology. Typical systems include polyurea-siloxane, polyurea-polyurethane, polyurea-polyester, and polyurea-polyimide hybrids. Feng and Wang et al. [74] reported

block copolymers composed of polyimide and urea segments prepared via a polymerization process, which significantly altered mechanical properties and glass transition behavior.

Non-isocyanate polyureas refer to systems in which isocyanates are excluded from the synthesis route, and urea linkages are formed via alternative precursors [75], representing an important direction toward greener polymer synthesis. Yu et al. [76] further optimized hard-segment structures by introducing urea bonds, achieving improved mechanical performance and self-healing capability.

From a polymer stability perspective, copolymerization is not a simple superposition of individual segment properties. Instead, it modifies chemical composition and interfacial organization, thereby tuning the microphase separation scale, hydrogen-bonding network stability, and environmental sensitivity of polyurea systems. For instance, incorporation of siloxane segments reduces surface energy and enhances hydrophobicity, weather resistance, and hygrothermal stability [77,78]. Polyurethane or polyester segments improve flexibility, processability, and interfacial compatibility, although hydrolysis-prone structures may be introduced [79,80]. Rigid polyimide segments contribute to improved thermal stability and high-temperature dimensional retention [81]. Therefore, copolymerized polyurea design requires balancing mechanical performance, environmental durability, and potential degradation risks.

Compared with copolymerized systems, non-isocyanate polyureas emphasize green, safer, and more sustainable network construction routes. With the development of CO₂ utilization and green polymer chemistry, the preparation of non-isocyanate polyurethane/polyurea networks from cyclic carbonates, urea-based intermediates, or other CO₂-derived precursors has become an important research direction [82,83]. CO₂-based polyols can provide favorable mechanical properties, thermal stability, flame retardancy, and chemical resistance. Compared with conventional polyether polyols, polyols containing 40 wt.% CO₂ content may reduce production costs by approximately 20-30% [84].

A widely used non-isocyanate route involves the reaction of CO₂ with epoxides to form five- or six-membered cyclic carbonates, followed by ring-opening reactions with polyamines to construct non-isocyanate polyurethane/polyurea networks containing hydroxyl, urea, or carbamate structures. These systems avoid the use of highly toxic isocyanates and provide reactive sites such as hydroxyl and urea groups, enabling further crosslinking, self-healing, reprocessability, and recyclability. However, non-isocyanate polyureas still suffer from relatively low reaction rates, limited regioselectivity, restricted polymerization efficiency, and difficulties in forming high-molecular-weight networks. Five-membered cyclic carbonates generally exhibit lower reactivity than isocyanate systems, while CO₂-derived six-membered cyclic carbonates can improve amine reactivity and enable

higher molecular weight PU formation [85-87]. In addition, alternative approaches using CO₂-derived intermediates with amines, dihalides, or aziridines have been explored to construct polyurea-based polymer backbones [88-90].

Overall, copolymerization design and non-isocyanate construction provide new structural platforms for stabilizing and sustainably designing polyurea protective coatings. The former focuses on improving weather resistance, thermal stability, interfacial adhesion, and damage tolerance through segment synergy, microphase structure regulation, and interfacial optimization. The latter extends the development of polyurea coatings toward greener pathways in terms of raw material safety, CO₂ utilization, network designability, and recyclability. For long-term service organic coatings, further evaluation is still required regarding barrier retention, interfacial stability, performance retention, and lifetime prediction reliability under hygrothermal, thermal-oxidative, UV, salt spray, and multi-factor coupled aging conditions.

2.2 Network Formation and Microphase Structure

The durability of polyurea protective coatings is governed not only by the chemical composition of raw materials but also by reaction kinetics during network formation, hydrogen-bonding assembly, and microphase separation behavior. The rapid reaction between isocyanates and amines enables fast film formation and convenient on-site application; however, it can also restrict chain diffusion and structural rearrangement. As a result, network inhomogeneity, incomplete microphase separation, residual stress, and interfacial defects may develop during curing. These initial structural features directly influence subsequent transport pathways for water, oxygen, and chloride ions within the coating. Under coupled hygrothermal, thermal-oxidative, UV irradiation, salt spray, and mechanical fatigue conditions, such heterogeneities can facilitate phase relaxation, interfacial debonding, and crack propagation, ultimately accelerating coating degradation and reducing long-term barrier performance. Accordingly, the microstructure of polyurea coatings should be understood as the combined outcome of urea bond formation, hydrogen-bonding association, hard-segment aggregation, microphase separation, and physical crosslinking. The interplay among these processes determines the continuity of the barrier network and the stability of the coating/substrate interface during long-term service.

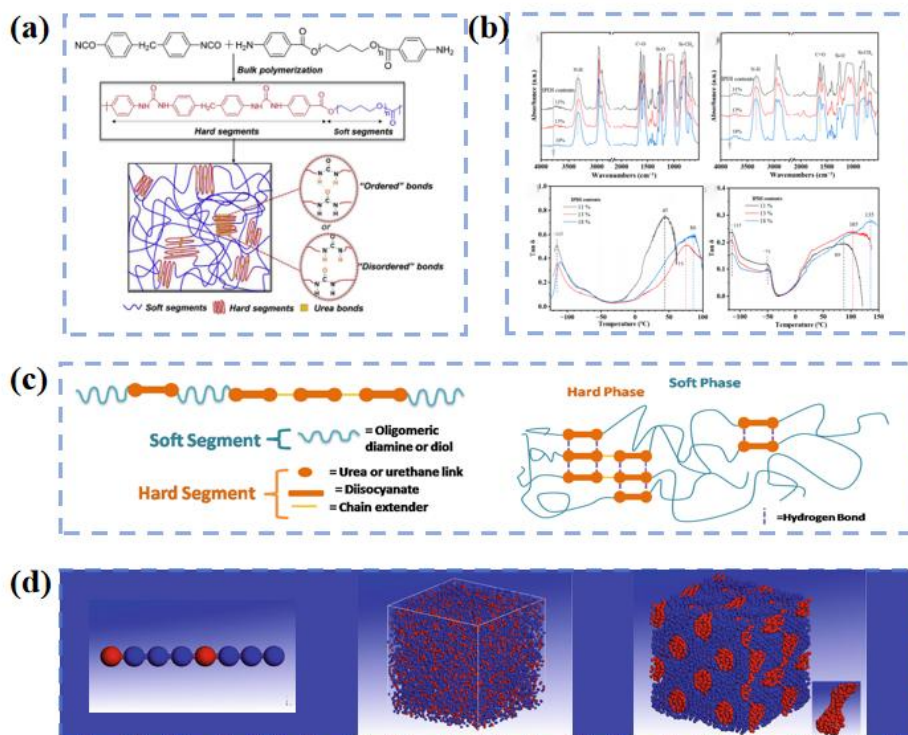


Fig. 3. (a) Synthesis route and schematic molecular structure of PUR1000 [21]; (b) Polyurea systems with different soft-segment molecular weights [94]; (c) Schematic illustration of the microphase separation model [62]; (d) Mesoscale simulation of polyurea morphology evolution [102].

2.2.1 Isocyanate-Amine Reaction and Network Formation

The fundamental formation reaction of polyurea involves the nucleophilic addition between isocyanate groups (—NCO) and amine groups (—NH_2 or —NHR), yielding urea linkages (—NH—CO—NH—). Compared with the isocyanate-hydroxyl reaction, the isocyanate-amine reaction exhibits significantly higher reactivity and typically proceeds rapidly at room temperature without additional catalysts. This enables spray-applied polyurea coatings to gel and form a preliminary film within seconds, which is a key advantage for on-site rapid construction.

During curing, isocyanate groups react simultaneously with terminal amino-functional soft segments and small-molecule amine chain extenders, leading to a rapid increase in molecular weight and progressive formation of branched, gelled, and crosslinked networks. Because the hard segments are mainly formed from isocyanates and amine chain extenders, while the soft segments are typically derived from flexible long-chain polyether amines, network formation is accompanied by hard-segment enrichment and soft/hard segment phase separation. In this sense, polyurea curing is not merely a covalent bond growth process, but a coupled evolution involving chemical reactions, hydrogen-bonding association, and phase structure development.

The rapidly formed urea linkages provide the structural basis for hard-segment formation. Meanwhile, thermodynamic incompatibility between hard and soft segments drives aggregation of urea-rich hard domains stabilized by hydrogen bonding, leading to dispersed hard domains within the soft matrix [92,93]. Li et al. [21] demonstrated that hard segments can self-assemble into stacked hard domains via hydrogen bonding, which act as reversible physical crosslinking points and provide structural reinforcement and mechanical stability to polyurea networks (Fig. 3a). However, under rapid spray and fast curing conditions, the reaction rate may exceed the diffusion and phase rearrangement rates of polymer chains. As a result, network heterogeneity, residual stress, and incomplete microphase development may be partially frozen into the final structure. These initial structural features can influence subsequent water/oxygen/chloride transport, interfacial degradation, and crack initiation during service. Therefore, polyurea network formation should be viewed as a coupled process involving urea bond generation, hard-segment aggregation, microphase separation, and physical crosslinking.

2.2.2 Hydrogen Bonding and Hard-Domain Formation

In polyurea systems, the urea group (—NH—CO—NH—) serves not only as a backbone linkage but also as a key driving unit for hard-segment aggregation and microphase separation. Owing to the coexistence of N-H donors and C=O acceptors, strong intermolecular hydrogen bonding can form between chains. This interaction promotes aggregation of urea-rich hard segments into hard domains, which function as reversible physical crosslinking points within the soft phase.

Hydrogen bonding directly governs the formation of hard microdomains and the resulting microphase-separated structure. Li et al. [21] described hard domains as hydrogen-bond-stabilized reversible physical crosslinks that preserve network integrity and regulate modulus, strength, and elastic recovery. Importantly, hydrogen bonding in urea groups does not exist in a single state; it can adopt both ordered and disordered association forms. With increasing temperature, ordered hydrogen bonds gradually dissociate or rearrange, leading to changes in hard-domain structure and microphase morphology. This indicates that hydrogen bonding acts not only as the driving force for hard-domain formation but also as a key factor controlling thermal stability and aging response.

Bao et al. [94] investigated polyurea systems with different soft-segment molecular weights and reported pronounced differences in hydrogen bonding and microphase structures between L-30D and H-130D, indicating that soft-segment length influences hard-segment organization. In addition, increasing isocyanate content raises the proportion of urea linkages and hard segments, leading to higher hard-domain T_g and more pronounced phase separation, as shown in Fig. 3(b).

For polyurea protective coatings, hydrogen-bond networks and hard-domain structures influence not only initial mechanical properties but also barrier retention and structural stability during service. Temperature rise can induce hydrogen bond dissociation and hard-domain rearrangement, while water ingress may compete with urea hydrogen bonds and weaken the stability of hard microdomains. These processes alter microphase structure, chain mobility, and transport pathways, further affecting adhesion retention, crack propagation, and long-term protective performance. Therefore, the stability of hydrogen bonding networks is a key basis for understanding aging behavior and stabilization design in polyurea coatings.

2.2.3 Formation Mechanism of Microphase Separation

Microphase separation in polyurea primarily originates from thermodynamic incompatibility between hard and soft segments. Hard segments are rich in urea groups with strong polarity and tend to aggregate through hydrogen bonding, whereas soft segments are typically composed of flexible polyether chains or other low-polarity segments with high chain mobility. Due to differences in polarity, solubility parameters, and intermolecular interactions, the system tends to phase-separate to minimize free energy [95-97]. However, because hard and soft segments are covalently linked, macroscopic phase separation is prevented, leading instead to nanoscale microphase-separated morphologies consisting of hard domains, soft phases, and interfacial regions.

He et al. [62] proposed that part of the hard segments self-assemble into distinct hard-phase regions, while a fraction remains dispersed or trapped within the soft phase, resulting in incomplete microphase separation characteristics (Fig. 3c). The degree of microphase separation is further influenced by chain mobility, viscosity, polymerization route, and thermal treatment conditions [98,99]. At elevated temperatures or under enhanced chain mobility, hard segments can more readily diffuse and aggregate into more well-developed domains [100]. In contrast, under rapid curing or high-viscosity conditions, chain rearrangement is restricted, and the system may deviate from equilibrium, leaving hard segments partially trapped in the soft phase [101]. For protective coatings, such non-equilibrium structures can influence phase relaxation, transport behavior, and crack initiation during service.

Hydrogen bonding further regulates microphase evolution. Mesoscopic simulations by Grujicic et al. [102] indicated that microphase separation evolves from an initially mixed state toward a segregated morphology, governed by hard-segment diffusion, local rearrangement, and domain growth (Fig. 3d). Li et al. [21] also observed that ordered hydrogen bonds within hard segments dissociate and reform during heating, inducing domain rearrangement and coarsening. These findings indicate that microphase morphology is governed not only by thermodynamic incompatibility between hard and soft segments but also by diffusion kinetics, curing rate,

hydrogen bond dynamics, and thermal history.

Accordingly, microphase separation in polyurea can be interpreted as the combined result of thermodynamic driving forces and kinetic constraints. Segmental incompatibility defines the phase-separation tendency, hydrogen bonding promotes hard-segment aggregation, and processing conditions determine the extent of structural development. For protective coatings, the resulting microphase structure directly affects mechanical response, thermal transitions, barrier performance, and long-term durability.

2.2.4 Relationship Between Microstructure and Properties

The service performance of polyurea protective coatings is closely linked to their hierarchical microstructure. Hard domains formed through hydrogen-bond-driven aggregation enhance modulus, strength, thermal resistance, and energy dissipation capability, while the continuous soft phase provides ductility, elastic recovery, low-temperature flexibility, and fatigue tolerance. Therefore, the macroscopic properties of polyurea coatings are not governed by a single structural component but arise from the synergistic interaction among hard-domain reinforcement, soft-phase deformation, and interfacial load transfer.

For long-term protective applications, the role of microphase structure extends beyond initial mechanical performance and directly affects water/oxygen/chloride transport pathways and crack propagation behavior. Moderate hard-domain aggregation improves thermal stability and dimensional retention, whereas excessive phase separation may induce local stress concentration and embrittlement. The continuous soft phase enhances flexibility but may also serve as a diffusion pathway for aggressive species. The interface between hard and soft phases simultaneously governs stress transfer and phase coordination and often becomes a site for damage accumulation under hygrothermal, salt spray, and cyclic loading conditions.

Therefore, structural design of polyurea protective coatings should not focus solely on high modulus, strength, or impact resistance. Instead, attention should be given to the stability of microphase architecture during long-term service. Hard-domain stability, soft-segment resistance to oxidation, hydrogen bond reconfiguration behavior, and interfacial integrity collectively determine barrier performance, adhesion retention, and service life.

2.3 Influence of Synthetic Routes on Coating Stability

The long-term performance of polyurea protective coatings is governed not only by molecular structure and microphase morphology, but also by the synthesis route and curing process. Different reaction pathways influence the formation kinetics of urea linkages, chain diffusion time, network homogeneity, phase development, and coating/substrate interface quality. These factors collectively determine the aging behavior of coatings under hygrothermal, UV, thermal-oxidative, salt spray, and mechanical loading conditions. From a durability perspective,

the synthesis route is not merely a method for constructing the polyurea network; it also defines the level of initial defects, barrier performance, and long-term stability. Variations in reaction kinetics and curing conditions can lead to differences in residual stress, interfacial integrity, and transport pathways for water, oxygen, and chloride ions, which ultimately govern coating degradation and adhesion retention during service.

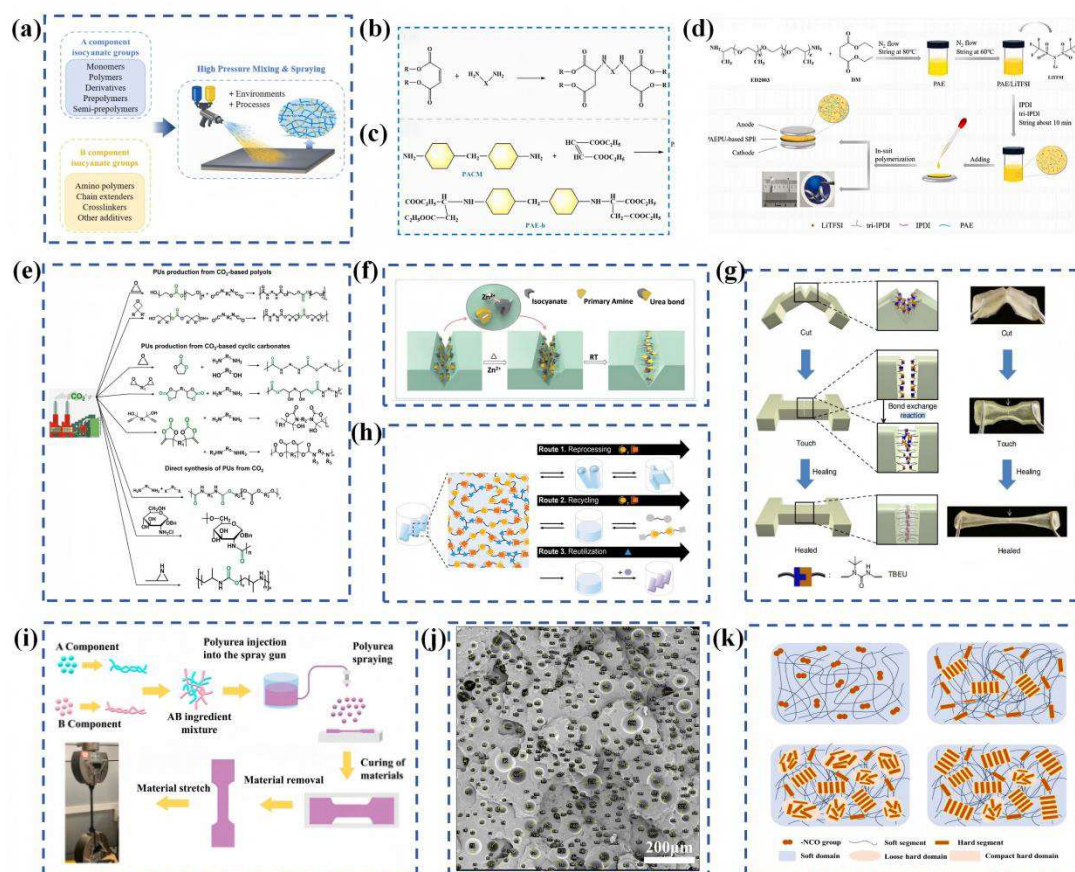


Fig. 4. (a) Conventional isocyanate-based two-component synthesis and rapid curing process of polyurea; (b) Synthetic route of polyurea [109]; (c) Preparation of polyurea elastomers [110]; (d) Synthesis of polyaspartic polyurea (PUA) [111]; (e) Representative pathways for CO₂-based polyurethane production [26]; (f) Self-healing mechanism in polyurea networks [125]; (g) Dynamic bond-mediated healing process [126]; (h) Covalent adaptable networks (CANs) enabling reprocessing and recyclability [124]; (i, j) Spray polyurea coating fabrication and application [133]; (k) Microphase-separated morphology of polyurea [134].

2.3.1 Conventional Isocyanate-Based Polyurea

Conventional isocyanate-based polyurea represents the most established synthesis route for polyurea protective coatings. It typically involves a two-component system, where diisocyanates or polyisocyanates serve as the A component and amine-terminated resins or polyamine chain extenders act as the B component. The rapid

addition reaction between isocyanate and amine groups leads to the formation of a crosslinked network dominated by urea linkages [59]. Owing to its high reactivity and extremely fast gelation kinetics, this system can cure rapidly at room temperature or even at lower temperatures, making it highly compatible with high-pressure two-component spray processes. As a result, it is widely used in waterproofing, anticorrosion, wear-resistant, and impact-resistant coatings. A typical two-component reaction and rapid film formation process is illustrated in Fig. 4(a).

The conventional isocyanate route offers broad formulation flexibility [103-105]. By adjusting the type of isocyanate, prepolymer molecular weight, structure of amine-terminated soft segments, and chain extenders, the hard-segment rigidity, soft-segment flexibility, crosslink density, and degree of microphase separation can be tailored. These structural variations directly affect modulus, strength, thermal resistance, mechanical performance, and impact resistance of the coating [106-108]. However, the fast reaction kinetics may also lead to insufficient mixing, incomplete substrate wetting, residual stress, and network heterogeneity. These initial defects can evolve into transport pathways for water, oxygen, and chloride ions under hygrothermal, salt spray, or fatigue conditions, promoting interfacial failure and crack initiation. In addition, the toxicity of isocyanate precursors and the irreversible nature of thermoset networks limit their sustainability and recyclability. Therefore, while conventional isocyanate-based polyurea remains the foundation of engineering applications, improvements in curing controllability, interfacial quality, and sustainability are still required.

2.3.2 Slow-Reaction Polyurea Systems

On the basis of conventional isocyanate-based systems, reducing the reactivity of the amine component is an effective strategy to improve curing uniformity and coating quality. Polyaspartic ester (PAE)-based polyurea represents a typical slow-reaction system. The sterically hindered secondary amine structure in PAE reduces the nucleophilicity of amine groups toward isocyanates, thereby extending pot life and application window.

Early studies [38] demonstrated that polyaspartic esters can react with aliphatic HDI trimers to form polyurea materials with improved weather resistance (Fig. 4b). Chen et al. [110] synthesized PAE-b via Michael addition between PACM and diethyl maleate, and further reacted it with H12MDI and amine-terminated polyethers to obtain polyurea elastomers (Fig. 4c). The resulting materials exhibited distinct microphase-separated structures and favorable mechanical performance. Lu et al. [111] further demonstrated that by adjusting the IPDI molar ratio and lithium salt concentration, the main-chain structure and crosslink density could be simultaneously regulated, enabling the construction of a PAE-based polyurethane (PUA) solid polymer electrolyte system (Fig. 4d). These results indicate that PAE structures provide advantages in processability and interfacial compatibility regulation.

From a curing kinetics perspective, the key advantage of PAE systems lies in extending the time window for chain diffusion, substrate wetting, and network rearrangement. Liu et al. [71] reported that, due to steric hindrance effects, the gel time of PAE-based coatings can be extended to approximately 30 min, and surface drying can still be achieved at $-10\text{ }^{\circ}\text{C}$. Edward P et al. [112] also pointed out that in steel protection applications, properly controlled application intervals can improve corrosion resistance. These findings suggest that a slower and controllable curing process helps reduce local crosslinking inhomogeneity, residual stress, and interfacial defects, thereby improving structural uniformity and long-term stability.

However, conventional spray-applied polyurea remains advantageous in applications requiring extremely rapid film formation and immediate service. In addition, ester groups introduced in PAE systems may introduce hydrolytic instability under hygrothermal conditions. Therefore, the significance of PAE polyurea lies not in replacing conventional systems, but in providing a kinetic regulation strategy to balance application window, interfacial quality, network homogeneity, and long-term durability.

2.3.3 Non-Isocyanate Polyurea

Non-isocyanate polyurea (NIPU/NIPUA) represents a key direction toward greener polyurea coating systems. This approach replaces toxic isocyanates with CO_2 utilization routes and alternative precursors such as cyclic carbonates, urea-based intermediates, and related monomers [113-116], thereby reducing raw material toxicity and enabling additional reactive sites for structural tuning, self-healing, and recyclability.

Among current approaches, the reaction between cyclic carbonates and polyamines is the most widely used route. Five- or six-membered cyclic carbonates undergo nucleophilic ring-opening with amines to form polymer networks containing hydroxyl, urea, or carbamate groups. Five-membered cyclic carbonate systems provide relatively high hydrogen-bond density but suffer from slow reaction kinetics, limited regioselectivity, and side reactions [117-120]. In contrast, six-membered or activated cyclic carbonates generally exhibit higher reactivity, improving network formation efficiency and mechanical performance [85-87].

Beyond cyclic carbonate chemistry, direct CO_2 -involved polymerization provides additional design flexibility for non-isocyanate polyurethane/polyurea systems. CO_2 can react with diamines, epoxides, or nitrogen-containing monomers to form linear or branched polymer structures with tunable molecular weight and network composition. For example, Cheng et al. [121] synthesized bicyclic carbonate intermediates from CO_2 and subsequently reacted them with diamines to produce polyhydroxy urethane structures with controllable molecular weight and architecture. Carre et al. [122] reported a solvent-free cyclic carbonate/diamine system, highlighting its potential for green processing. Łukaszewska et al. [123] showed that non-isocyanate polyurethane networks exhibit high

hydrophilicity and pronounced water uptake, indicating that dimensional stability and mechanical retention under hygrothermal conditions still require careful evaluation. Ou et al. [26] summarized various CO₂-based polyurethane synthesis routes, as shown in Fig. 4(e).

Overall, NIPU/NIPUA systems provide safer and more sustainable routes for polyurea coating design and enable the incorporation of hydroxyl, urea, carbamate structures, and dynamic sites. However, their practical application is still limited by reaction efficiency, molecular weight control, network integrity, and long-term water resistance. For protective coatings, the introduction of hydroxyl, ester, or carbamate groups may significantly alter water uptake behavior, hydrogen-bonding states, and hydrolysis sensitivity. Therefore, future studies should not only emphasize green synthesis advantages but also systematically evaluate barrier retention, adhesion stability, and service life under hygrothermal, thermal-oxidative, UV, salt spray, and multi-factor coupled aging environments.

2.3.4 Dynamic Polyurea Networks

Dynamic polyurea networks provide an alternative strategy to conventional irreversible thermoset systems. The key concept is the introduction of reversible dynamic bonds into the backbone or crosslinking points, enabling bond exchange, local reconfiguration, or topological rearrangement under thermal, photochemical, or specific chemical stimuli. This imparts self-healing, reprocessability, and recyclability while maintaining structural integrity.

Recently, hindered urea bonds (HUBs) and reversible urea exchange reactions have attracted considerable attention. Lyu et al. [124] constructed non-isocyanate covalent adaptable networks (CANs) based on dynamic HUBs, enabling reprocessing, chemical recycling, and reuse (Fig. 4(h)). Wang et al. [125] introduced Zn²⁺ catalysis to facilitate reversible dissociation and recombination of urea bonds under heating, enhancing self-healing and reprocessing capability (Fig. 4(f)). Hanze et al. [126] demonstrated dynamic repair of polyurethane-urea networks based on reversible dissociation and recombination of HUBs, supported by both schematic mechanisms and macroscopic healing behavior (Fig. 4(g)). In addition, hydrazone bonds [127], reversible Diels-Alder structures [128], and thiol radical association-dissociation systems [129-131] also provide useful molecular strategies for dynamic polyurea design.

For protective coatings, the value of dynamic networks lies not only in damage healing and recyclability, but also in crack closure, interfacial damage recovery, and local stress relaxation. However, excessive dynamicity may also lead to creep, reduced thermal stability, network relaxation, and deterioration in long-term mechanical retention. Therefore, dynamic polyurea design should not focus solely on healing efficiency. Instead, it is necessary

to consider bond exchange kinetics, service temperature window, medium stability, and post-aging property retention. Further evaluation is required regarding structural stability, healing efficiency decay, and reprocessing reliability under thermal-oxidative, hygrothermal, UV, salt spray, and fatigue aging conditions.

2.4 Curing Process, Initial Defects, and Interfacial Quality

The structural formation of polyurea protective coatings is governed not only by molecular composition but also by curing kinetics and processing conditions. Different curing regimes alter chain diffusion, substrate wetting, hydrogen-bonding assembly, and phase rearrangement time scales, thereby influencing network homogeneity, pore defects, residual stress, and coating/substrate interface adhesion. Rapid curing facilitates fast film formation during on-site application, but it also tends to preserve kinetically trapped, non-equilibrium structures. In contrast, slow or controlled curing provides additional time for chain rearrangement and interfacial wetting, which can improve structural uniformity.

2.4.1 Rapid Curing and Structural Heterogeneity

Spray polyurea represents one of the most typical processing routes for polyurea coatings, characterized by high-pressure impingement mixing, atomized spraying, and ultrafast gelation. In this process, component A (isocyanate prepolymer) and component B (amine-terminated resin) collide at high velocity in the spray gun mixing chamber, are immediately atomized, and rapidly undergo spreading, reaction, and preliminary film formation. Tripathi et al. [132] reported that the isocyanate-amine reaction exhibits extremely fast kinetics, with gelation typically occurring within tens of seconds. Zhang et al. [133] also described spray polyurea formation as a process involving high-temperature, high-pressure mixing and atomization of two reactive components (Fig. 4i).

From a structural evolution perspective, spray polyurea is a typical rapid curing system. Because the reaction rate often exceeds the rates of chain diffusion and phase rearrangement, gelation can occur before the system reaches thermodynamic equilibrium. As a result, parts of the structure are frozen in a kinetically controlled state. Li et al. [21] showed that hard segments form hydrogen-bonded physical crosslinking points dispersed within the soft matrix, and their evolution is governed by thermodynamic driving forces, hydrogen bonding, and chain mobility. Accordingly, the microphase structure of spray polyurea is strongly dependent on processing history.

Rapid curing may also lead to multiscale structural heterogeneity. Due to limited mixing and short reaction times, local regions may exhibit differences in conversion, non-uniform hard-domain distribution, or incomplete hydrogen-bonding assembly. Zhang et al. [133] further demonstrated that spraying temperature and pressure influence internal void formation and pore size distribution (Fig. 4j), indicating that processing conditions directly determine the initial defect state. Kang et al. [134] reported that hydrogen bonds evolve from disordered to ordered

states during curing, driving hard-domain formation and microphase separation (Fig. 4k).

Therefore, rapid curing is not only an advantage for processing efficiency but also a potential source of long-term durability variability. Non-uniform networks, voids, residual stress, and interfacial defects can modify water/oxygen/chloride transport pathways and promote interfacial failure and crack initiation under hygrothermal, salt spray, or fatigue conditions.

2.4.2 Slow Curing and Structural Uniformity

Compared with rapid spray curing, slow-curing systems provide extended reaction and flow time, allowing more sufficient chain diffusion, substrate wetting, and molecular rearrangement prior to gelation. As a result, hard-segment aggregation, hydrogen-bond formation, and microphase separation can proceed in a more thermodynamically favorable manner, reducing the structural heterogeneity commonly observed in fast-curing systems.

Under slow-curing conditions, hydrogen bonding between urea groups has sufficient time to form and reorganize, and hard segments gradually aggregate within the soft matrix, leading to more well-defined microphase-separated structures [62,135]. Compared with rapid curing systems, slow curing generally improves network homogeneity, enhances substrate wetting, and strengthens coating/substrate interface adhesion, while reducing local crosslinking heterogeneity and residual stress accumulation. These structural features are beneficial for long-term coating stability and durability.

However, slow curing does not necessarily guarantee superior structure. The final network is still influenced by reaction activity, system viscosity, film thickness, temperature gradients, and environmental humidity. Excessively slow or incomplete curing may lead to insufficient crosslink density, phase coarsening, or residual small-molecule entrapment, which can negatively affect mechanical retention, water resistance, and long-term protective performance. Therefore, the advantage of slow curing lies in providing sufficient time for diffusion, wetting, and phase rearrangement rather than simply minimizing reaction rate. For polyurea protective coatings, the key is to balance reaction completion, processing window, interfacial quality, and long-term durability.

2.4.3 Influence of Curing Rate on Performance and Stability

Different curing kinetics alter the formation pathway of polyurea networks and subsequently determine both initial structure and long-term stability. In rapid curing systems, the reaction rate exceeds the rates of chain diffusion and hydrogen-bond rearrangement, leading to kinetically trapped, heterogeneous microphase structures. In contrast, slow or controlled curing provides sufficient time for chain mobility, substrate wetting, and phase rearrangement, generally resulting in more uniform network structures [136,137]. Fig. 5 schematically illustrates

the differences in structural evolution under different curing kinetics. Rapid curing tends to generate kinetically frozen heterogeneous networks, whereas slow or controlled curing facilitates chain diffusion, hydrogen-bond reorganization, and microphase homogenization.

From a microstructural perspective, rapid curing limits hydrogen-bond assembly and hard-segment aggregation, leading to non-uniform hard-domain sizes, poorly defined soft/hard interfacial regions, and the presence of voids and localized defects [138]. These heterogeneous structures increase residual stress and stress concentration sites, which may evolve into pathways for aggressive species penetration and initiation sites for interfacial failure and crack propagation under thermal-oxidative, hygrothermal, salt spray, or fatigue aging conditions. In comparison, slow or controlled curing generally reduces local crosslinking heterogeneity and residual stress, improving network integrity and interfacial quality.

These structural differences are ultimately reflected in coating durability. Rapidly cured coatings may exhibit higher initial strength and enhanced energy dissipation capacity, but their kinetically frozen heterogeneous structure can reduce long-term property retention. Relatively uniform slow-cured networks are more favorable for barrier performance and environmental stability, although they may not be suitable for applications requiring instant film formation and immediate service. Therefore, the key design principle for polyurea coatings is not simply to maximize or minimize curing rate, but to achieve a balance among curing kinetics, processing window, structural uniformity, coating/substrate interface quality, and long-term protective performance.

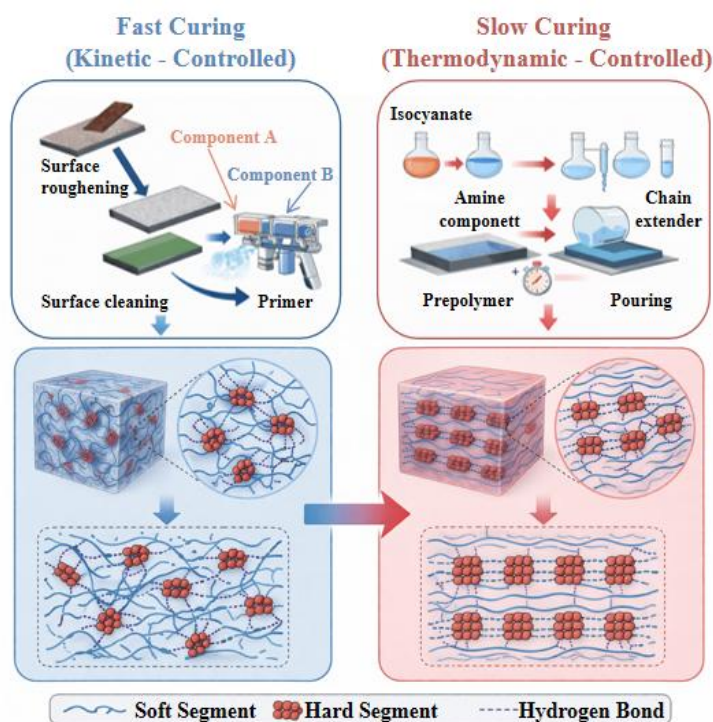


Fig. 5. Schematic illustration of curing kinetics-dependent structural evolution in polyurea.

3 Aging and Failure Mechanisms of Polyurea Protective Coatings

3.1 Damage and Energy Dissipation under Dynamic Loading

Polyurea protective coatings exhibit favorable energy dissipation and buffering capability under extreme dynamic loading conditions, including high-velocity impact, cavitation erosion, severe friction, and blast-induced shock. This performance is closely related to their phase-separated hard/soft segment architecture. Hard segments aggregate through urea-based hydrogen bonding to form nanoscale hard domains, while soft segments constitute a continuous flexible matrix. Together, they form a microphase-separated structure that enables load-bearing, deformability, and partial elastic recovery. Under dynamic loading, energy dissipation arises from the coupled contributions of soft-segment chain deformation, hard-domain load support, and reversible breaking/reformation of hydrogen bonds. Chain mobility in the soft phase accommodates large strain, while hard domains act as physical constraints that distribute stress and delay localized failure. Meanwhile, hydrogen bond dissociation and reformation within the hard phase provide an additional reversible energy dissipation pathway. For protective coating applications, the response under dynamic loading is not only relevant to instantaneous impact resistance but also governs residual damage, coating/substrate interface integrity, and subsequent environmental aging behavior. Microstructural damage accumulated during impact may modify transport pathways for water, oxygen, and chloride ions, thereby influencing long-term coating degradation under coupled mechanical and environmental conditions.

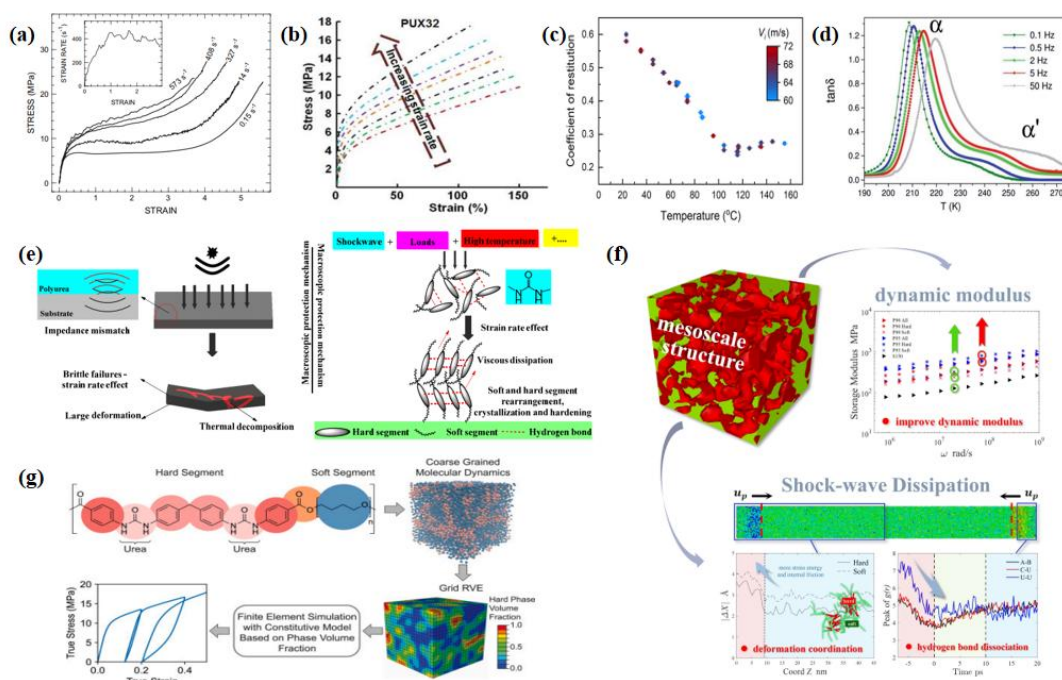


Fig. 6. (a) Stress-strain curve [139]; (b) Stress-strain curve [140]; (c) Maximum energy absorption capacity [141]; (d) Tan δ curve [142]; (e) Microphase-separated structure [57]; (f) Coarse-grained molecular dynamics simulation [41]; (g) Hard domains under loading conditions [42].

3.1.1 Mechanical Response under High-Strain-Rate Loading

Under impact, blast, and high-velocity penetration conditions, polyurea exhibits pronounced strain-rate sensitivity, with mechanical response increasing with loading rate. This rate-dependent behavior provides the basis for its transient load-bearing capacity and impact energy dissipation. However, from a long-term service perspective of protective coatings, residual stress and microstructural damage generated under high-rate loading may also influence subsequent fatigue response and environmental aging.

Previous studies have established the dynamic mechanical behavior of polyurea over a wide range of strain rates. As shown in Fig. 6(a), Roland et al. [139] reported that within the high-strain-rate regime of 10^2 - 10^3 s⁻¹, the stress-strain curves shift upward and the initial modulus increases significantly, indicating a typical strain-rate-induced stiffening behavior. Meanwhile, the increase in yield strength and reduction in failure strain suggest a transition from a ductile response to a more rigid-like behavior under rapid loading. Tripathi et al. [140] further demonstrated that in the low-to-intermediate strain-rate range of 10^{-4} - 10^{-1} s⁻¹, increasing strain rate still leads to elevated stress levels (Fig. 6(b)), confirming that rate-hardening behavior persists across several orders of magnitude.

Mechanistically, strain-rate sensitivity originates primarily from the viscoelastic nature of polyurea and the relaxation behavior of polymer chains. At low strain rates, soft segments have sufficient time for molecular relaxation and rearrangement, and the material behaves in a rubbery state. At high strain rates, the loading time becomes much shorter than the relaxation time of polymer chains, restricting segmental mobility and driving the system toward a glass-like response, thereby increasing stiffness and strength. Meanwhile, the hydrogen-bonding network cannot reorganize in time under rapid loading, and its rupture and delayed reformation become important energy dissipation pathways.

At even higher strain rates or under impact loading, strain-rate-induced dynamic vitrification may occur. As shown in Fig. 6(c), Sun et al. [141] reported that polyurea exhibits a peak energy absorption capacity at specific temperatures, which is associated with the matching between molecular relaxation time and loading time scale during impact. This indicates that energy dissipation is governed not only by viscoelasticity but also by dynamic phase transition behavior. Reinecker et al. [142] further identified two distinct relaxation peaks in the tan δ spectrum (Fig. 6(d)), corresponding to α relaxation of free soft segments and a constrained α' (or α_2) relaxation

near hard-segment interfaces. The α_2 relaxation is associated with restricted chain mobility within microphase-separated hard domains and exhibits significantly slower dynamics than free-chain relaxation. When the loading rate approaches the relaxation time scale of these constrained segments, enhanced energy dissipation is observed.

Therefore, strain-rate-induced stiffening and dynamic vitrification enhance the resistance of polyurea coatings to instantaneous impact, but they may also leave residual stress and localized deformation at soft/hard phase interfaces. Under repeated impact or cyclic dynamic loading, these regions may progressively evolve into fatigue cracks and interfacial damage, ultimately affecting adhesion retention and barrier performance.

3.1.2 Microphase Structure and Hydrogen Bond Evolution

The outstanding impact resistance and energy dissipation capability of polyurea originate from its dynamic microphase-separated structure [57,41]. Due to thermodynamic incompatibility between soft and hard segments, a two-phase morphology forms, consisting of a flexible soft matrix and hard segments aggregated into hard domains via hydrogen bonding. As shown in Fig. 6(e), Toader et al. [57] demonstrated that hard domains and the surrounding soft phase jointly form a typical microphase-separated architecture, where energy dissipation under impact is achieved through dynamic hydrogen-bond responses and interfacial wave scattering. This “hard-domain reinforcement-soft-phase buffering” architecture provides the structural basis for efficient energy dissipation under dynamic loading.

At low strain rates, the hydrogen-bond network within hard segments remains relatively stable, and the material exhibits a rubber-like response. Under high-strain-rate impact, however, the loading duration is significantly shorter than the relaxation time of chain segments, preventing timely reorganization of hydrogen bonds. As a result, ordered hydrogen bonds within hard domains preferentially dissociate, leading to local relaxation and partial disintegration of hard-domain structures. Yao et al. [143] reported that hydrogen bond dissociation and reformation occur during impact, effectively dissipating energy while delaying crack propagation and stress localization. Using coarse-grained molecular dynamics, Yao et al. [41] further showed that hydrogen bonds in hard segments undergo pronounced rupture during impact, accompanied by local structural perturbation and increased internal dissipation, thereby promoting energy dissipation and stress attenuation (Fig. 6(f)).

Meanwhile, hard domains are not static during dynamic loading but undergo continuous structural evolution. Under impact stress, pre-existing hard domains may experience local deformation, fragmentation, rearrangement, and re-aggregation, resulting in reorganization of microphase interfaces. In situ SAXS and molecular simulation studies [144] have revealed changes in hard-domain spacing, interfacial reorientation, and local phase

rearrangement during dynamic loading, indicating strong adaptive behavior of the microphase structure. Yang et al. [42] further reported that hard domains may undergo fibrillation, reorientation, and reassembly under loading, thereby influencing stress transfer pathways and energy dissipation mechanisms, as shown in Fig. 6(g).

From a long-term service perspective, microphase structure and hydrogen bonding evolution govern not only instantaneous energy dissipation but also post-impact structural recovery. Higher hard-segment aggregation enhances stiffness and load-bearing capacity; however, excessive phase separation may induce stress concentration and interfacial embrittlement. Moderate microphase separation provides a balanced structure, enabling cooperation among hard-domain reinforcement, soft-phase deformation, and hydrogen-bond-mediated dissipation. Under repeated impact or cyclic loading, progressive accumulation of hard-domain fragmentation, hydrogen bond rupture, and interfacial relaxation may create pathways for crack propagation, aggressive species penetration, and interfacial failure.

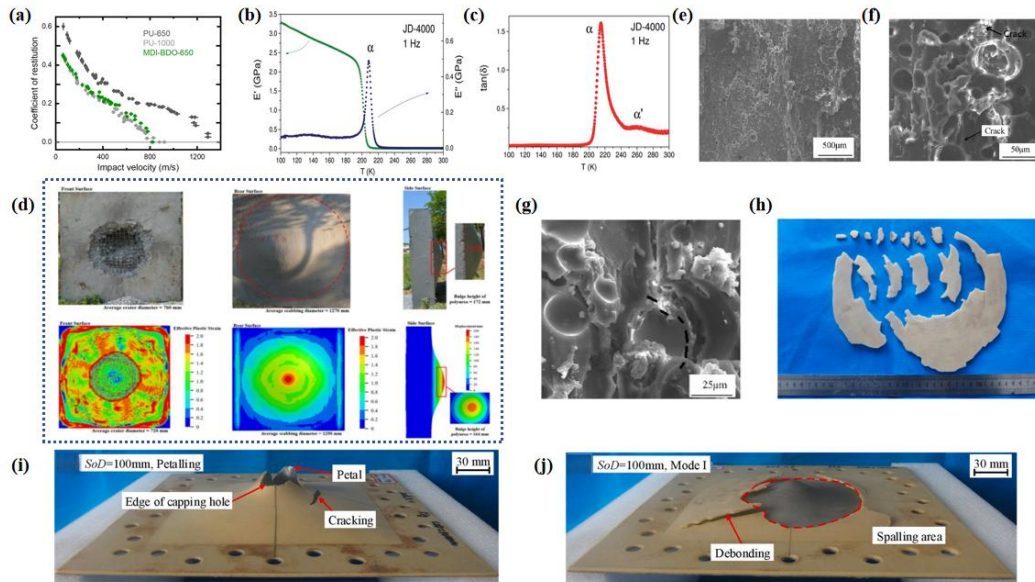


Fig. 7. (a) Coefficient of restitution variation curve [145]; (b, c) DMA results [142]; (d) Blast resistance performance [149]; (e-g) SEM images [150]; (h-j) Polyurea under extreme loading conditions [154].

3.1.3 Impact Energy Dissipation Mechanism

The outstanding impact resistance of polyurea arises from a multiscale energy dissipation mechanism spanning molecular, mesoscale, and macroscopic levels. Under dynamic impact loading, soft segments are first stretched and oriented, dissipating part of the input energy through viscoelastic deformation. Meanwhile, hydrogen-bonded networks within the hard segments undergo continuous dissociation and reformation, providing an additional pathway for energy consumption. Roland et al. [139] were among the first to attribute this strain-rate sensitivity to restricted chain mobility and the rapid response of hydrogen-bond networks under high-rate loading.

Subsequently, Sun et al. [145], based on ultrafast particle impact experiments and spectroscopic analysis, further demonstrated that the dynamic stiffening behavior of polyurea is closely related to hydrogen bonding interactions and chain dynamics. Under high-frequency impact conditions, suppressed segmental relaxation leads to a pronounced increase in transient stiffness, as shown in Fig. 7(a). Recent multiscale simulation studies have further indicated that glassy hard domains may undergo fibrillation, orientation evolution, and local phase transitions during dynamic loading, thereby altering stress transfer and energy dissipation pathways. Yang et al. [42] reported that the dynamic evolution of hard domains and reconstruction of microphase interfaces constitute key structural bases for efficient impact energy dissipation in polyurea systems.

With increasing impact intensity, pre-existing hard domains may undergo local deformation, fibrillation, fragmentation, and re-aggregation, accompanied by dynamic rearrangement of microphase interfaces, which collectively generate new stress redistribution pathways. Grujicic et al. [146,147] demonstrated through mesoscale simulations that hard-segment aggregates significantly modify shock wave propagation, reduce local stress concentration, and enhance attenuation of impact waves. In addition, Reinecker et al. [142] identified a pronounced α' relaxation process in constrained chain regions near microphase interfaces using DMA measurements, corresponding to a secondary glass transition. This indicates that cooperative chain dynamics at interfacial regions play a critical role in dynamic energy dissipation, as shown in Fig. 7(b,c).

At the macroscopic scale, polyurea further dissipates impact energy through large deformation, acoustic impedance mismatch, and wave reflection at interfaces [27,148]. Under blast and high-velocity impact conditions, polyurea transforms localized concentrated loading into distributed stress fields through a coupled mechanism involving chain-level dissipation, hard-domain reorganization, and interfacial stress redistribution. Experimental and numerical studies have shown that polyurea coatings significantly enhance shock wave attenuation and blast resistance of structures, as illustrated in Fig. 7(d) [149].

It should be noted that impact energy dissipation does not imply full structural recovery. Chain orientation, hydrogen bond rupture, hard-domain reorganization, and interfacial deformation may leave residual damage, which can accumulate under repeated impact or cyclic loading. For protective coatings, post-impact barrier performance, coating/substrate interface integrity, and long-term retention of mechanical properties should therefore be considered alongside instantaneous impact resistance.

3.1.4 Damage Evolution and Failure after Impact

Although polyurea exhibits excellent dynamic energy dissipation under high strain-rate conditions, complex damage evolution and failure processes still occur under extreme impact loading. In the early stage of impact, local

stress concentration preferentially induces cavitation and crazing near soft/hard interfacial regions, which subsequently evolve into microcracks and localized damage zones. Liu et al. [150] used SEM and micro-CT analysis to show that high strain-rate compression leads to extensive cavitation, crazing, and microcrack formation in polyurea, accompanied by clear crack propagation behavior, as shown in Fig. 7(e-g). These results indicate that the progressive coalescence of cavities and crazes represents an initial stage of damage evolution.

With increasing impact severity, localized plastic deformation becomes increasingly confined, leading to pronounced shear localization. Grujicic et al. [151] demonstrated through molecular-scale and mesoscale simulations that dynamic rearrangement of hard domains and stress concentration under high-velocity impact promote shear band formation and local instability. Meanwhile, Choi et al. [152,153] reported that cavitation jet impact induces significant localized heat accumulation in polyurea, and the resulting thermo-mechanical coupling activates chain mobility and local thermal softening, thereby accelerating structural degradation and damage propagation. As damage evolves, microcracks preferentially propagate along soft/hard interfaces, accompanied by interfacial debonding and crack coalescence, eventually leading to through-thickness failure.

Chen et al. [154] further observed pronounced interfacial delamination, fragmentation, and spalling under extreme loading conditions, as shown in Fig. 7(h-j). Under localized blast loading, coating detachment and fragmentation occur at the coating/substrate interface, while spalling behavior further compromises structural integrity and impact resistance. These impact-induced defects have important implications for long-term durability. Cavitation, crazing, shear bands, and interfacial debonding can act as defect precursors under subsequent hygrothermal, salt spray, or fatigue environments, accelerating water/oxygen/chloride transport, weakening hydrogen-bond networks, and promoting crack growth. Therefore, residual damage after impact should be considered a critical factor in lifetime prediction of polyurea protective coatings.

3.2 Thermal-Oxidative and UV Aging Mechanisms

3.2.1 Thermal-Oxidative Aging and Chain Scission

The performance degradation of polyurea under long-term thermal-oxidative environments is primarily associated with chain scission induced by oxidation, weakening of the hydrogen-bonding network, and deterioration of the microphase structure. Che et al. [16], in a marine atmospheric aging study, observed pronounced changes in characteristic functional groups such as N-H, C=O, and C-O-C with increasing exposure time, indicating continuous oxidative reactions and progressive degradation of hydrogen-bonding interactions. Concurrently, surface yellowing, roughening, and microcrack propagation were observed, as shown in Fig. 8(a).

Mayer-Trzaskowska et al. [19] further combined FTIR, TGA, and surface morphology analyses and reported

that thermal aging continuously promotes surface structural degradation and reduces interfacial stability in polyurea/polyurethane-urea systems. Their morphological observations revealed evident crack propagation, localized embrittlement, and interfacial damage after aging, as shown in Fig. 8(b), indicating a gradual loss of stability in the original microphase-separated structure.

In addition, Yang et al. [42], based on multiscale simulations and SAXS correlation analysis, demonstrated that the dynamic performance of polyurea is strongly governed by the stability of hard-segment aggregates. Under sustained thermal exposure, the loosening of hard domains and evolution of microphase interfaces progressively destabilize the “hard-domain reinforcement-soft-phase dissipation” architecture, thereby reducing energy dissipation capability and long-term service stability.

From a broader perspective, Xie et al. [155], in a review on polyurethane elastomer degradation, further highlighted that elevated temperatures enhance oxygen diffusion and chain mobility, accelerating radical oxidation reactions. This ultimately leads to chain scission, degradation of crosslinked networks, and loss of microstructural integrity. Therefore, thermal-oxidative aging of polyurea coatings can be interpreted as a coupled process involving chain oxidation, hydrogen-bond weakening, and microphase structural degradation.

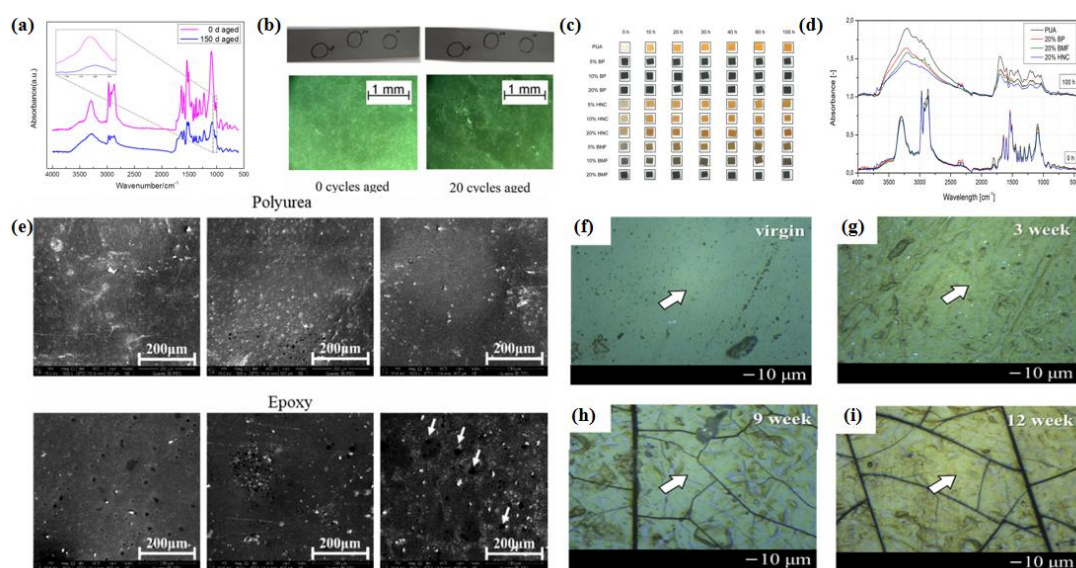


Fig. 8. (a) FTIR spectra [16]; (b) Comparison diagram [19]; (c, d) Aging tests [156]; (e) SEM image [157]; (f-i) Optical microscopy images [158].

3.2.2 UV Aging and Surface Failure

Polyurea coatings undergo pronounced photo-oxidative degradation under long-term UV irradiation, which originates from UV-induced chain scission, free-radical oxidation reactions, and progressive deterioration of the surface structure. Barczewski et al. [156], in an accelerated UV aging study of polyurea, reported that with

increasing UV exposure time, the coating surface gradually exhibited yellowing, roughening, and microcrack propagation, accompanied by surface embrittlement and an increase in localized defects, as shown in Fig. 8(c,d).

FTIR analysis further confirmed that UV irradiation continuously induces photodegradation of both urea linkages and soft-segment structures, leading to evident variations in characteristic groups such as N-H and C=O. These changes indicate a progressive destabilization of the hydrogen-bonding network within the coating. As the original network is disrupted, the structural integrity of the near-surface region is gradually weakened.

Wang et al. [157], based on UV-condensation aging experiments, further demonstrated that UV exposure significantly increases the oxidation level of the polyurea surface, leading to the formation of an oxidized and embrittled surface layer. SEM observations revealed the progressive development of surface voids, defects, and heterogeneous interfacial regions, while FTIR results showed a continuous increase in carbonyl-related oxidation products, as shown in Fig. 8(e). Due to the modulus mismatch between the oxidized surface layer and the underlying flexible matrix, stress tends to concentrate at the near-surface region, thereby promoting crack initiation and propagation. In addition, aromatic polyureas, owing to the higher UV absorption capability of benzene rings, generally exhibit more severe yellowing and surface degradation.

Kuwashiro et al. [158], based on a coupled photo-oxidation and nano-mechanical study, further revealed that long-term UV irradiation not only induces surface oxidation and chain scission, but also alters local hydrogen-bonding structures and modulus distribution. Optical microscopy and nanoindentation results showed an increase in surface crack density and a localized increase in modulus after UV aging (Fig. 8(f-i)). This indicates that UV exposure gradually embrittles the surface layer and reduces its resistance to crack propagation. For outdoor protective coatings, such surface cracking compromises barrier integrity and increases the probability of water, oxygen, and corrosive species ingress into the bulk coating.

3.2.3 Thermo-Oxidative-UV Coupled Aging

In practical service environments, polyurea coatings are often exposed simultaneously to heat, oxygen, and UV irradiation, resulting in coupled aging behavior characterized by synergistic degradation. Xie et al. [155] reported that polyurethane/polyurea elastomers undergo typical free-radical photo-oxidative chain reactions under thermo-oxidative-UV conditions, including hydroperoxide formation, carbonyl accumulation, and chain scission. Elevated temperature further accelerates oxygen diffusion and radical mobility, thereby enhancing surface oxidation and promoting bulk structural degradation.

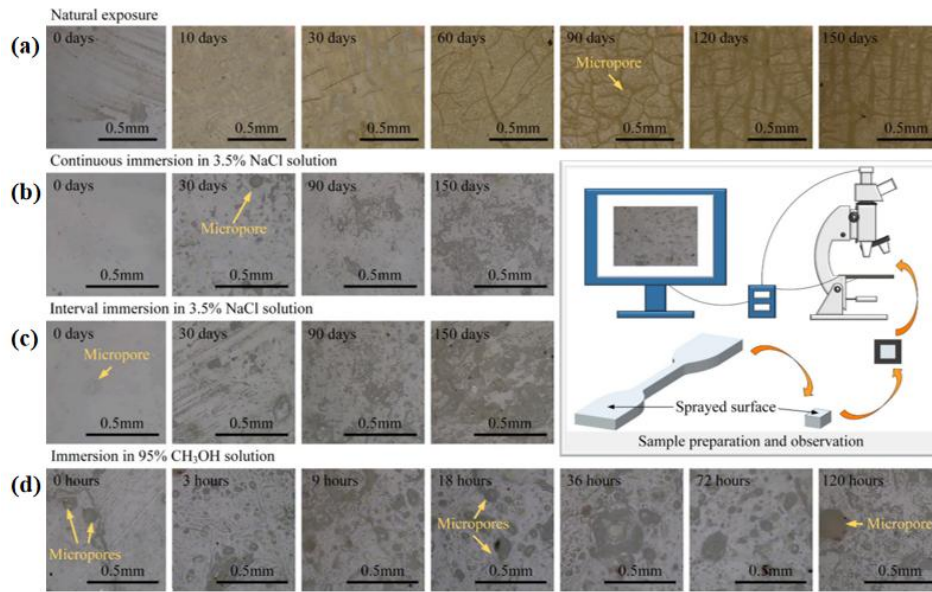


Fig. 9. Comparison of environmental aging [159]

Additionally, Zhang et al. [159] investigated blast-resistant polyurea coatings and found that after exposure to natural weathering, salt spray, and hygrothermal aging, the coatings exhibited pronounced yellowing, embrittlement, and surface crack propagation. Meanwhile, both tensile properties and impact resistance decreased significantly, as shown in Fig. 9. These results indicate that thermal, oxidative, and UV-related factors collectively degrade the soft-segment architecture, hydrogen-bonding network, and microphase morphology of polyurea, driving the coating from a ductile, energy-dissipating state toward a brittle failure mode.

Accordingly, failure of polyurea protective coatings under coupled thermo-oxidative and UV environments cannot be attributed to a single photodegradation or thermal oxidation pathway. Instead, it results from the combined effects of surface oxidation, chain scission, hydrogen-bond weakening, microphase relaxation, and crack propagation. As oxidation-induced brittle layers and surface cracks develop, both barrier performance and adhesion retention gradually deteriorate, leading to an increased risk of interfacial failure under hygrothermal, salt spray, or corrosive exposure conditions.

3.3 Hygrothermal and Marine-Induced Interfacial Degradation

3.3.1 Water Diffusion and Chain Rearrangement

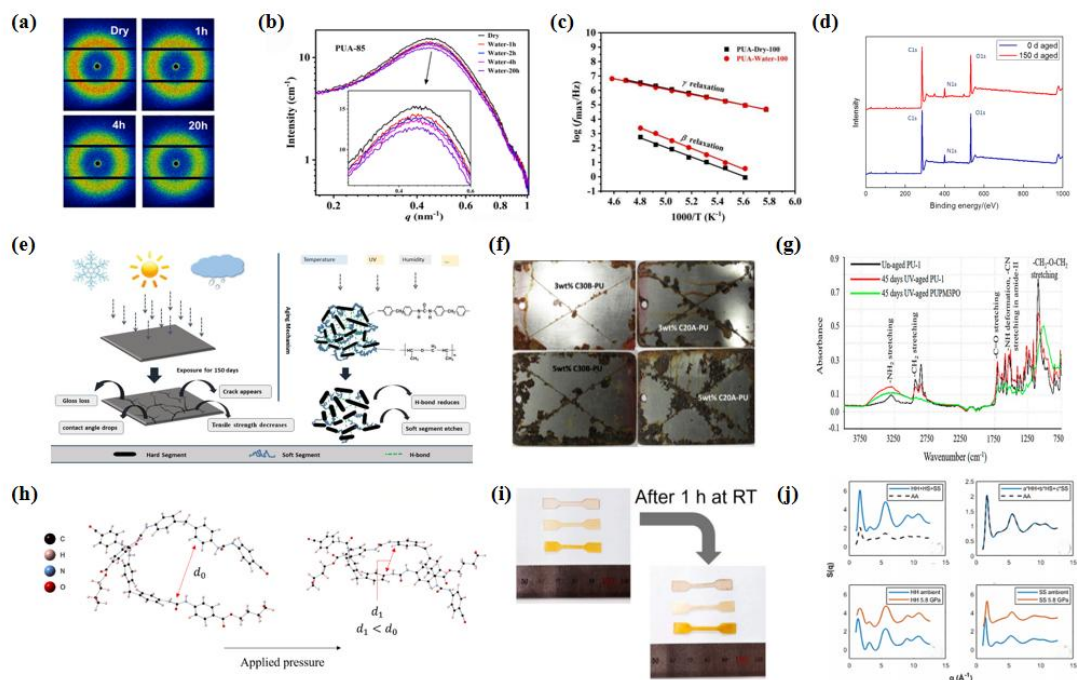


Fig. 10. (a, b) SAXS patterns [18]; (c) Relationship between the maximum frequency and (1000/T) [18]; (d) XPS spectra [16]; (e) Schematic mechanism diagram [16]; (f) Salt spray corrosion test [160]; (g) FTIR spectra [17]; (h) Depiction of interchain spacing as indicated by the FSDP [164]; (i) Comparison of cyclic tensile tests and room-temperature resting conditions [165]; (j) Molecular dynamics simulation [166].

Polyurea coatings undergo water uptake and structural rearrangement under hygrothermal conditions, which is primarily driven by continuous disruption of hydrogen-bonding networks and microphase-separated morphology by water molecules. Song et al. [18], using molecular dynamics simulations combined with SAXS analysis, reported that water molecules preferentially migrate into the soft/hard phase interfacial regions and free-volume domains. They competitively interact with urea groups, weakening the original hydrogen-bonding network within hard segments, as shown in Fig. 10(a,b). With increasing water uptake, the aggregation of hard segments becomes progressively loosened, accompanied by degradation of the microphase interface and pronounced plasticization of polymer chains.

Further DRS analysis indicated that the β -relaxation process is significantly enhanced after moisture absorption, demonstrating that water diffusion increases local chain mobility and facilitates segmental rearrangement and interfacial relaxation, as shown in Fig. 10(c). Continuous water penetration also induces local swelling and an increase in intermolecular spacing, resulting in a reduction in storage modulus and a decay in dynamic energy dissipation capability.

Che et al. [16], in a marine environmental aging study, further observed that hygrothermal exposure

accelerates surface crack initiation and microphase degradation in polyurea coatings, accompanied by yellowing, softening, and interfacial embrittlement, as shown in Fig. 10(d). With prolonged water ingress, the original “hard-domain reinforcement-soft-phase dissipation” architecture becomes unstable, leading to a progressive loss of long-term service stability. Overall, hygrothermal degradation of polyurea coatings can be understood as a coupled process involving water diffusion, hydrogen-bond weakening, microphase relaxation, and interfacial damage evolution.

3.3.2 Salt Spray Corrosion and Interfacial Degradation

In marine and salt spray environments, polyurea coatings are continuously exposed to chloride (Cl^-) penetration, hygrothermal cycling, and atmospheric corrosion, resulting in progressive degradation of interfacial stability and microphase integrity. Che et al. [16] reported that after salt spray exposure, polyurea coatings exhibited pronounced yellowing, surface roughening, and crack propagation, along with mechanical property deterioration and weakened hydrogen-bonding interactions, as shown in Fig. 10(e). Prolonged aging leads to progressive relaxation of the microphase-separated structure and a marked reduction in interfacial stability.

Verma et al. [160] further demonstrated through salt spray corrosion tests that aggressive species can diffuse along intrinsic defects and interfacial regions, inducing localized swelling, blistering, and interfacial roughening, as shown in Fig. 10(f). FTIR results confirmed a gradual reduction in characteristic N-H and C=O peak intensities after long-term exposure, indicating continuous disruption of the hydrogen-bonding network by chloride ingress.

Mayer-Trzaskowska et al. [19], in a study on polyurethane/polyurea coating degradation, reported that NaCl exposure reduces coating adhesion strength and promotes surface cracking and interfacial delamination. With continued chloride penetration, hydrated interfacial layers or localized corrosion zones may form at the coating/substrate interface, ultimately leading to adhesion loss and coating failure. Therefore, salt spray degradation should be understood not only as polymer aging, but as a coupled process involving chloride transport, barrier breakdown, interfacial delamination, and underfilm corrosion.

3.3.3 Fatigue and Environment-Load Synergistic Failure

In long-term service, polyurea coatings are often subjected to cyclic loading combined with hygrothermal and salt spray exposure, resulting in pronounced environment-fatigue synergistic failure behavior [161,162]. Pal et al. [17] found through FTIR and mechanical analysis that environmental exposure weakens hydrogen-bonding networks and hard segment structures, promoting microcrack propagation and chain scission, as shown in Fig. 10(g). Under cyclic loading, stress progressively concentrates at soft/hard phase interfaces, accelerating interfacial debonding and structural instability.

The key feature of synergistic degradation lies in defect amplification. Hygral and saline environments induce plasticization, swelling, hydrogen-bond weakening, and adhesion loss, while cyclic loading drives these weakened regions into cracks, voids, or interfacial separation zones. Once cracks coalesce or continuous transport pathways form, water, oxygen, and Cl^- ions can more rapidly reach the substrate surface, leading to severe underfilm corrosion and coating failure. Therefore, the service life of polyurea coatings under complex environments depends not only on intrinsic material stability, but also on the retention of barrier integrity and interfacial robustness under fatigue loading.

3.4 Structural Damage under Extreme Environments

3.4.1 Low-Temperature Embrittlement and Chain Freezing

At reduced temperatures, segmental mobility of the soft phase in polyurea is significantly restricted, leading to a pronounced glassy response [27,163]. Sun et al. [141] demonstrated via temperature-controlled high-velocity particle impact tests that the impact response of polyurea is closely related to the constrained α_2 relaxation of soft segments. As temperature decreases, chain relaxation kinetics slow dramatically, and the material transitions from a rubbery state to a glass-like response.

Meanwhile, low temperature further reduces free volume and chain mobility. Eastmond et al. [164], using in-situ X-ray scattering, observed that decreasing temperature leads to reduced free volume and suppressed segmental rearrangement, while locally ordered structures remain relatively stable, as shown in Fig. 10(h). Macroscopically, Zhou et al. [165] reported that soft segments gradually lose flexibility at low temperature, while hydrogen-bonded hard domains dominate the mechanical response, resulting in increased strength but reduced elongation at break. Under repeated impact or cyclic loading, stress concentration is more likely to develop at soft/hard interfaces, promoting crack initiation and propagation, as shown in Fig. 10(i).

For protective coatings, low-temperature embrittlement is not only associated with reduced mechanical performance but also with increased crack susceptibility and interfacial damage. Reduced deformability of the soft phase enhances stress localization at both soft/hard interfaces and coating/substrate interfaces, leading to microcrack growth under mechanical loading. Therefore, low-temperature failure is primarily governed by chain freezing, loss of toughness, interfacial stress concentration, and barrier deterioration.

3.4.2 Structural Evolution under High Pressure

Deep-sea hydrostatic pressure alters the microphase structure of polyurea coatings. Eastmond et al. [166], using in-situ energy-dispersive X-ray diffraction (EDXD) combined with molecular dynamics simulations, found that increasing pressure up to ~6 GPa causes a continuous shift of the first diffraction peak toward lower scattering

distances, indicating reduced spacing between hard domains. Further analysis revealed that pressure mainly compresses inter-domain spacing, while internal hard-domain structure remains relatively stable (Fig. 10(j)).

The reduction in free volume restricts chain mobility and increases material density, potentially enhancing stiffness. For deep-sea protective coatings, such pressure-induced densification may reduce certain types of species transport, while simultaneously altering interfacial stress distribution and energy dissipation behavior [167]. Under combined conditions of low temperature, seawater exposure, or mechanical loading, pressure-induced microphase rearrangement may further affect adhesion retention and crack evolution. Therefore, coating stability under high pressure should be evaluated in terms of microphase structure, interfacial state, and seawater transport simultaneously.

3.4.3 Radiation and Atomic Oxygen-Induced Damage

Radiation exposure affects color, surface morphology, and local mechanical stability of polyurea coatings. Guo et al. [58] investigated γ -ray irradiation effects and observed progressive color transition from light yellow to deep red with increasing dose, accompanied by an increase in brittle regions in cross-sections, as shown in Fig. 11(a). This behavior was attributed to irradiation-induced oxidation and embrittlement of soft segments, while hard segments remained relatively stable. FTIR analysis showed minimal changes in main functional groups, indicating limited bulk chemical reconstruction, although local damage accumulation and mechanical degradation still occurred.

In addition to radiation, atomic oxygen (AO) is a dominant degradation factor for polymers in low Earth orbit. Jung et al. [168], based on ReaxFF molecular dynamics simulations, reported that highly reactive atomic oxygen impacts polymer surfaces at velocities of ~ 7.4 km/s, continuously driving surface oxidation reactions and producing volatile species such as CO and H₂O, resulting in mass loss and surface erosion, as shown in Fig. 11(b).

Overall, degradation of polyurea coatings in space environments is mainly governed by radiation-induced soft-segment embrittlement, surface oxidation, and atomic oxygen erosion. These processes reduce surface integrity and accelerate crack formation and barrier failure. To improve long-term space durability, surface protection strategies such as POSS, SiO₂, siloxane, or ceramic-forming fillers may be introduced to enhance resistance against irradiation and atomic oxygen attack.

3.5 Synergistic Failure under Multi-Factor Environments

3.5.1 Temperature-Load Coupled Damage

The dynamic response of polyurea is not only strain-rate dependent but also highly sensitive to temperature. Roland et al. [139] reported that yield stress and modulus increase significantly with strain rate, showing a typical

strain-hardening behavior under high-rate loading, as shown in Fig. 11(c). This is attributed to restricted chain relaxation, which drives the material toward a glass-like response.

Liu et al. [169], using SHPB tests, further showed that compressive strength increases with strain rate (1400-5700 s⁻¹), while increasing temperature from 20 °C to 80 °C significantly reduces load-bearing capacity, as shown in Fig. 11(d-f). These results indicate that strain-rate strengthening and thermal softening jointly govern the dynamic mechanical response.

Sun et al. [141] further demonstrated that polyurea exhibits a pronounced energy absorption peak at a specific temperature range under high-velocity impact, attributed to a dynamic glass transition under coupled thermal and loading time scales, as shown in Fig. 11(g). This suggests that maximum energy dissipation occurs when the loading time scale matches the chain relaxation time.

Therefore, thermo-mechanical coupling should not be interpreted solely in terms of instantaneous strength. Temperature governs chain relaxation and hydrogen-bond stability, while mechanical loading drives deformation and crack evolution. Their coupling determines damage accumulation during impact, fatigue, and high-temperature service.

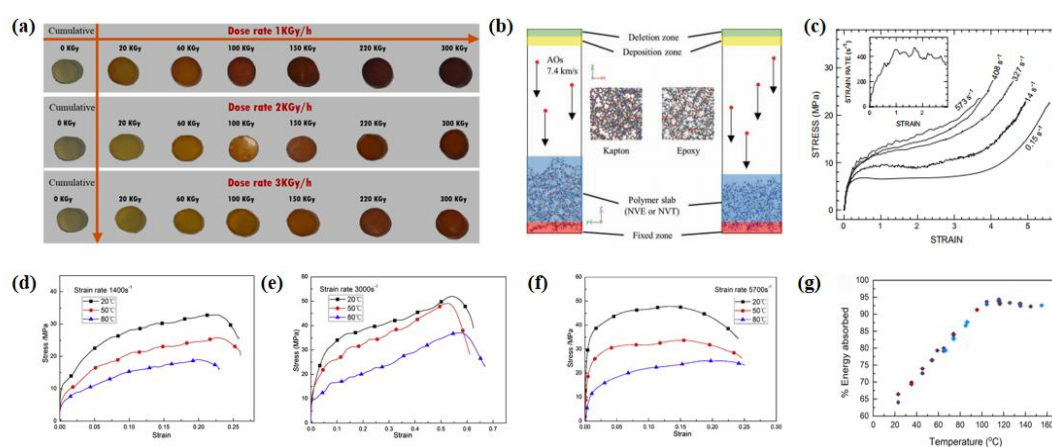


Fig. 11. (a) Effect of γ -radiation on polyurea coatings [58]; (b) Molecular dynamics simulation [168]; (c) Stress and strain [139]; (d-f) Variation of compressive strength with strain rate [169]; (g) Variation of energy percentage with temperature [141].

3.5.2 Multi-Factor Aging and Lifetime Prediction

In practical service environments, polyurea coatings are simultaneously exposed to temperature, moisture, mechanical stress, and aggressive species, leading to coupled degradation behavior. Peng et al. [170], in a study on polyurea waterproofing coatings, reported that the combined effects of temperature and water exposure continuously reduce the adhesion strength between polyurea and concrete substrates, accompanied by a transition

in failure mode from interfacial debonding to cohesive failure within the polyurea layer. With increasing aging time, interfacial integrity progressively deteriorates, resulting in continuous loss of service performance.

In addition, Yang et al. [42], through a combined molecular dynamics and finite element analysis, demonstrated that macroscopic mechanical degradation is closely linked to microphase evolution. Under accumulated deformation and environmental exposure, hard-segment aggregates gradually fracture, while soft/hard interfacial regions undergo continuous rearrangement. This structural evolution ultimately leads to reduced energy dissipation capacity and mechanical stability.

Fig. 12 can be used to summarize the cross-scale failure process of polyurea protective coatings under multi-factor environments. Water, oxygen, chloride ions, and UV irradiation initially weaken hydrogen-bonding interactions and disrupt ordered hard-segment packing. Subsequently, oxidative scission of soft segments, interfacial relaxation, and reduced chain entanglement density lead to diminished toughness and impaired load transfer capability. Finally, these microscale defects evolve into macroscopic cracks, interfacial debonding, and coating failure. Therefore, lifetime prediction of polyurea coatings should not rely on a single aging indicator. Instead, it should integrate structural evolution, adhesion retention, barrier performance degradation, and crack propagation behavior. Future efforts should combine aging experiments, in-situ characterization, multiscale simulations, and field service data to establish a reliable lifetime prediction framework under multi-factor coupled environments.

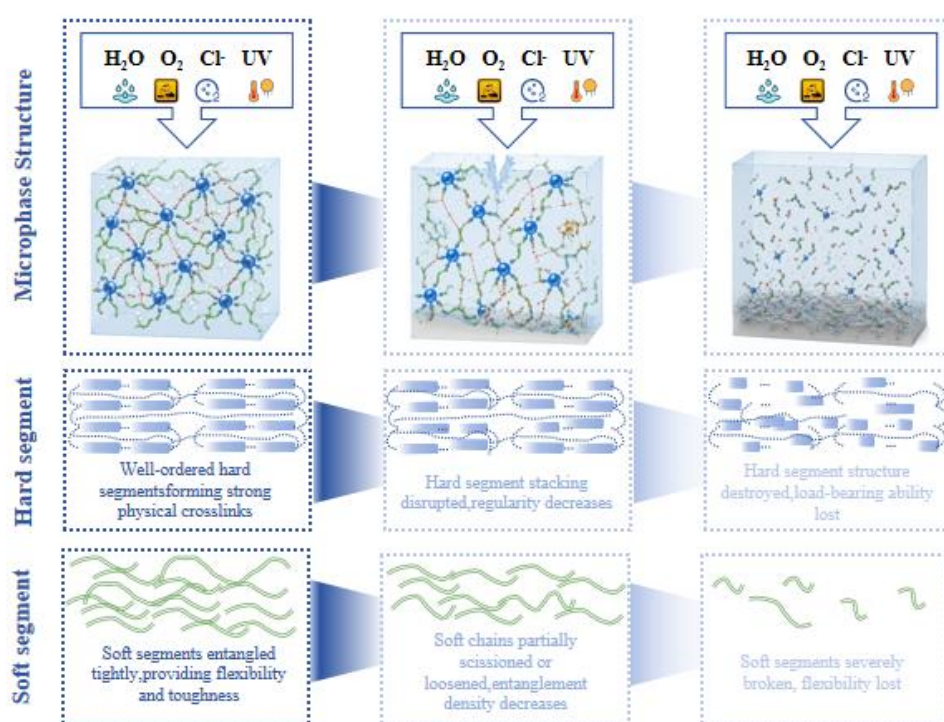


Fig. 12. Schematic illustration of the degradation and failure evolution of polyurea materials.

3.6 Structural Degradation and Stability-Oriented Design

3.6.1 Relationship between Structural Evolution and Performance Deterioration

The service behavior of polyurea coatings under extreme environments such as impact, hygrothermal exposure, marine conditions, low temperature, and irradiation is manifested as variations in mechanical response, corrosion resistance, interfacial stability, and service life. However, these macroscopic changes originate from molecular structure evolution, hydrogen-bonding network rearrangement, and microphase morphology transformation [21,171]. Accordingly, the macroscopic performance of polyurea cannot be adequately interpreted using isolated parameters such as strength, modulus, or elongation at break. Instead, it should be understood through the hierarchical response transfer across molecular, supramolecular, microphase, and macroscopic scales.

At the molecular scale, hard-segment content, soft-segment architecture, chain extender type, and molecular weight collectively determine chain mobility, hydrogen-bond density, and phase separation degree [172]. Hard segments primarily contribute to load-bearing capacity, thermal stability, and physical crosslinking, whereas soft segments provide chain mobility, low-temperature flexibility, and energy dissipation space. At the microphase scale, hard-domain size, spatial distribution, and the stability of hard/soft interfaces further govern stress transfer efficiency, crack propagation behavior, and energy dissipation mechanisms [41].

Therefore, performance degradation of polyurea coatings in complex environments is not governed by a single structural factor, but results from the progressive influence of environmental loading on chain mobility, hydrogen-bond stability, microphase architecture, and interfacial integrity. Establishing the relationships among molecular structure, microphase morphology, mass transport, and macroscopic protective performance is essential for subsequent stability-oriented design.

3.6.2 Design Principles for Polyurea Stabilization

For polyurea systems designed for extreme environmental protection, improving a single property such as strength, toughness, or corrosion resistance is insufficient to ensure long-term service stability. Different application scenarios are dominated by distinct failure mechanisms: impact and blast protection rely on high-strain-rate energy dissipation and crack suppression [41]; marine and hygrothermal environments are governed by water/ion transport and interfacial aging; low-temperature service requires sufficient chain mobility retention; while thermal-oxidative or irradiation environments depend primarily on intrinsic chemical stability.

Accordingly, polyurea design should be guided by service conditions and failure modes, achieving a balance among hard-segment reinforcement, soft-segment dissipation, hydrogen-bond stability, microphase interfacial

integrity, and environmental durability [173]. Excessive hard-segment content may enhance modulus and thermal resistance but increase brittleness, whereas an overly flexible soft phase may compromise dimensional stability and barrier performance. Thus, the optimization objective should not be single-property maximization, but rather multi-functional synergy.

Interfacial stability should also be treated as a key design parameter [57,174]. Many failure processes do not originate from insufficient bulk strength but from hydrogen-bond network relaxation, microphase interfacial instability, defect growth, or coating/substrate interfacial failure. Consequently, improving microphase integrity, reducing initial defects, strengthening interfacial adhesion, and delaying aggressive species penetration are often more critical than simply increasing initial mechanical strength.

3.6.3 Service-Life-Oriented Design in Engineering Applications

Future development of polyurea protective coatings should gradually shift from empirical formulation optimization toward service-demand-oriented design. For marine engineering, bridges, offshore structures, transportation infrastructure, aerospace systems, and impact-resistant protective applications, dominant failure modes such as salt spray penetration, hygrothermal debonding, UV-induced embrittlement, low-temperature cracking, or post-impact damage propagation should first be identified. Material design parameters, including hard/soft segment ratio, curing strategy, interfacial treatment, and filler modification, should then be defined accordingly.

Multiscale characterization and modeling approaches are essential for establishing structure-lifetime relationships. Techniques such as FTIR, DMA, SAXS, AFM, in-situ mechanical testing, EIS, salt spray exposure, and adhesion measurements can track chemical evolution, microphase morphology changes, barrier performance degradation, and interfacial stability during aging. Meanwhile, molecular simulations and finite element analysis provide mechanistic insights into transport behavior, stress concentration, and crack propagation. Data-driven screening, inverse design, and digital twin strategies will be further discussed in subsequent sections.

The long-term performance of polyurea protective coatings should not rely on improvement of a single property. Instead, it should be built on stable molecular architecture, controllable microphase structure, reliable interfacial adhesion, and durable barrier performance. Integrating structure design, film formation, interfacial engineering, and service environment is therefore essential for improving coating durability and enhancing the reliability of lifetime prediction.

4 Stability Enhancement and Life Extension Strategies for Polyurea Protective Coatings

4.1 Nanofiller Barrier Effect and Interfacial Reinforcement

4.1.1 Regulation of Hydrogen-Bonding Network and Microphase Morphology by Nanofillers

The stability of polyurea protective coatings is strongly governed by the hard-segment hydrogen-bonding network and microphase separation structure. The role of nanofillers extends beyond simple stiffness enhancement; interfacial interactions between fillers and the polymer matrix can alter hydrogen-bond organization, hard-domain aggregation, and soft/hard interfacial states, thereby influencing barrier performance and long-term durability.

Li et al. [21] systematically investigated the relationship between hydrogen bonding and polyurea performance using multiscale characterization. They found that the dissociation of ordered hydrogen bonds in hard segments directly reduces hard-domain connectivity and induces microphase reconstruction, leading to decreased modulus and strength. As shown in Fig. 13(a), progressive hydrogen-bond dissociation increases hard-domain spacing and causes noticeable coarsening, confirming that the hydrogen-bonding network is a key factor governing microphase stability. This study established a direct correlation among hydrogen-bond structure, microphase morphology, and macroscopic mechanical response.

Pangon et al. [55] used AFM and SAXS to study the effect of soft-segment variation on microphase structure. When the soft-segment architecture changed, originally continuous and ordered hard domains gradually transformed into dispersed and disordered structures. As shown in Fig. 13(b), the degree of hard-segment aggregation decreased significantly and the interphase became less distinct. This highlights the sensitivity of polyurea microphase structure to local molecular interactions, suggesting that nanofiller-induced modifications to hydrogen-bond environments can produce similar structural regulation effects.

In recent years, graphene, carbon nanotubes, and POSS have been widely introduced into polyurea systems. Tzelepis et al. [135] reported that the reinforcing efficiency of graphene nanosheets depends strongly on hard-segment content. At higher hard-segment ratios, graphene participates more effectively in the hard-domain network, enhancing stress transfer across the microphase structure and improving stiffness and structural stability.

Meng et al. [39] further prepared polyaspartic polyurea composites using isocyanate-functionalized graphene. As shown in Fig. 13(c), the modified graphene forms a more stable interfacial interaction with the polyurea matrix and promotes reconstruction of the hydrogen-bonding network. Beyond mechanical enhancement, the system also

exhibited improved self-healing, corrosion resistance, and thermal conductivity, indicating that interfacial hydrogen-bond regulation can simultaneously improve structural stability and multifunctionality.

Similar effects have been reported for other nanofiller systems. Chin et al. [175] found that multi-walled carbon nanotubes act as physical crosslinking nodes that promote hydrogen-bond formation and restrict chain mobility, thereby enhancing network stability. Raftopoulos et al. [176] reported that POSS particles not only interact with polymer chains but also modify the degree of microphase separation, influencing chain dynamics and glass transition behavior.

Overall, the effect of nanofillers on polyurea is not limited to mechanical reinforcement. It arises from coupled contributions of filler surface chemistry, interfacial hydrogen bonding, hard-domain organization, and microphase morphology. For protective coatings, filler design should prioritize dispersion stability, interfacial compatibility, and microphase integrity rather than simply increasing filler loading.

4.1.2 Barrier Effect of Nanofillers on Water/Oxygen/Cl⁻ Transport

After incorporation into polyurea, nanofillers introduce additional interfacial structures that modify transport pathways for water, oxygen, and chloride ions. For protective coatings, this barrier effect is often more critical than mechanical reinforcement. Well-dispersed fillers increase the tortuosity of diffusion pathways, reduce permeation rates, and delay chloride penetration toward the coating/substrate interface.

Meng et al. [39] reported that isocyanate-modified graphene in polyaspartic polyurea forms a clear interfacial transition region rather than a sharp interface. This structure facilitates stress transfer from the matrix to graphene nanosheets, improving load-bearing capacity and interfacial stability.

Beyond load transfer, nanoscale interfaces also influence crack propagation behavior. Liu et al. [150] observed in SiC/polyurea nanocomposites that crack growth is impeded and deflected by particle interfaces, increasing crack path tortuosity and fracture energy dissipation, as shown in Fig. 13(d). Compared with neat polyurea, the composite exhibits higher dynamic strength and improved resistance to failure.

For corrosion protection, interfacial structures also serve as barriers against aggressive species penetration. Zhang et al. [173] introduced sulfonated graphene into waterborne polyurea and found that the two-dimensional nanosheets form a “tortuous pathway” effect within the coating, significantly extending diffusion paths for water and ions, as shown in Fig. 13(e).

The barrier efficiency of nanofillers strongly depends on dispersion state and interfacial compatibility. Uniformly dispersed 2D or 1D nanofillers increase diffusion tortuosity, whereas agglomeration introduces voids, interfacial defects, and stress concentration sites, which can instead facilitate water and Cl⁻ transport. Therefore,

corrosion resistance should be evaluated not only by filler type and loading, but also by dispersion quality, interfacial adhesion, water uptake behavior, salt spray resistance, and adhesion retention.

4.1.3 Influence of Nanofillers on Crack Blunting and Interfacial Stress Transfer

The excellent impact resistance of polyurea under shock, blast, and high-strain-rate loading originates from synergistic energy dissipation across multiple scales. Unlike conventional rigid protective materials that rely on a single deformation mode, polyurea nanocomposites establish continuous energy dissipation pathways from molecular to phase to crack scales, enabling progressive load attenuation [177-179].

At the molecular level, hydrogen bonds between hard segments form a dynamic physical crosslinked network. Tzelepis et al. [135] reported that hydrogen bonding drives the formation of continuous hard domains, while soft segments preserve chain mobility, together forming a typical microphase-separated structure. Under impact loading, reversible hydrogen-bond dissociation and reformation dissipate energy through molecular friction and conformational rearrangement, delaying local stress concentration (Fig. 13(f)).

At the mesoscale, nanofillers further regulate stress transfer pathways and microphase stability. Qian et al. [66] found that well-dispersed graphene nanosheets form effective interfacial bonding with polyurea, promoting load transfer from matrix to reinforcement. In contrast, agglomerated graphene oxide introduces defects that degrade mechanical performance. Interfacial hydrogen bonding, filler dispersion, and polymer molecular weight collectively determine reinforcement efficiency (Fig. 13(g)).

Crack evolution connects microscopic structure to macroscopic failure. Liu et al. [150] used micro-CT to analyze compression failure in polyurea nanocomposites, revealing sequential damage evolution from void formation to microcrack initiation, crack propagation, and catastrophic fracture. Nanoparticles promote crack deflection and branching, increasing crack path length and energy dissipation contribution (Fig. 13(h)).

Therefore, the influence of nanofillers on crack propagation is governed by dispersion quality, interfacial adhesion, and microphase stability. For protective coatings, ideal nanofillers should provide interfacial compatibility, crack blunting capability, and long-term environmental stability while avoiding agglomeration-induced defect formation.

4.1.4 Applications and Design Considerations of Nanoreinforced Polyurea

Research on nanoreinforced polyurea has gradually shifted from simple mechanical strengthening toward multifunctional protective applications. Graphene, carbon nanotubes, and nano-SiC have been widely incorporated into polyurea systems, showing promising performance in impact resistance, corrosion protection, self-healing, and thermal/electrical conductivity [180,181]. Zhao et al. [177] summarized that nanofillers not only improve

mechanical properties but also enhance interfacial stability and environmental durability, enabling polyurea to evolve from a single protective material into a multifunctional structural system.

In protective applications, Toader et al. [182] reported that carbon nanotube-reinforced polyurea coatings enhance load-bearing capacity under dynamic impact and reduce local deformation (Fig. 13(i)). In corrosion protection, Zhang et al. [173] demonstrated that sulfonated graphene introduces a more tortuous diffusion pathway, improving long-term corrosion resistance.

The key to nanoreinforced polyurea is not filler content but interfacial effectiveness. Excess filler tends to agglomerate, weakening interfacial bonding and introducing voids or defect sites. Proper interfacial engineering enables nanofillers to contribute to barrier enhancement, stress transfer, crack blunting, and environmental stability. Future design should therefore focus on surface modification, dispersion stability, coating/substrate adhesion, salt spray durability, and long-term property retention rather than single-property optimization.

4.2 Dynamic Networks and Self-Healing Polyurea

4.2.1 Dynamic Urea Bonds and Reversible Networks

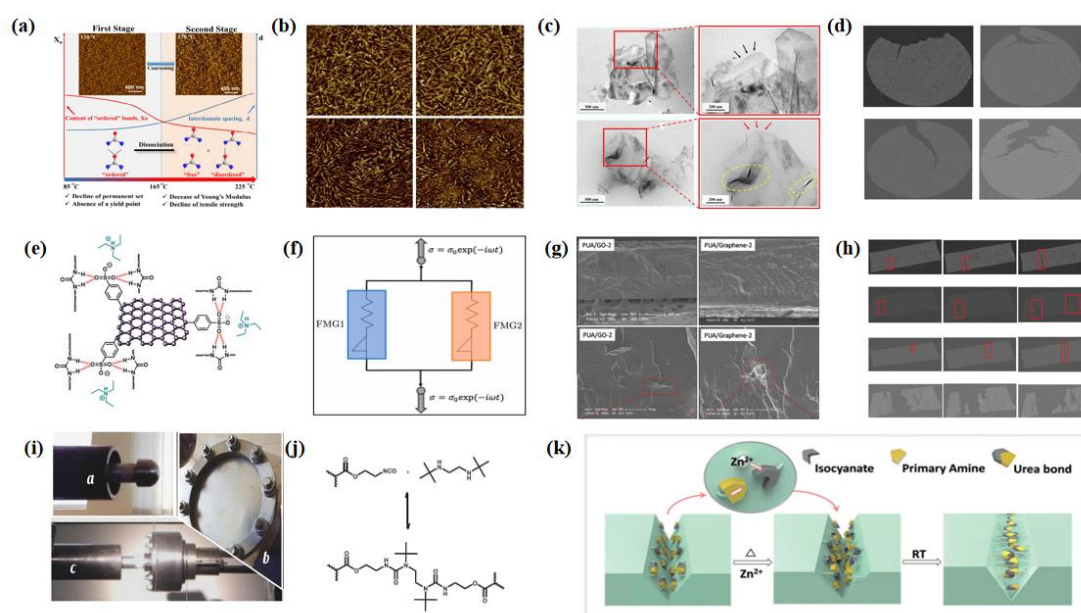


Fig. 13. (a) Schematic mechanism diagram [21]; (b) AFM image [55]; (c) SEM image [39]; (d) SEM image [150]; (e) Dissociation mechanism [173]; (f) Schematic illustration of two FMGs [135]; (g) SEM image [66]; (h) SEM image [150]; (i) Configuration of the Split Hopkinson Pressure Bar (SHPB) apparatus [182]; (j) Reversible reaction process [185]; (k) Schematic mechanism diagram [125].

Conventional polyurea networks are relatively stable and typically do not recover spontaneously after damage. To improve healing and structural reconfiguration capability, dynamic urea bonds or other reversible linkages have

been introduced into the network, enabling bond exchange and reconstruction under thermal, light, or catalytic stimuli [183,184]. For protective coatings, such dynamic chemistry provides a potential route for crack closure, local stress relaxation, and interfacial restoration.

Ying et al. [126] first proposed a hindered urea bond (HUB) strategy. By introducing bulky substituents near the urea nitrogen, the resonance stabilization of the urea group is weakened, enabling reversible dissociation into isocyanate and amine under mild conditions, followed by reformation of urea bonds. This reversible process endows the network with exchangeable crosslinking sites, enabling reconstruction of the polymer architecture.

Based on this concept, Zechel et al. [185] developed reprocessable polyurea networks relying on dynamic urea chemistry. They observed that thermal stimulation triggers chain reconnection and network recovery, enabling crack healing and partial restoration of mechanical performance (Fig. 13(j)). In addition to steric design, Wang et al. [125] demonstrated that $\text{Zn}(\text{OAc})_2$ can catalyze reversible urea bond dissociation by forming Zn-O coordination interactions, which lower the dissociation energy barrier and promote dynamic bond exchange. This strategy enables conventional polyurea systems to achieve self-healing and reprocessability without requiring specially engineered hindered structures, expanding the design space for engineering applications (Fig. 13(k)). These studies indicate that dynamic urea chemistry provides a molecular-level healing pathway, although practical performance still depends on the balance among exchange kinetics, network strength, and service conditions.

4.2.2 Crack Healing and Interfacial Recovery

The core of self-healing in polyurea is not merely crack closure, but whether interfacial molecular interactions and load-transfer pathways can be re-established. Healing processes typically involve hydrogen-bond reorganization, dynamic covalent exchange, and chain migration [186]. For protective coatings, recovery of a continuous barrier layer after crack closure is a key metric of healing efficiency.

Wang et al. [187] designed a dual-dynamic polyurea system and found that the synergy between UPy quadruple hydrogen bonds and urea hydrogen bonds enhances chain diffusion and interfacial reconnection. After crack formation, dynamic hydrogen bonds can reform at the damaged interface, enabling rapid structural recovery (Fig. 14(a)).

Beyond hydrogen bonding, dynamic covalent chemistry can further strengthen network reconstruction. Li et al. [188] introduced aromatic disulfide bonds into a crosslinked polyurea network and observed that disulfide exchange, together with hydrogen-bond reorganization, promotes crack healing and network reconfiguration (Fig. 14(b)). Once the damaged surfaces recontact, continuous exchange of dynamic crosslinking points enables partial restoration of mechanical integrity.

In coating systems, self-healing is not limited to crack closure but also involves recovery of protective functionality. Tian et al. [189] developed a polyurea composite coating based on hydrogen bonding and Diels-Alder chemistry. After crack closure, a continuous barrier layer can be re-established, restoring corrosion and cavitation resistance (Fig. 14(c-e)). Chen et al. [190] further reported that coupling disulfide exchange with shape-memory effects enables a continuous process of crack closure, interfacial reconstruction, and property recovery. These results indicate that evaluation of self-healing coatings should not rely solely on crack disappearance, but also on the recovery of water resistance, salt spray resistance, adhesion, and barrier performance.

4.2.3 Influence of Dynamic Networks on Lifetime and Stability

The incorporation of dynamic networks not only enables self-healing but also slows damage accumulation and improves long-term service stability under harsh environments. Luo et al. [191] reported that self-healing polyurea systems can continuously repair local damage through chain diffusion, hydrogen-bond reorganization, and bond exchange, thereby reducing performance decay and extending service life.

From a network perspective, dynamic bond exchange facilitates local stress relaxation and topological reconstruction. The disulfide-based polyurea system developed by Li et al. [188] exhibited pronounced stress relaxation behavior, indicating that dynamic crosslinking networks can mitigate stress concentration and improve damage tolerance (Fig. 14(f)). In addition, Li et al. [192] found that a relatively loose hard-segment packing structure favors chain mobility and interfacial reconstruction, thereby improving healing efficiency and structural stability (Fig. 14(g)).

For protective coatings, dynamic networks can also restore barrier integrity after damage. Tian et al. [189] reported that hydrogen-bond/Diels-Alder dual-dynamic polyurea coatings retain good corrosion and cavitation resistance after healing, indicating that dynamic chemistry can extend the effective service lifetime of protective systems. However, increasing dynamic bond content often reduces network rigidity. Zechel et al. [185] emphasized that a trade-off exists between healing efficiency and mechanical strength. Therefore, the design of dynamic polyurea coatings should balance healing efficiency, mechanical retention, barrier performance, and service temperature window.

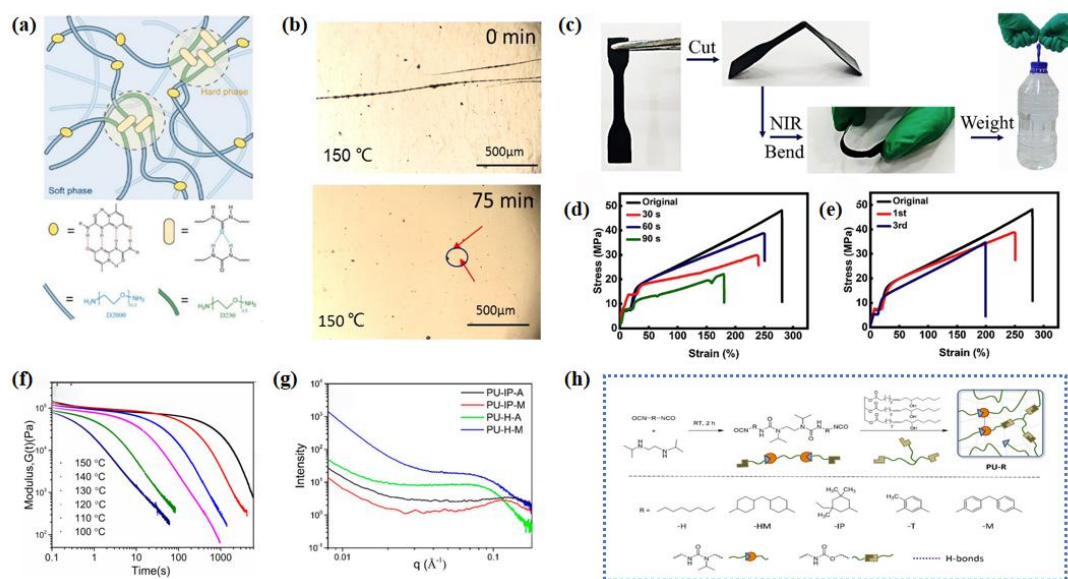


Fig. 14. (a) Schematic mechanism diagram [187]; (b) Healing image [188]; (c-e) Self-healing behavior of Pue-FD [189]; (f) Stress relaxation curve [188]; (g) SAXS pattern [192]; (h) Synthesis of a dynamic covalent polyurea network [194].

4.2.4 Design Challenges of Dynamic Polyurea Networks

Although dynamic networks endow polyurea with self-healing and structural reconfiguration capability, their long-term service stability remains insufficiently validated. Most existing studies focus on crack healing, reprocessing, and short-term property recovery under laboratory conditions, while systematic data under humid, salt spray, UV, thermal-oxidative, and cyclic loading environments are still limited [188,193].

A key unresolved issue lies in the coupling between dynamic chemistry and microphase separation. The mechanical performance of polyurea primarily originates from the physical crosslinked network formed by hard-segment aggregation. The introduction of dynamic bonds inevitably alters hard-domain packing and hydrogen-bonding interactions. Chen et al. [194] reported that dynamic polyureas derived from different isocyanate architectures exhibit distinct exchange mechanisms and network evolution behaviors, indicating that the performance of dynamic systems depends not only on the dynamic bonds themselves, but also on the underlying microphase structure (Fig. 14(h)).

In addition, most current dynamic polyurea systems lack long-term service data. Zhang et al. [183] pointed out in a recent review that research in this area is still largely concentrated on self-healing efficiency and reprocessability, whereas systematic evaluation of performance retention under cyclic loading, environmental aging, and repeated healing cycles remains scarce.

For protective coating applications, future studies should place greater emphasis on post-healing EIS behavior,

salt spray resistance, water uptake, adhesion retention, and crack re-propagation characteristics. Only when barrier performance and coating/substrate interfacial stability can be maintained after repeated healing events can dynamic polyurea coatings be considered viable for long-term protective applications.

4.3 Stability Issues of Functional Polyurea Systems

4.3.1 Conductive and Electromagnetic Shielding Polyurea

Pristine polyurea is inherently electrically insulating, which limits its application in electromagnetic interference (EMI) shielding, electrostatic dissipation, and in-service structural monitoring. By incorporating conductive fillers such as carbon nanotubes (CNTs), graphene, graphene nanoplatelets (GNPs), MXene, carbon black, metallic nanowires, or intrinsically conductive polymers, a continuous or semi-continuous conductive network can be established within the polyurea matrix. Such networks enable electromagnetic attenuation through reflection, absorption, and multiple scattering. Meanwhile, the electrical resistance response can reflect strain evolution, crack propagation, interfacial damage, and conductive network rearrangement, providing a route for structural health monitoring.

Wang et al. [195] developed a multilayer polyurea composite system based on CNTs and carbon fiber (CF) fabrics. A hybrid three-dimensional conductive network formed by well-dispersed CNTs and layered carbon fibers enhanced both electrical conductivity and EMI shielding effectiveness while maintaining flexibility (Fig. 15a). The study also indicated that strong interfacial adhesion between polyurea and carbon fibers improves stress transfer and structural stability. Similarly, Meng et al. [39] introduced isocyanate-functionalized graphene nanoplatelets (IP-GNPs) into polyaspartic polyurea, strengthening interfacial interactions between fillers and matrix and constructing a more stable conductive network (Fig. 15b). Surface functionalization of graphene not only reduces the percolation threshold but also improves thermal conductivity, self-healing capability, and corrosion resistance.

Conductive networks can also be used for damage detection during service. Yu et al. [196] incorporated functionalized graphene nanoplatelets into a sprayable polyurea system, achieving a coating with both structural protection and strain-sensing capability (Fig. 15c). Owing to hydrogen bonding and covalent interactions between graphene and the polymer matrix, a stable conductive pathway was formed at relatively low filler loading, enabling measurable electrical resistance changes under deformation. This indicates that conductive polyurea can function not only as an EMI shielding material but also as a platform for monitoring crack initiation, strain localization, and structural degradation.

Beyond carbon-based fillers, conductive polymers have also been used for polyurea functionalization. Bi et al. [197] combined polyaniline (PANI) with reduced graphene oxide to construct hybrid conductive fillers, achieving

simultaneous enhancement in EMI shielding and flame retardancy (Fig. 15d). Gheybi et al. [198] incorporated PANI-CsC@TiO₂ into polyaspartic polyurea, producing coatings with antistatic, anticorrosion, and antibacterial functions. Chin et al. [175] further reported that non-functionalized MWCNTs can be uniformly dispersed in aliphatic polyurea under sonication, forming electron transport pathways while promoting hydrogen bonding and restricting chain mobility.

From the perspective of polymer degradation and stability, conductive fillers influence not only conductivity or shielding efficiency but also microphase structure, stress transfer behavior, mass transport pathways, and crack evolution. A well-dispersed conductive network can simultaneously enhance EMI shielding, damage sensing, and interfacial reinforcement. However, filler agglomeration or poor interfacial compatibility may introduce defect sites, accelerating fatigue damage and environmental aging. Therefore, evaluation of conductive polyurea should extend beyond initial shielding performance to include conductive stability, sensing reliability, and mechanical retention after thermal aging, hygrothermal exposure, salt spray, UV irradiation, and cyclic loading.

4.3.2 Strain-Sensing Polyurea

Embedding conductive fillers such as graphene nanoplatelets, liquid-exfoliated graphene, or carbon nanotubes into the polyurea matrix enables the formation of strain-sensitive conductive pathways. Under tensile loading, impact, or localized cracking, changes in contact resistance, tunneling distance, and network connectivity lead to measurable electrical resistance variations. This piezoresistive behavior enables real-time strain monitoring, crack detection, and structural health assessment of polyurea coatings [199,200].

Yu et al. [196] developed a sprayable self-sensing coating by incorporating functionalized graphene (HT-GNP) into a polyurea system. The coating exhibited rapid resistance response and recovery under deformation and maintained sensing capability after hygrothermal, salt spray, and UV aging (Fig. 15e). This suggests that appropriate filler functionalization and interfacial engineering are critical for preserving conductive network continuity under harsh environments. Rahim Jan et al. [201] used liquid-exfoliated graphene coatings to monitor local strain and microcrack formation in composite structures, enabling structural health monitoring in complex geometries (Fig. 15f).

From a degradation and durability standpoint, the value of strain-sensing polyurea lies not only in electrical signal generation but also in early-stage damage identification. Crack initiation, interfacial debonding, fatigue accumulation, and local stress concentration can all trigger conductive network rearrangement or failure, making resistance signals an indirect indicator of coating degradation. However, challenges remain, including filler agglomeration, baseline drift, interfacial instability, and the trade-off between conductivity and flexibility. Future

studies should focus on signal stability, repeatability, and failure thresholds after thermal oxidation, hygrothermal exposure, salt spray, UV aging, and cyclic loading to improve long-term reliability of self-sensing polyurea coatings.

4.3.3 Shape Memory and Stimuli-Responsive Polyurea

Shape memory and stimuli-responsive behaviors provide polyurea coatings with the capability of damage recovery and deformation adaptation. When subjected to impact, large deformation, or localized damage, the ability to recover the original geometry under external stimuli (e.g., heat, light, or electricity) can mitigate crack propagation and delay structural failure. In polyurethane-urea systems, Ji et al. [202] reported that soft segment crystallization can act as a temporary fixing phase, while hydrogen-bonding networks within hard segments maintain permanent shape stability. Shape recovery is typically accompanied by restored chain mobility and reformation of hydrogen-bonding networks.

In polyurea systems, Liu et al. [203] introduced supramolecular networks based on dual and quadruple hydrogen bonding, enabling simultaneous shape memory and self-healing functions. During deformation, reversible hydrogen-bond dissociation and reformation dissipate applied stress while facilitating structural reconstruction in damaged regions. Xiang et al. [204] further incorporated dynamic disulfide bonds into polyurea networks, developing thermoplastic polyurea with integrated shape memory, self-healing, and reprocessability (Fig. 15g). In this system, disulfide exchange provides network rearrangement capability, while hydrogen bonding maintains structural integrity, enabling shape recovery and repeated processing under relatively mild conditions.

Multistimuli-responsive designs further extend deformation control strategies in polyurea. Liu et al. [205] developed a conductive filler-based shape memory polyurea system capable of reversible deformation driven by thermal, optical, and electrical stimuli (Fig. 15h). Chen et al. [206] constructed hierarchical networks through synergistic covalent crosslinking and hydrogen bonding, where permanent covalent networks provide structural stability and dynamic hydrogen bonds enable energy dissipation and shape recovery, resulting in shape memory performance while maintaining strength and toughness (Fig. 15i).

From a long-term durability perspective, the significance of shape memory and stimuli-responsive functions lies in enhancing post-damage deformation recovery and structural integrity rather than introducing “smart” behavior alone. Future work should focus on property retention under repeated deformation-recovery cycles, dynamic bond exchange kinetics, stimulus-response thresholds, and reliability after thermo-oxidative aging, hygrothermal exposure, UV irradiation, and fatigue loading. Only when stable recovery capability is maintained under complex service environments can such systems be considered viable for long-term protection and

service-life extension.

4.3.4 Antibacterial and Antifouling Polyurea Surfaces

In marine service environments, microbial adhesion, biofouling, and contaminant deposition accelerate surface degradation and may promote localized corrosion, interfacial failure, and loss of protective performance. Although polyurea coatings exhibit high mechanical strength and chemical resistance, pristine systems generally lack active antibacterial and antifouling functionality. Therefore, introducing low-surface-energy components, bioinspired micro/nanostructures, antimicrobial agents, or self-healing units has become an effective strategy for improving marine durability through synergistic antibacterial, antifouling, and anticorrosion functions [190,207].

Tian et al. [189] reported a hydrogen- and Diels-Alder bond-based epoxy-modified polyurea (PUE-FD) coating integrating functionalized reduced graphene oxide (FrGO) and 4,5-dichloro-2-n-octyl-isothiazolinone (DCOIT), achieving combined anticavitation, anticorrosion, and antibacterial performance. The sheet-like FrGO structure physically inhibits microbial adhesion and suppresses bacterial growth through oxidative activity, while DCOIT disrupts microbial cell membranes and enzyme activity to enhance antibacterial efficiency. The coating exhibited a bacterial removal rate above 99% and nearly complete microalgae removal (Fig. 15j).

Gao et al. [208] developed a self-healing superhydrophobic polyurea/TiO₂ coating in which low-surface-energy components and hierarchical micro/nanostructures generate a Cassie state, reducing underwater adhesion and improving self-cleaning performance (Fig. 15k). During droplet rolling, surface contaminants are removed, limiting fouling accumulation. This strategy integrates antifouling and self-healing functions, offering a potential route for long-term marine and deep-sea protection. Zhang et al. [209] reported an ambient-cured cardanol-derived polyurea coating that simultaneously exhibits antibacterial and anticorrosion properties, demonstrating the feasibility of bio-based systems for environmentally compatible protective coatings. In addition, full-ocean-depth poly(oxime-urethane) coatings provide a reference for antifouling/anticorrosion integration in deep-sea environments.

It should be noted that antibacterial and antifouling functionality does not necessarily guarantee long-term stability. Filler agglomeration, insufficient interfacial adhesion, uncontrolled release of antimicrobial agents, mechanical damage to superhydrophobic structures, and surface chemical evolution under prolonged seawater exposure may all weaken protective performance. Future studies should therefore evaluate surface integrity, antibacterial/antifouling efficiency decay, adhesion retention, and corrosion protection lifetime under long-term immersion, salt spray, mechanical abrasion, and biofouling conditions, rather than relying solely on initial antibacterial efficiency or static contact angle.

4.3.5 Performance Trade-Offs in Multifunctional Polyurea Systems

With polyurea systems evolving from single protective coatings toward multifunctional platforms integrating conductivity, sensing, anticorrosion, antifouling, and environmental responsiveness, increasing structural complexity inevitably emerges. From the perspective of polymer degradation and stability, the key challenge is not the addition of more functional components, but achieving a balance among functionality enhancement, microphase stability, interfacial integrity, and long-term service reliability.

Conductive functionality typically relies on percolated networks formed by fillers such as graphene or carbon nanotubes. Noh et al. [210] indicated that conductive elastomers must balance electrical percolation with elastic compliance, since excessive filler loading restricts chain mobility and reduces flexibility. De Focatiis et al. [211] further observed that conductive networks undergo rearrangement and hysteresis during cyclic deformation, leading to drift in piezoresistive response. Similar issues exist in polyurea systems: while conductive fillers improve EMI shielding or sensing capability, filler agglomeration and interfacial defects may also act as initiation sites for fatigue cracking and aggressive species penetration.

For strain-sensing systems, a trade-off exists between sensitivity and long-term stability. Amjadi et al. [212] reported that high-sensitivity flexible sensors often rely on conductive pathway rupture, crack propagation, or tunneling effects to generate resistance changes, yet these mechanisms may lead to signal degradation under prolonged cyclic loading. In protective and antifouling systems, functional additives can also alter interfacial structure and transport pathways. Montemor [213] noted that multifunctional protective coatings are evolving from single-barrier systems toward synergistic designs integrating anticorrosion, self-healing, and antifouling functions. Thomas et al. [214] further highlighted that while nanoparticles and functional additives improve surface performance, they may also introduce interfacial competition, dispersion instability, and reduced long-term durability.

Therefore, the design of multifunctional polyurea should shift from “initial performance enhancement” toward “post-aging functional retention”. Future studies should systematically assess filler functionalization, interfacial compatibility, microphase stability, and long-term spatial distribution of functional components, while correlating them with mechanical behavior, conductivity/sensing stability, corrosion resistance, antifouling efficiency, and interfacial integrity under thermo-oxidative, hygrothermal, salt spray, UV, and cyclic loading conditions. Only when structural and functional performance can be maintained after long-term exposure can multifunctional polyurea coatings truly contribute to durability improvement in extreme environments.

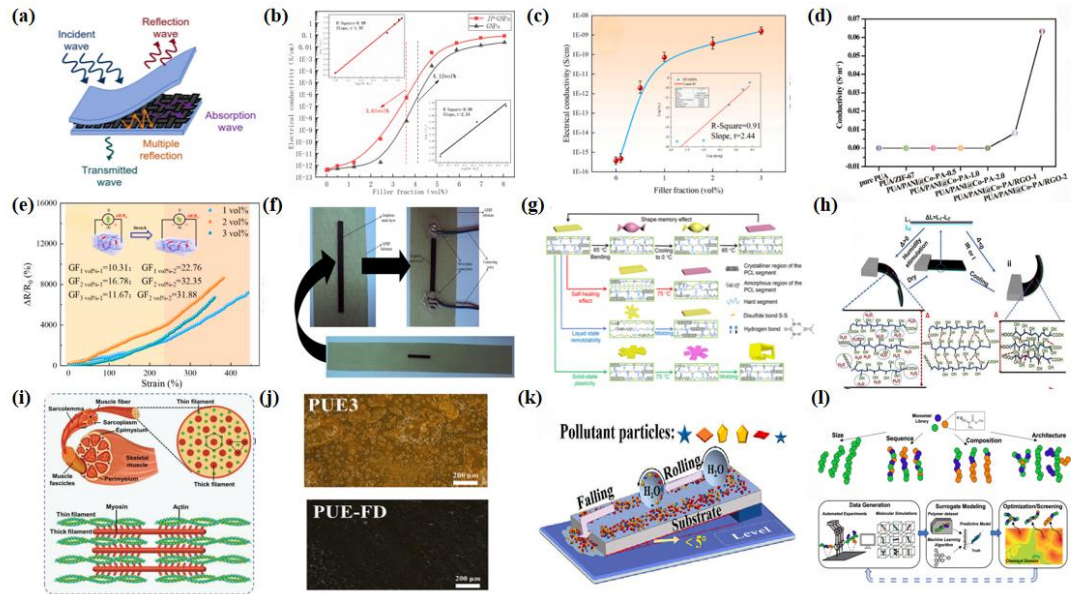


Fig. 15. (a) EMI shielding mechanism [195]; (b) Electrical conductivity [39]; (c) Relationship between electrical conductivity and graphene content [196]; (d) Conductivity curves [197]; (e) Relative resistance variation [196]; (f) GFRP laminate composite specimens [201]; (g) Schematic illustration of polyurea [204]; (h) Mechanism of reversible deformation of actuator [205]; (i) Illustration from Ref. [206]; (j) Digital micrographs [189]; (k) Mechanism [208]; (l) Considerations and approach to polymer-based biomaterials design [215].

4.4 Data-Driven Lifetime Prediction and Formulation Design

4.4.1 Aging Data and Performance Prediction

With polyurea protective coatings evolving toward multifunctional applications such as anticorrosion, self-healing, sensing, and extreme-environment protection, their formulation complexity, microphase structure, and service conditions have increased substantially. Conventional formulation optimization relies largely on trial-and-error experimentation, making it difficult to establish quantitative relationships among molecular structure, curing kinetics, microphase morphology, and long-term performance. In this context, machine learning and materials informatics provide complementary tools for correlating structural parameters with degradation behavior and property evolution.

The foundation of data-driven design lies in the digital representation of polymer structures. Patel and Webb [215] emphasized that polymer properties are governed not only by chemical composition but also by molecular weight, chain sequence, topology, and processing history. Accordingly, complex polymer architectures must first be converted into computable numerical descriptors before constructing structure-property mappings (Fig. 15(l)). Traditional polymer informatics approaches typically use features such as functional group composition, polarity

parameters, molecular volume, aromatic content, and hydrogen-bond donor/acceptor counts to establish quantitative structure-property relationship (QSPR) models for property prediction.

For polyurea systems, descriptor selection should reflect their intrinsic microphase-separated morphology. The macroscopic performance of polyurea originates primarily from soft-hard segment microphase separation and hydrogen-bonded hard segment domains. Therefore, parameters such as hard segment content, hydrogen-bond density, isocyanate chemistry, chain flexibility, and polar group distribution can serve as key structural variables. Averochkin et al. [216] proposed a physics-informed descriptor framework combining van der Waals volume, bonding characteristics, polarity parameters, and quantum-chemical features for polymer property prediction. Their results indicated that physically interpretable descriptors not only improve model interpretability but also clarify the contribution of structural variables to thermal and mechanical properties.

With the advancement of machine learning, polymer representation has gradually shifted from manual feature engineering to automated feature learning. Gurnani et al. [217] developed the PolyGNN model, which represents polymer repeat units as graph structures and uses graph neural networks to learn atomic connectivity and topological features, thereby avoiding information loss associated with manually defined descriptors (Fig. 16(a)). Compared with conventional QSPR models, graph-based approaches better capture nonlinear structure-property relationships in complex polymer systems and show improved applicability for property prediction and material screening.

Building on this, Kuenneth and Ramprasad [218] introduced the polyBERT model, which treats polymer SMILES strings as a chemical language and employs Transformer architectures to extract structural features for rapid property prediction and high-throughput screening (Fig. 16(b)). Unlike descriptor-based approaches, this method does not require predefined structural parameters and can learn latent structure-property relationships directly from large datasets, providing an alternative pathway for polyurea design in complex chemical spaces.

For polyurea protective coatings, machine learning applications should not be limited to predicting T_g , modulus, or thermal stability. They should be extended to coating-relevant metrics such as water uptake, salt spray resistance, EIS parameters, adhesion retention, crack density, and post-aging mechanical performance. Lu and Jayaraman [219] demonstrated that machine learning can also support automated analysis of microscopy images, scattering data, and spectroscopic signals, which is relevant for identifying microphase evolution, hydrogen-bond rearrangement, and aging-induced damage in polyurea systems. However, publicly available polyurea datasets remain limited, and many models are trained on polyurethane or generic polymer datasets. Therefore, establishing dedicated databases that integrate formulation, curing conditions, microphase structure, aging environments, and

coating performance is necessary to improve the reliability of lifetime prediction for polyurea coatings [43,44].

4.4.2 Multiscale Simulation and Formulation Optimization

The durability of polyurea protective coatings is governed by coupled effects of molecular structure, hydrogen-bonding networks, microphase separation, filler dispersion, and coating/substrate interfacial behavior. These factors span molecular, mesoscale, and macroscopic coating scales, making it difficult to establish clear quantitative relationships through experiments alone. Multiscale simulation therefore provides a useful framework for interpreting structural evolution and guiding formulation optimization [172,215,220].

At the mesoscale, Liu et al. [24] developed a coarse-grained polyurea model to investigate the influence of soft-hard segment architecture on microphase separation morphology. Their results showed that chain connectivity and hard segment aggregation behavior significantly affect hard domain connectivity and phase morphology, thereby influencing mechanical response and energy dissipation. Zheng et al. [171] constructed a hybrid atomistic/coarse-grained model that retains urea hydrogen-bonding information and revealed that hydrogen bonding governs both hard segment organization and chain relaxation behavior. These findings suggest that hydrogen bonds serve not only as structural units for hard domain formation but also as key bridges linking molecular structure to macroscopic properties.

To enable cross-scale prediction from microstructure to macroscopic response, Yang et al. [42] integrated molecular dynamics-derived structural parameters into a representative volume element (RVE) framework to establish a mapping between microphase organization and mechanical properties. Their results indicated that hard domain reorganization is closely associated with yield strength, flow stress, and strain-rate sensitivity, demonstrating that multiscale modeling can significantly shorten the design-to-performance evaluation cycle.

With the growth of polymer databases and machine learning tools, research focus has further shifted toward inverse design. Unlike conventional forward optimization (“structure-to-property”), inverse design starts from target properties and identifies molecular structures and formulations that satisfy predefined requirements. Wu et al. [221] applied Bayesian optimization to construct a mapping between polymer structure and thermal conductivity and successfully identified candidate structures with target properties.

On this basis, Nanjo et al. [222] developed the SPACIER platform, which integrates molecular dynamics simulations, machine learning models, and Bayesian optimization into a unified framework for iterative structure generation, property prediction, and parameter optimization (Fig. 16(c)). This approach enables automatic adjustment of structural variables based on target properties and continuous model refinement using simulation feedback.

Further, Qiu et al. [223] proposed the PolyTAO generative model, which uses Transformer networks to learn structure-property relationships and directly generates candidate polymer structures based on target performance requirements (Fig. 16(d)). Compared with traditional high-throughput screening, this approach expands the search space beyond existing material libraries, enabling exploration of broader chemical design spaces.

However, applications of these methods to polyurea coatings remain at an early stage. Key limitations include the scarcity of publicly available datasets, difficulties in accurately representing hydrogen bonding, microphase separation, and dynamic network behavior, and inconsistencies in aging conditions, testing protocols, and performance metrics across studies. A more practical direction is to integrate experimental aging data, EIS results, salt spray performance, water uptake, adhesion retention, microscopy characterization, and multiscale simulation outputs into a unified formulation-structure-durability database tailored for polyurea protective coatings.

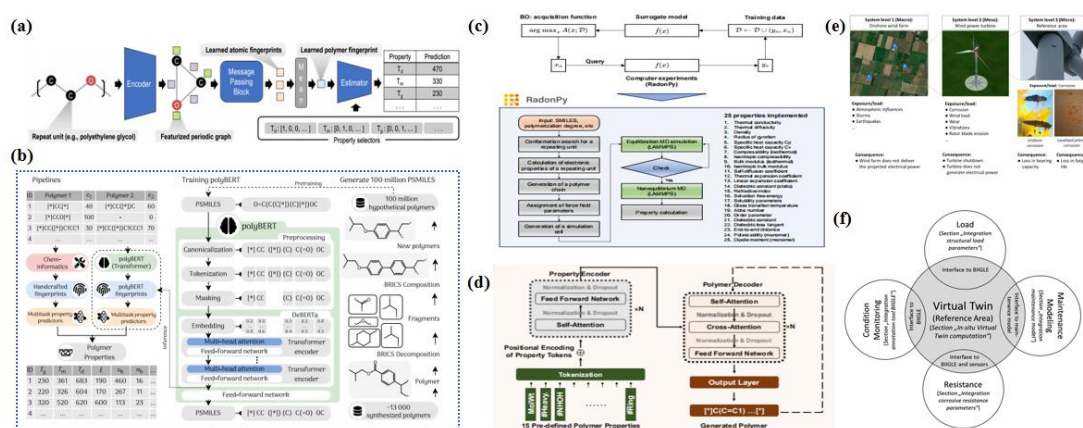


Fig. 16. (a) PolyGNN architecture [217]; (b) Polymer informatics with polyBERT [218]; (c) SPACIER workflow: Bayesian optimization (BO) is utilized to identify polymers with desired properties [222]; (d) PolyTAO generative model [223]; (e) Engineering system structure [227]; (f) Digital twin framework associated with the present study [227].

4.4.3 Digital Twin and Service Life Prediction

During long-term service, polyurea protective coatings are simultaneously exposed to multiple environmental and mechanical factors, including temperature, humidity, UV irradiation, salt spray, mechanical loading, and substrate conditions. Conventional lifetime prediction methods mainly rely on accelerated aging tests and empirical models, which are insufficient to capture environmental fluctuations, microstructural evolution, and interfacial degradation processes in real service conditions. Digital twin (DT) technology provides an alternative framework by integrating physical models, experimental data, in-situ monitoring signals, and environmental information into a unified virtual system for tracking coating degradation and estimating maintenance schedules

[224,225].

Within a digital twin framework, lifetime prediction depends on three categories of data. The first includes environmental and loading conditions recorded by in-service sensors [226], such as temperature, humidity, salt deposition, and UV exposure [227]. The second involves microstructural descriptors of the coating, including polyurea microphase separation, hard/soft segment ratio, and filler dispersion state [228]. The third comprises experimental and historical degradation datasets used to train machine learning models for predicting degradation kinetics and service life [229-231]. As shown in Fig. 16(e,f) [227], digital twin systems typically define a reference region and integrate heterogeneous data streams into a unified representation.

When combined with multiscale simulation, digital twins can bridge microstructural evolution and macroscopic lifetime degradation. Microphase morphology and interfacial states can be used as input parameters to interpret water/oxygen/ion transport, crack propagation, and adhesion loss. Machine learning models can assist in defect recognition, degradation rate prediction, and failure time estimation, while field monitoring data continuously update and calibrate model outputs. From an engineering perspective, the value of digital twin systems does not lie in replacing aging experiments, but in supporting coating thickness design, formulation selection, maintenance scheduling, and failure warning thresholds.

At present, the application of digital twins to polyurea coatings remains limited. Data formats and testing conditions are not standardized across studies, and the linkage between microstructure and macroscopic performance is still insufficiently established. Moreover, model generalization under marine, deep-sea, high-UV, or complex mechanical environments lacks experimental validation. Practical implementation is further constrained by sensor reliability, data quality, and computational cost. Therefore, future research should prioritize the establishment of standardized aging databases and the integration of physics-based models with machine learning approaches, enabling predictions that not only estimate lifetime but also explain degradation mechanisms.

As illustrated in Fig. 17, functional development of polyurea materials is gradually shifting from single protective functions toward multifunctional integration. Future design should focus on: (i) improving the accuracy and timeliness of field data acquisition through high-precision sensing and automated data processing; (ii) integrating physics-driven multiscale models with machine learning algorithms to achieve interpretable degradation prediction; and (iii) developing scalable digital twin platforms applicable to different service environments and coating systems, thereby enabling engineering optimization and predictive maintenance.

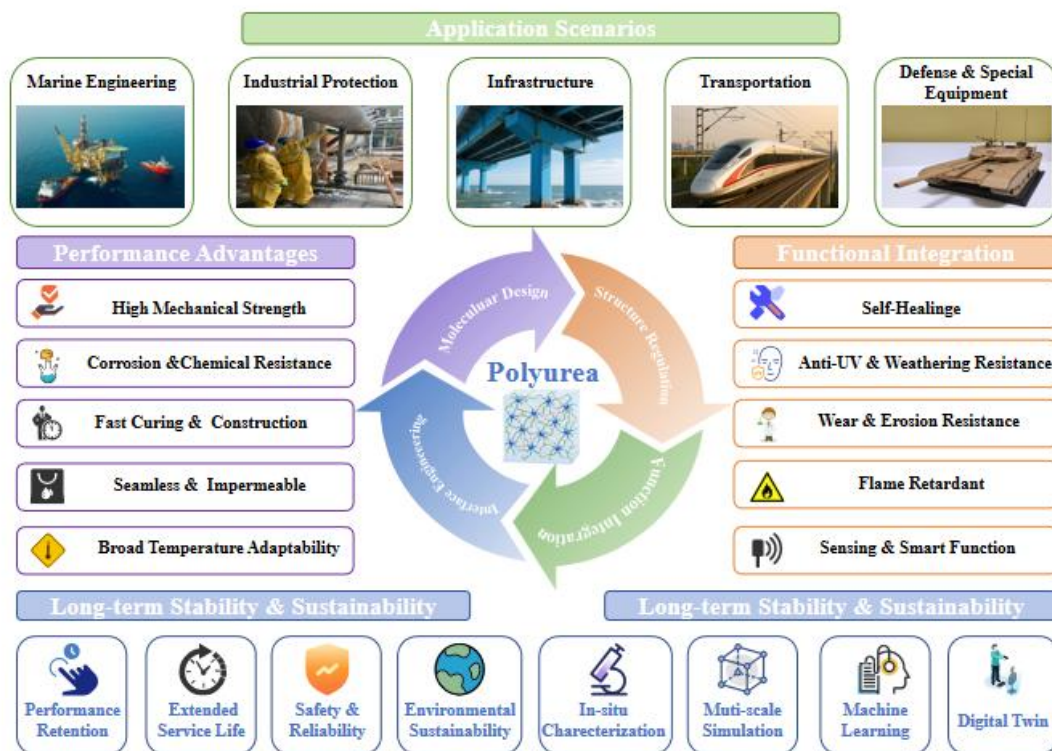


Figure 17. Overview of the multifunctionality, performance characteristics, and stability of polyurea materials.

5. Conclusions and Future Perspectives

5.1 Main Conclusions

This review summarizes the long-term durability of polyurea protective coatings from the perspectives of structure formation, service aging, failure mechanisms, and stabilization strategies. Overall, the protective performance of polyurea coatings is not governed solely by initial strength or elongation at break, but is controlled by the combined effects of hard/soft segment architecture, urea-based hydrogen-bonding networks, microphase separation morphology, curing process, and coating/substrate interface stability. Hard segments provide load-bearing capacity and physical crosslinking, while soft segments contribute to flexibility and energy dissipation. The hydrogen-bonding network and microphase structure govern stress transfer, water/oxygen/ion transport, and crack propagation behavior.

During long-term service, performance degradation of polyurea coatings is rarely driven by a single chemical degradation pathway. Thermo-oxidative and UV exposure mainly induce surface oxidation, chain scission, yellowing, embrittlement, and microcrack formation. Hygrothermal and salt spray environments facilitate

water/oxygen/chloride penetration, weaken hydrogen-bonding networks, and accelerate interfacial failure at the coating/substrate interface. Mechanical fatigue, impact, low temperature, high pressure, and irradiation further disturb microphase structures, promote local stress concentration, and accelerate crack propagation. Therefore, long-term failure of polyurea coatings should be understood as the coupled result of molecular degradation, hydrogen-bond evolution, microphase relaxation, medium transport, and interfacial debonding.

Current stabilization strategies mainly include molecular structure regulation, curing optimization, nanofiller barrier enhancement, interface engineering, dynamic network design, and self-healing approaches. Nanofillers can extend diffusion pathways for water, oxygen, and chloride ions while improving stress transfer and crack deflection resistance. Dynamic bonds and self-healing networks enable crack closure and partial recovery of local damage. Reprocessable and non-isocyanate routes also provide possibilities for greener and full life-cycle coating design. However, whether these strategies truly improve service life must be validated through long-term immersion, salt spray, hygrothermal aging, UV exposure, EIS, adhesion retention tests, and post-aging structural characterization.

5.2 Current Challenges

Several key issues remain unresolved in the study of polyurea protective coatings. First, the mechanisms of multi-factor coupled aging are not yet fully understood. Most studies focus on single-factor conditions such as thermo-oxidation, UV irradiation, hygrothermal exposure, or salt spray, whereas real service environments involve simultaneous variations in temperature, moisture, oxygen, chloride ions, mechanical loading, and radiation. Synergistic interactions among these factors may lead to failure pathways that differ significantly from those observed under single aging conditions.

Second, continuous structural evolution during aging lacks in-situ characterization. Many studies still rely on comparisons between pre- and post-aging mechanical properties or surface morphologies, with insufficient real-time tracking of hydrogen-bond networks, hard segment aggregation, microphase interfaces, transport behavior, and interfacial debonding. As a result, it remains difficult to establish quantitative relationships linking molecular-level changes to barrier degradation and interfacial failure.

Third, durability evaluation standards are not yet unified. Aging protocols, coating thickness, substrates, surface preparation methods, salt spray duration, immersion media, UV intensity, and failure criteria vary significantly across studies, limiting comparability. For organic protective coatings, relying only on tensile strength or elongation at break is insufficient. A more comprehensive evaluation should include EIS response, water uptake, adhesion retention, salt spray resistance, coating defect evolution, and corrosion propagation area.

Fourth, lifetime prediction models still lack reliable data support. Although accelerated aging reduces testing time, results do not always correlate with real service conditions. Most existing models are empirical and limited in describing multi-factor coupling, nonlinear degradation, and interfacial failure evolution. Machine learning and digital twin approaches show promise, but require high-quality, standardized, and reusable aging databases.

In addition, some modification strategies may introduce new stability issues. Nanofiller aggregation can act as defect initiation sites. Excessive dynamic bond content may reduce network rigidity and creep resistance. Non-isocyanate systems may increase water sensitivity due to hydroxyl, ester, or urethane-related structures. Multifunctional fillers may also compromise flexibility, adhesion, and long-term barrier performance.

5.3 Future Research Directions

Future research on polyurea protective coatings should shift from improving initial properties toward extending service life. First, more realistic multi-factor aging evaluation systems should be developed. For marine engineering, transportation infrastructure, industrial corrosion protection, bridge structures, and advanced equipment, coupled effects of hygrothermal exposure, salt spray, UV irradiation, thermal cycling, mechanical fatigue, and impact damage should be considered, along with identification of dominant failure mechanisms under different environments.

Second, in-situ characterization of coating structure and interfacial failure should be strengthened. Techniques such as in-situ FTIR, SAXS, AFM, DMA, SEM, XPS, micro-CT, EIS, and adhesion testing can be used to track hydrogen-bond evolution, hard domain development, transport behavior, crack propagation, and interfacial debonding. Integrating these results with mechanical and electrochemical data can help distinguish whether failure originates from matrix degradation, barrier deterioration, or interfacial damage.

Third, formulation design and processing routes should be further optimized. At the molecular level, isocyanate structure, soft segment chemistry, hard segment content, and hydrogen-bond density can be tuned. At the microphase level, hard domain distribution and interfacial stability should be controlled. At the coating level, curing kinetics, substrate wetting, thickness control, surface pretreatment, and multilayer architectures require careful optimization. For organic coating systems emphasized in *Progress in Organic Coatings*, adhesion stability, transport resistance, and corrosion propagation inhibition should be prioritized.

Fourth, self-healing and dynamic network designs should evolve from “crack closure” toward “recovery of protective function”. Future studies should focus on post-repair EIS performance, salt spray resistance, adhesion retention, crack re-growth behavior, and degradation after multiple healing cycles, rather than relying solely on surface morphology recovery or single-cycle mechanical restoration.

Finally, standardization of lifetime prediction and data infrastructure should be promoted. A unified database integrating accelerated aging tests, long-term immersion, field exposure, microstructural characterization, electrochemical measurements, and multiscale simulations is required. Machine learning and digital twin approaches should be combined with physically based models and real service data to avoid purely empirical predictions.

Overall, the future development of polyurea protective coatings should not be limited to higher strength or additional functions. Instead, a balanced integration of barrier performance, interfacial stability, damage recovery capability, process controllability, and environmental durability is required. Only through the coupling of structural design, coating processes, and service-oriented evaluation can polyurea coatings be reliably applied in long-term corrosion protection under complex service environments.

Credit authorship contribution statement

Declaration of Competing Interest

Acknowledgements

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