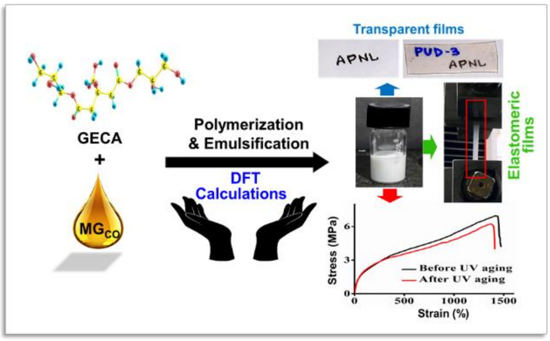
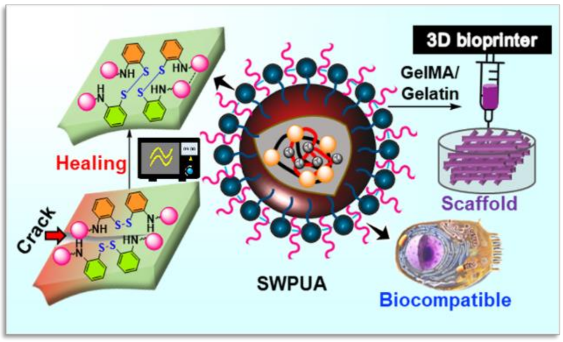
Summary and Future Scope

Highlights

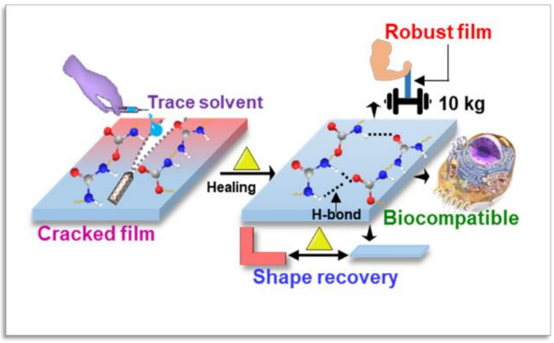
This chapter provides a succinct overview of the smart water borne polyurethanes (WPUs) and their nanocomposites developed during the current investigation. The outcomes of the ongoing investigation are conveyed through chapter-wise summaries, culminating in conclusions drawn from these findings. Based on the outcomes of the present research, the chapters also outline various future possibilities and perspectives. The highlights of the thesis, chapter wise from **Chapter 2** to **Chapter 6** are shown in the given graphics.



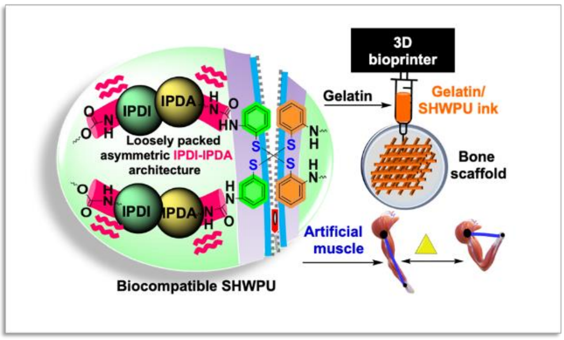
Chapter 2



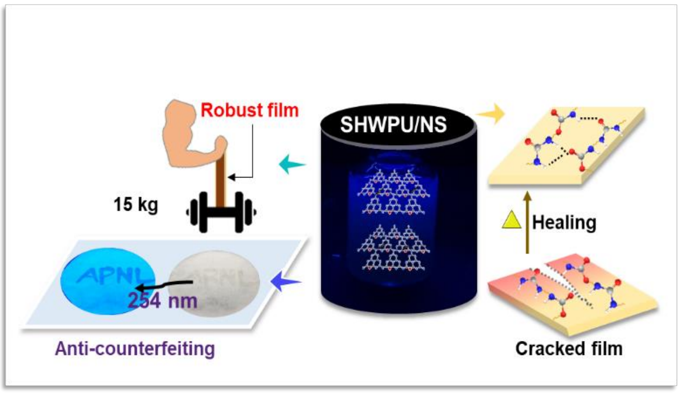
Chapter 3



Chapter 4



Chapter 5



Chapter 6

7.1. Summary and Conclusions

The thesis provides a detailed explanation of the development of self-healable waterborne polyurethane (SHWPU) and its nanocomposites, highlighting their versatility for various advanced applications. The thesis consists of a total of seven chapters.

Chapter 1: It offers an extensive introduction to WPU and its pivotal role in contemporary materials science. It covers polymerization pathways and mechanisms, the influence of tailor-made catalysts, effective modification techniques, and prospects for the future of WPU. Furthermore, this chapter highlights the utilization of various instrumentation techniques for characterizing WPUs and their nanocomposites. It also provides a concise overview of various smart attributes such as shape memory (SM), self-healing (SH), and fluorescent properties, along with their potential applications. In the end, the objectives and the research plan are outlined in alignment with the scope and prospects of the present scenario of the field.

Chapter 2: In this chapter, the use of glycerol ester of citric acid (GECA) is detailed as an internal emulsifier for the formulation of high-performance biobased anionic WPU dispersions. Density Functional Theory (DFT) calculations demonstrate that GECA exhibits reactivity similar to that of conventional bis(hydroxy methyl) propionic acid (DMPA). The synthesis of GECA is achieved through an esterification reaction involving citric acid and glycerol. A series of GECA-based WPU dispersion was prepared by pre-polymerization techniques. The films derived from this particular WPU displayed exceptional stretchability, favorable tensile strength, remarkable toughness, excellent thermal stability, moderate to high transparency, and commendable resistance to chemicals and UV radiation. Importantly, WPU films also demonstrated significant biodegradability when exposed to *P. aeruginosa* and *B. subtilis* bacterial strains.

Chapter 3: This chapter unveils a straightforward yet highly effective approach rooted in the triple synergistic interplay of a 'dynamic hard domain,' 'multiple hierarchical hydrogen bonding,' and the creation of a 'semi-interpenetrating network (IPN).' This method aims to resolve the enduring challenge of balancing high healing efficiency with mechanical strength. Based on this approach, a series of self-healable waterborne poly(urethane/acrylic) (SWPUA) hybrid dispersions and films were prepared by using 2-aminophinyl disulfide (2-APDS) as the ‘dynamic hard domain’, monoglyceride of castor oil (MG_{CO}) as a chain extender, GECA as an internal emulsifier and different acrylate monomers with other preferred reactants (polyols/diamines and diisocyanate). The resultant films exhibited microwave responsive SH ability, good mechanical robustness, high thermal stability, biocompatibility, and biodegradability.

Chapter 4: Taking inspiration from the cuticle of mussel byssus, an asymmetric alicyclic structure i.e., isophorone diisocyanate-isophorone diamine (IPDI-IPDA) moiety was incorporated into the hard domain of the WPU matrix. This amendment led to the creation of a range of transparent, elastomeric WPUs with SM and SH properties, and remarkable characteristics including unparalleled toughness, exceptional stretchability, high fracture energy, reprocessability, biocompatibility, and biodegradability. These results can be attributed to the presence of densely packed, hindered urea-based hydrogen bonds generated by the IPDI-IPDA system and the chemical cross-linking facilitated by GECA. Thus, the overall findings suggest that the developed WPU elastomer holds promise as a potential intelligent biomaterial, suitable for applications such as sutures and coatings for biomedical devices.

Chapter 5: This chapter unveils yet another straightforward but highly effective strategy to create a resilient self-healable WPU (SHWPU) elastomer, possessing high SH efficiency as well as other crucial properties necessary to consider it as an advanced material. Notably, this strategy is based on the synergistic effects of three key elements, namely, 'dynamic hard domains (2-APDS),' 'asymmetric IPDI-IPDA architecture,' and the 'shape memory effect (SME)' within a single elastomer. The loosely arranged IPDI-IPDA moieties, in combination with the SM Effect (SME), facilitate reversible S-S metathesis reactions, leading to both excellent healing efficiency and substantial mechanical strength simultaneously. Capitalizing on its impressive shape-recovery capabilities, the elastomer was evaluated for its potential use in simulating "artificial muscle" contractions. Furthermore, a range of 3D printable ink formulations comprising gelatin and SHWPU was developed, having potential applicability in the development of bone scaffolds.

Chapter 6: In the last work, we have successfully prepared a series of photoluminescent nanocomposites by incorporating S and Mo co-doped g-C_3N_4 (Mo@S-CN) nanohybrids as reinforcing agents within the SHWPU matrix. Transmission electron microscopy (TEM) images revealed that the Mo@S-CN nanohybrid consists of g-C_3N_4 nanosheets and MoO_x nanorods, forming a complex lamellar structure. Conspicuously, the introduction of Mo@S-CN nanohybrid not only enhances the inherent characteristics of the original SHWPU significantly but also imparts fluorescence activity to the nanocomposite (SHWPU/NS). Additionally, the aqueous dispersion of the Mo@S-CN nanohybrid and SHWPU/NS nanocomposite were evaluated for applications in bioimaging and anti-counterfeiting. Therefore, these materials exhibit significant promise and have the potential to pave the way for innovative advancements in the field of advanced smart materials, applicable across a diverse range of uses.

Chapter 7: This chapter offers an overview of our ongoing research by providing a summary of each individual chapter, along with concise concluding remarks. Additionally, it outlines the potential future directions and scope of our current investigation.

The significant outcomes of the current investigation are briefly summarized in the following section.

i) The present study establishes that bio-based internal emulsifiers (e.g., GECA) and chain extenders (e.g., MG_{CO}) can be used in place of petroleum-based precursors during the synthesis of WPU. Also, DFT confirms the equivalent reactivity of hydroxyl groups present in GECA and DMPA.
ii) The present study ensures that multifunctional smart WPUs can be synthesized through judicious molecular engineering.
iii) The present study shows that an optimal WPU film can be stretched up to 6300% from its original shape and the film exhibited the record highest toughness of 436.1 MJ m^{-3}.
iv) The present study reveals that an optimal SHWPU film is so tough that a dumbbell of 25 kg, which is 53648 times heavier than the weight of the film can be successfully lifted without any crack. Also, a healed SHWPU film after the first cycle of healing, can easily lift 8 kg without any damage.
v) The present study divulges that SWPUA and SHWPU dispersions can be used as the main component for 3D-printable bone scaffolds.
vi) The present study confers that the aqueous dispersion of Mo@S-CN nanohybrid and SHWPU/NS nanocomposites can be used for bioimaging and anti-counterfeiting applications, respectively.

7.2. Future scopes

The present thesis offers a thorough and systematic exploration of the development of smart WPUs and their promising advanced applications. Though, the presented research addresses several fascinating features within a single polymeric system, there is still ample room for further investigation aimed at designing more advanced materials. Drawing from the current findings, a few potential research avenues in this field are outlined below.

i) Initiating trials for the large-scale (industrial scale) production of WPUs.
ii) Exploring molecular engineering techniques for enhancing the SH efficiency WPUs at room temperature.

iii) Clinical trial for real-life application of drug loaded WPUs as suture for quick recovery of wound.

iv) Incorporation of suitable nanomaterials with energy efficient methods for introducing more advanced properties e.g., EMI shielding, flame retardancy, human motion sensing, into the WPU.

v) Recycling of used WPU and nanocomposites into the starting materials, e.g., polyols, using innovative techniques.