



ROLE OF CHEMISTRY IN WATERBORNE POLYURETHANE FILMS

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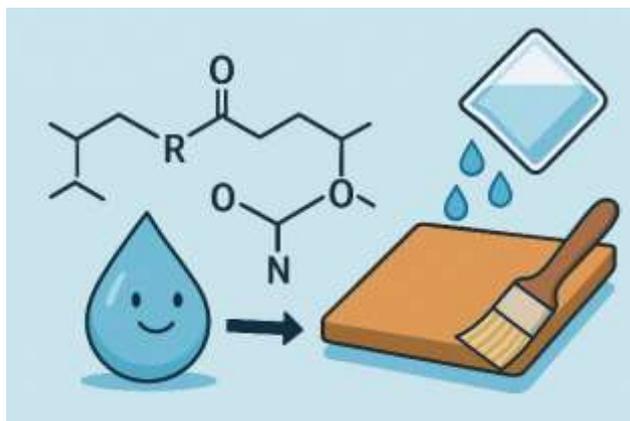
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ABSTRACT

Waterborne polyurethane (WPU) films have emerged as eco-friendly alternatives to solvent-based coatings due to their low volatile organic compound (VOC) emissions, adjustable mechanical properties, and wide industrial applicability. The chemistry of WPU plays a decisive role in dictating film performance, including adhesion, flexibility, chemical resistance, and durability. This review highlights the fundamental chemistry of waterborne PU dispersions, mechanisms of film formation, and the influence of molecular design on their structural and functional properties. The review highlights progress in environmentally friendly synthesis approaches, innovations in material crosslinking, and recent methods for modifying nanocomposites. It also examines how these developments support new uses across fields such as surface coatings, sustainable packaging, biomedical technologies, and energy-related systems.

Keywords: Waterborne polyurethane, Eco-friendly coatings, Film formation mechanisms, Nanocomposites, Green synthesis.



INTRODUCTION

Polyurethane (PU) materials constitute a highly adaptable family of polymers and are incorporated into a broad range of products, including protective coatings, structural adhesives, sealants, elastomeric components, and various biomedical devices. Their appeal stems from their customizable mechanical behaviour and strong resistance to chemical

degradation. Conventional production of PU films typically involves solvent-based routes that require significant amounts of organic solvents. Although these approaches produce films with desirable performance, concerns regarding solvent emissions—especially VOC release—and associated health issues have encouraged the development of more environmentally responsible processing methods [1-2]. Waterborne

polyurethane (WPU) systems have emerged as an environmentally benign counterpart to solvent-borne formulations. By dispersing PU in water rather than in organic solvents, these systems significantly reduce VOC emissions while maintaining desirable film properties such as elasticity, adhesion, and durability [3]. The development of WPU films is thus closely linked to innovations in polymer chemistry, particularly the synthesis and structural modification of polyurethane prepolymers and their dispersion stabilization in aqueous media [4]. The role of chemistry is central to tailoring the performance of waterborne PU films. Factors such as the chemical structure of polyols, the choice of isocyanates, the incorporation of internal emulsifiers, and the use of chain extenders govern the colloidal stability, film formation, and ultimate mechanical strength of the coatings [5]. Furthermore, advanced chemical strategies—such as introducing renewable polyols, ionic and non-ionic hydrophilic segments, or nanocomposite fillers—have expanded the scope of WPU films in applications ranging from protective coatings and packaging to biomedical devices and flexible electronics [6-7]. In this review, we highlight the crucial role of chemistry in the design, synthesis, and performance optimization of waterborne PU films. Particular emphasis is placed on the relationship between chemical structure and film properties, as well as recent advances that integrate green chemistry principles for sustainable development. By consolidating current knowledge, this work aims to provide insights into future directions for environmentally friendly, high-performance PU film technologies.

CHEMISTRY OF WATERBORNE POLYURETHANE DISPERSIONS

Fundamental Structure

Polyurethanes (PUs) are versatile polymers produced through polyaddition reactions between diisocyanates and polyols. Their architecture is generally segmented, comprising flexible “soft” domains derived from polyether, polyester, or polycarbonate diols, and rigid “hard” domains formed by diisocyanates and low-molecular-weight chain extenders. While soft segments impart elasticity and processability, hard segments contribute to mechanical strength, thermal stability, and phase separation behavior [8-9].

Transition to Waterborne Systems

Traditional PU synthesis has relied heavily on organic solvents, raising environmental and safety concerns. To

address this, waterborne polyurethane (WPU) dispersions have been developed, where water serves as the primary medium. Achieving water dispersibility requires introducing hydrophilic functionality into the polymer backbone. A common strategy involves internal emulsification through ionic groups, often introduced using chain extenders such as dimethylolpropionic acid (DMPA). Following neutralization, these ionic groups enable stable colloidal dispersions. Alternatively, non-ionic routes, such as the incorporation of polyethylene glycol (PEG), provide steric stabilization with lower ionic content, thereby modifying particle size and film properties [10-11].

Film Formation Process

The formation of coherent PU films from aqueous dispersions occurs through a multistage process. Initially, water evaporation increases particle packing density. As the soft segments retain mobility, dispersed particles coalesce into a more continuous phase. Subsequently, interdiffusion of chains and, in some systems, chemical crosslinking consolidates the film, yielding cohesive integrity and durability. The extent and efficiency of film formation are strongly influenced by the selection of chain extenders, crosslinkers, and the balance between ionic and non-ionic stabilizing groups [12-13].

INTERMEDIATES AND TECHNOLOGY IN WATERBORNE POLYURETHANE COATINGS

Waterborne polyurethane (WPU) coatings are typically based on polyether, polyester, and polyacrylate soft segments combined with aliphatic isocyanates for enhanced UV resistance [14]. The primary intermediates used in WPU formulations include polyols, isocyanates, curatives, and specialty intermediates such as dimethylolpropionic acid (DMPA), caprolactam, and caprolactones [15]. Among polyether systems, PTMEG-based polyurethanes provide superior mechanical strength, flexibility, and water resistance, making them suitable for components subjected to movement or vibration. Polyester and polyacrylate systems, including polycaprolactone and polycarbonate derivatives, deliver high overall performance and exterior durability, along with excellent gloss retention [16].

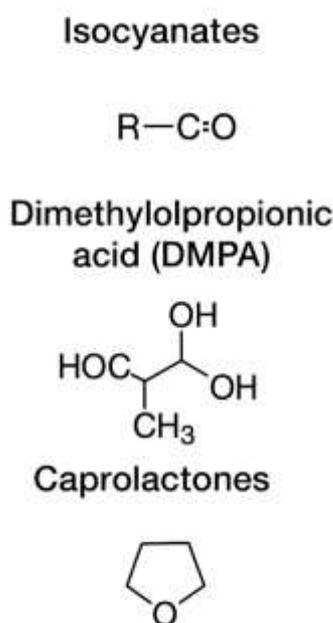
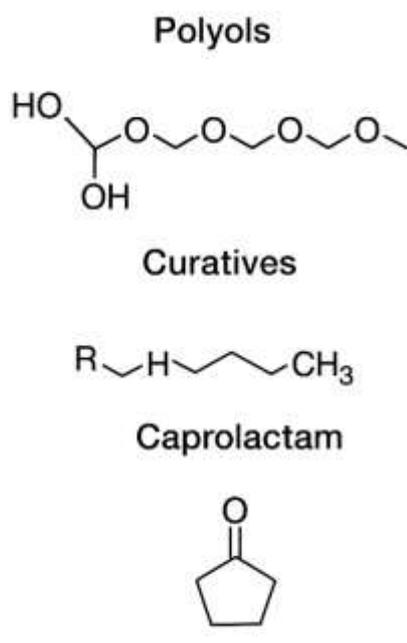
Waterborne Polyurethane Dispersion (PUD)

Modern PUD technology allows polyurethane particles to be dispersed in water, achieving properties comparable to solvent-based systems without the



environmental and health hazards [17]. Internal emulsification is often achieved using carboxylated diols such as DMPA, which is co-reacted with polyols and isocyanates and neutralized using tertiary amines or ammonium hydroxide. DMPA concentrations of 4–8% by prepolymer weight enhance particle dispersion and film formation, resulting in non-ionic polymer films upon drying [18]. While most PUDs are anionic, cationic PUDs can also be formulated using tertiary amine-diols like N-methyldiethanolamine (MDEA), offering improved adhesion to hydrophobic surfaces.

Two-Component (2K) Systems



In 2K WPU systems, isocyanate-terminated prepolymers react with polyamine curatives such as ethylenediamine (ED) or diethylenetriamine (DETA), providing faster curing compared to water alone (Rhee et al., 2021). Hydroxyl-terminated dispersions can also be crosslinked using blocked polyisocyanates, which remain inactive during dispersion but thermally unblock during curing to react with hydroxyl groups. Common blocking agents include MEKO, DMP, and ϵ -CAP, which dictate the deblocking temperature and curing profile (Xu & Li, 2020).

One-Component (1K) Systems

Thermally cured 1K WPU coatings utilize prepolymers with protective groups, enabling single-component formulations that cure upon heating. The choice of polyol, isocyanate, and NCO/OH ratio controls coating properties, while the protecting group governs the thermal cure profile (Kumar et al., 2019). High molecular weight, anionically modified polyurethanes containing DMPA can form water-dispersible systems under shear using neutralizing agents like triethylamine (TEA) or ammonia, resulting in uniform air-dried films.

INFLUENCE OF CHEMISTRY ON FILM PROPERTIES

Mechanical Performance

The mechanical behavior of polymeric films is largely dictated by the balance between rigid and flexible segments within the polymer backbone. Increasing the proportion of hard segments generally raises the material's tensile strength and stiffness; however, this adjustment often reduces its ability to stretch before failure [19-20]. Balancing the two segment types is therefore important for tailoring the final mechanical properties.

Thermal Stability

Thermal performance is strongly influenced by the chemical structure of the diisocyanates employed. Aromatic diisocyanates such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) generally impart rigidity and high-temperature

resistance to the films. In contrast, aliphatic diisocyanates such as isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) provide superior resistance to ultraviolet degradation, making them favourable for outdoor applications [21-22].

Hydrophobicity and Barrier Properties

Surface hydrophobicity and barrier function are improved through incorporation of specific chemical moieties. Long-chain fatty acids, fluorinated groups, and silicone-based segments are commonly introduced to enhance water repellency and chemical resistance, thereby extending the durability of polymer films under harsh environments [23-24].

Crosslinking Chemistry

Crosslinking plays a vital role in improving solvent resistance, dimensional stability, and long-term durability. Conventional strategies rely on aziridine, carbodiimide, or epoxy-based crosslinkers. Recent developments have focused on self-crosslinking waterborne polyurethane (WPU) systems containing reactive pendant groups, which enable in-situ curing without the need for external agents [25-26].

ADVANCES IN THE CHEMISTRY OF WATERBORNE POLYURETHANE FILMS

Bio-based Polyols

The shift from conventional petrochemical polyols to renewable alternatives such as castor oil, lignin, and carbohydrate-derived diols has significantly contributed to the sustainability of waterborne polyurethane (WPU) formulations. These bio-based

polyols not only reduce reliance on fossil resources but also maintain desirable mechanical and chemical properties, making them viable for high-performance applications [27-28].

Nanocomposite Modifications

The integration of nanoscale fillers—including graphene oxide, nanoclay, and silica—into WPU matrices has been shown to enhance mechanical robustness, barrier properties, and flame resistance. Such nanocomposite approaches exploit the high surface area and functional versatility of nanomaterials, allowing for tailored property enhancement in waterborne coatings [29-30].

Green Synthesis Approaches

Emerging strategies in WPU chemistry aim to minimize environmental and health impacts. Non-isocyanate polyurethanes (NIPUs) and solvent-free polymerization techniques are being actively investigated as eco-friendly alternatives, offering reduced toxicity while maintaining the performance standards of conventional polyurethane films [31-32].

APPLICATIONS OF WATERBORNE PU FILMS

Waterborne polyurethane (WPU) films have garnered significant attention due to their versatile applications (Figure-1) across various industries, attributed to their eco-friendly nature, excellent mechanical properties, and adaptability. These films are synthesized by dispersing polyurethane polymers in water, eliminating the need for organic solvents and thereby reducing environmental impact [33].



Figure- 1

Coatings and Paints

WPUs are extensively utilized in coatings and paints, offering corrosion protection, durable wood finishes, and automotive coatings. Their ability to form films at

ambient temperatures and exhibit excellent adhesion to diverse substrates makes them ideal for protective and decorative applications [34].



Adhesives and Sealants

In the realm of adhesives and sealants, WPUs are favoured for their high flexibility and strong bonding capabilities to a wide range of substrates. Their application spans from packaging materials to medical devices, providing reliable and durable adhesion [35].

Packaging

WPUs serve as effective barrier films in packaging, particularly for food and pharmaceutical products. Their biodegradability and non-toxic nature ensure that they meet the stringent requirements for materials in direct contact with consumables [36].

Biomedical Applications

The biomedical field benefits from WPUs due to their biocompatibility and tunable degradation properties. They are employed in wound dressings, drug delivery systems, and implants, offering flexibility and support for tissue regeneration [37].

Energy Devices

WPUs are also utilized in energy devices, including flexible films for membranes, sensors, and protective layers. Their mechanical strength and flexibility contribute to the efficiency and durability of energy-related applications [38]. Waterborne polyurethane films are integral to a multitude of applications, providing sustainable and high-performance solutions across industries.

FUTURE PROSPECTIVES

Advancements in the field of waterborne polyurethane (WPU) films are steering towards more sustainable, functional, and scalable applications. The future directions can be categorized into four primary areas:

Development of Fully Bio-Based wpus

The shift towards sustainability is prompting the exploration of fully bio-based WPU. Utilizing renewable resources such as vegetable oils, lignin, and plant-based polyols, researchers are developing WPU that not only reduce reliance on petrochemical derivatives but also enhance biodegradability and reduce environmental impact. For instance, studies have demonstrated the successful incorporation of lignin nanoparticles into WPU composites, resulting in

materials with improved mechanical properties and environmental benefits [39].

Smart Coatings with Self-Healing, Antimicrobial, or Responsive Functionalities

The integration of smart functionalities into WPU films is a burgeoning area of research. Self-healing capabilities, achieved through dynamic covalent bonds or microencapsulation techniques, enable the material to autonomously repair damage, thereby extending the lifespan of coatings. Additionally, antimicrobial properties are being introduced to prevent microbial growth on surfaces, which is particularly beneficial in medical and food packaging applications. Responsive functionalities, such as UV-curable and light-healing properties, are also being incorporated, allowing for coatings that can adapt to environmental stimuli [39-41].

Scale-Up of Non-Isocyanate and Green Synthetic Routes

The traditional synthesis of polyurethanes involves isocyanates, which pose health and environmental risks. As a result, there is a concerted effort to develop non-isocyanate polyurethanes (NIPUs) through green synthetic routes. These methods utilize alternative reactants such as cyclic carbonates and diamines derived from renewable sources, eliminating the need for toxic isocyanates. The scalability of these processes is a critical focus, with research aiming to optimize reaction conditions and improve the economic feasibility of large-scale production [39].

Integration of WPU Films into High-Value Devices for Sustainable Technologies

WPU is increasingly being integrated into high-value applications, particularly in the realm of sustainable technologies. Their versatility allows for use in coatings for electronics, sensors, and wearable devices. The development of flexible, transparent, and conductive WPU films is enabling their application in areas such as smart packaging, environmental monitoring, and health diagnostics. The incorporation of WPU into these devices not only enhances performance but also contributes to the reduction of environmental footprints through the use of sustainable materials [39-40]. In conclusion, the future of WPU films lies in their evolution towards fully

renewable, multifunctional, and scalable materials [41] that contribute to sustainable technological advancements. Continued interdisciplinary research and development will be pivotal in realizing these objectives.

Conclusion

The performance and applicability of waterborne polyurethane (WPU) films are fundamentally governed by their underlying chemical architecture. The careful design of soft and hard segments dictates not only mechanical flexibility and toughness but also thermal and chemical resistance, while hydrophilic modifications influence water dispersibility, adhesion, and surface interactions. Crosslinking strategies further enhance dimensional stability, barrier properties, and durability under operational conditions. Recent advances in monomer engineering, incorporation of functional groups, and utilization of environmentally benign synthesis routes highlight the potential of tailoring WPU films for highly specific performance criteria. Moreover, the integration of green chemistry principles—such as renewable monomers, reduced solvent usage, and energy-efficient processing—promises to expand the sustainability and industrial feasibility of these materials. Looking forward, continued innovation in the molecular design and functionalization of WPUs will likely drive the development of next-generation films with enhanced mechanical, thermal, and barrier properties, facilitating their broader adoption across coatings, biomedical, packaging, and electronic applications. This underscores the critical role of chemistry-driven strategies in shaping the future landscape of high-performance, environmentally responsible polymeric materials.

Conflict of Interest: Authors have no conflict of interest.

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