CHAPTER 7

Summary and Conclusions

Scientists, engineers, and researchers across diverse fields are attracting attention to vegetable oil-based polymers, which have emerged as a promising class of materials. They reduce the use of petroleum sources and are considered an eco-friendly alternative for sustainable development. The inherent chemical structure of VOs, comprising triglycerides with varying fatty acid chains, provides a versatile platform for creating polymers with tailored functionalities. VO-based polymers offer several advantages, including biodegradability, renewability, and reduced environmental impact. Their unique chemical properties, such as the presence of double bonds, hydroxyl groups, and ester linkages, allow for extensive chemical modifications to suit specific applications. However, challenges like limited thermal stability and mechanical strength require careful optimization during synthesis and application. The role of VO-based polymers as stabilizers, modifiers, and structural frameworks can be managed through the properties of VO. By modifying polymer properties, such as functional groups or chain architectures, researchers can achieve desired mechanical, thermal, and chemical characteristics in VO-based polymers. These modifications often lead to superior performance, making VO-based polymers suitable for applications ranging from coatings and adhesives to biomedical materials and environmentally friendly packaging.

In the present thesis work, non-edible castor oil (CO) and mahua oil (MO) were used as renewable sources for synthesizing VO-based polyurethanes (PUs) and waterborne polyurethanes (WPUs). CO, rich in ricinoleic acid, provides hydroxyl groups essential for direct reaction with isocyanates, enabling the formation of urethane linkages without prior modifications. MO, known for its high acid value and fatty acid composition, was chemically modified to create polyols suitable for PU synthesis. Various PUs and WPUs were thoroughly characterized and evaluated for their applications, such as antimicrobial activity, coatings, and packaging. The thesis comprises six chapters detailing the synthesis processes, characterization techniques, and application studies, highlighting the potential of VO-based polymers in advancing sustainable materials science. To summarize the present thesis work, mainly six chapters are reported.

Chapter1: General Introduction

This chapter provides an overview of bio-based polymers using the renewable resources as alternatives to petroleum-based polymers, emphasizing their environmental benefits and sustainable potential. It discusses VOs, especially non-edible oils like CO and MO, as versatile feedstocks for PU synthesis due to their chemical properties and abundant

availability. The chapter highlights the synthesis and applications of PUs and WPUs derived from these CO and MO, showcasing their eco-friendly nature and utility in coatings, adhesives, and antimicrobial materials.

Chapter 2: Extraction and physico-chemical properties of non-edible vegetable oils

The chapter shows the extraction and physicochemical characterization of NEVOs, emphasizing their eco-friendly nature and industrial relevance. CO and MO, extracted primarily through mechanical pressing, are highlighted as sustainable resources for polymer synthesis. Mechanical pressing ensures the purity of the extracted oils, reduces environmental impact, and provides by-products like seed cake, which can be repurposed as biofertilizers. The physicochemical properties, including acid value, hydroxyl value, iodine value, saponification value, and specific gravity, are meticulously measured to assess the oils' suitability for PU polymer synthesis. CO's high ricinoleic acid content (~89.73%) with a hydroxyl group at the 12th carbon position enhances its reactivity, while MO's high oleic acid content (~39.62%) offers stability and flexibility for industrial applications. Advanced analytical techniques like GC-MS are used to determine the fatty acid composition, further guiding the oils' potential in chemical and polymerization reactions. The chapter emphasizes the role of CO and MO as renewable alternatives to petroleum-based resources, fostering innovation in material science while promoting environmental sustainability and resource conservation.

Chapter 3: Development of polyurethane (urethane-modified polyesteramide) polymer using mahua oil and castor oil

Using non-edible sustainable resources such as MO and CO, the urethane-modified polyesteramide (UmPEA) resins were successfully developed. Here, MO reacted with diethanolamine to form fatty amide (MFA), which was converted to polyesteramide (PEA) polyol with itaconic acid. Mixtures of synthesized PEA and CO as polyols were successfully reacted with isocyanate to prepare the UmPEA resins. All the synthesized polymers were well characterized by ATR-FTIR and NMR techniques. The developed UmPEA films show good resistance against HCl, NaOH, and NaCl, and except for UmPEA5, all films were found insoluble in most organic solvents. Results of the DSC analysis showed an increase in the Tg value from 56.1°C to 69.1°C of UmPEA films with the increased content of CO. TGA studies showed the two-stage degradation of UmPEA resins at different heating rates of 10°C/min, 15°C/min, and 20°C/min, respectively. At a 10°C/min heating rate, the % decomposition was

found to be 41.98% to 34.66% up to 360°C and 94.64% to 94.44% up to 470°C for UmPEA5 to UmPEA1 films, which clearly indicated the decrease in % decomposition with an increase in the amount of CO. A similar trend was found in other studied heating rates as well. Because of the higher amount of CO in the resin, high thermal stability is attributed to the higher cross-linking densities through the high hydroxyl numbers and double bond content. The high thermal stability of the UmPEA films is also confirmed by the activation energy value of the decomposition of the UmPEA film determined through the Kissinger method. The lowest CO content UmPEA5 film has Ea values of 4.31 kJ mol^{-1} (Tp_1) and 101.38 kJ mol^{-1} (Tp_2), while the higher CO content UmPEA1 film showed Ea values of 224 kJ mol^{-1} (Tp_1) and 226 kJ mol^{-1} (Tp_2), respectively. High activation energy is required for degradation of UmPEA resin with a high content of CO, as it is the cross-linking network structure in the resin. The morphologies of UmPEA1 to UmPEA3 films showed a homogenous and smooth surface, while the UmPEA4 and UmPEA5 films displayed rough surfaces. Overall, these findings prove that the sustainable bioresources MO and CO-based polyols were successfully developed into urethane-modified polyesteramide resins with isocyanates, which promise potency in coating applications. ***This work has been published in the Journey of Applied Polymer sciences (Wiley),* 2023,141(5), e54872.(*doi.org/10.1002/app.54872*).**

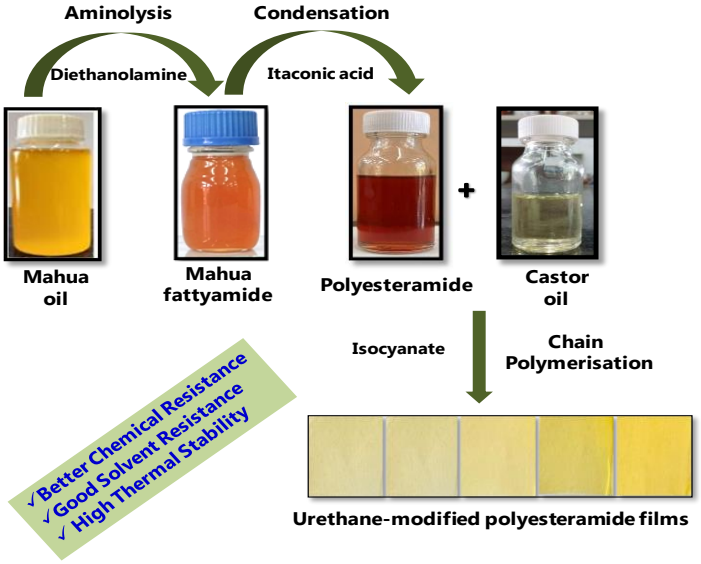

Figure 7.1. Graphical representation of development of PU (urethane-modified polyesteramide) polymer using MO and CO

Chapter 4: Development of waterborne polyurethane polymers using castor oil

In this chapter, WPUs are highlighted as an environmentally friendly alternative to traditional PUs, as many volatile organic solvents are replaced with water. In the present work, the inherent antibacterial properties of curcumin were utilized by adding it as a chain

extender, along with renewable resources like CO, to develop WPUCs. The WPUCs were synthesized using CO as a polyol, isocyanate, dimethylolpropionic acid (DMPA) as an emulsifier, and curcumin in varying mole ratios as a chain extender for coating polyester/cotton (PE/C) blend textiles. The WPUC dispersions had particle sizes ranging from 80.1 nm to 48.2 nm, with zeta potentials between -61.7 mV and -52.2 mV. The characteristic phenolic –OH group peak of curcumin at 3510 cm^{-1} was observed, and its disappearance in the ATR-FTIR spectrum after curcumin was added to the PU prepolymer confirmed its successful integration into the polymeric chain of WPUCs.

The effects of WPUC coatings on PE/C blend fabrics showed significant improvements in washing and rubbing fastness, while a slight decrease in light fastness indicated favorable properties for textile applications. Enhanced stiffness of the fabric was evidenced by increased resistance to air permeability and a noticeable rise in bending modulus. Additionally, the coatings improved abrasion resistance, enhancing the durability of the PE/C fabric, and tensile strength was also notably improved.

Antibacterial activity tests demonstrated a remarkable increase in activity (%R), ranging from 83.12% to 99.99%, attributed to the strong penetration and excellent compatibility between the fabric and WPUCs. Furthermore, higher curcumin content in the polymeric chain led to significant improvements in antibacterial performance, leveraging curcumin's inherent antibacterial nature. Overall, these newly developed WPUCs are eco-friendly, bio-based antibacterial coatings with promising applications for textile fabrics. ***This work has been published in the Journey of Applied Polymer sciences* (Wiley), *2023, 141(24), e55509.(doi.org/10.1002/app.55509).***

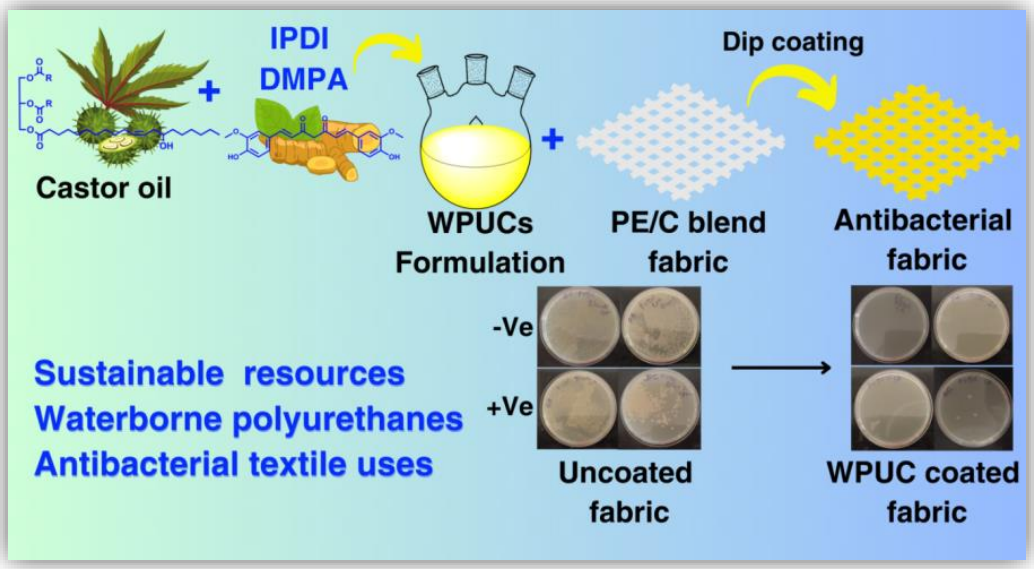

Figure 7.2. Graphical representation of developed WPU polymer using CO and curcumin

Chapter 5: Development of waterborne polyurethane-urea dispersion using castor oil.

In this chapter work, various waterborne polyurethane-urea polymers (WPUUs) were prepared by using CO as a polyol with isocyanate, DMPA as an emulsifier, and 1,8-diaminooctane (OA) with different weight percentages as a chain extender.

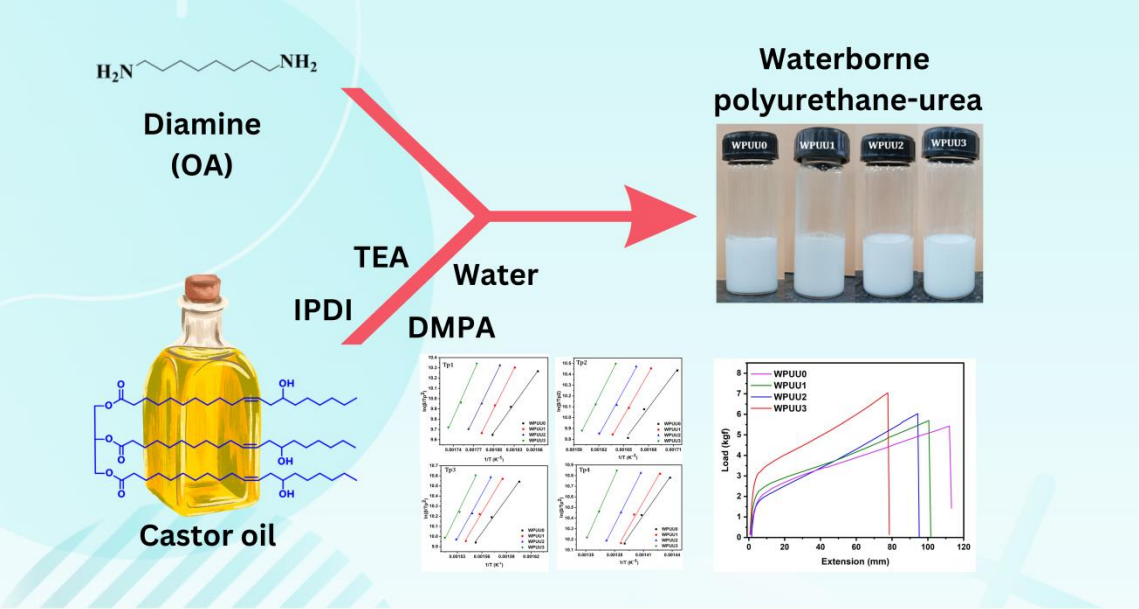

Figure7.3. Graphical representation of synthesized WPUU dispersions

The WPUU dispersions had particles ranging in size from 130.6 to 109.6 nm. The characteristic peak observed at 1636 cm^{-1} corresponds to the urea C=O stretching. After the addition of OA to the PU-prepolymer, the appearance of the peak at 1636 cm^{-1} in the ATR-FTIR spectrum confirmed the successful insertion of OA into the polymeric chain of WPUU. Results of the DSC analysis showed an increase in the Tg value from 36.8°C to 57.4 °C of WPUU films with the increased content of OA. TGA studies showed the four-stage degradation of WPUU at different heating rates of 10, 15, and 20°C/min, respectively. The high thermal stability of the WPUU films is confirmed by the activation energy value of the decomposition of the WPUU film determined through the Kissinger method. The lowest OA content WPUU0 film has Ea values of 76.47 kJ mol^{-1} (Tp1), 84.88 kJ mol^{-1} (Tp2), 93.13 kJ mol^{-1} (Tp3), and 107.67 kJ mol^{-1} (Tp4), while the higher OA content WPUU3 film showed Ea values of 123.98 kJ mol^{-1} (Tp1), 126.32 kJ mol^{-1} (Tp2), 137.04 kJ mol^{-1} (Tp3), and 168.65 kJ mol^{-1} (Tp4), respectively. High activation energy is required for the degradation of WPUU with a high content of OA, as it is the cross-linking network structure in the polymer. The morphologies of all films showed a homogenous and smooth surface. These WPUU films exhibited better properties in chemical resistance, thermal stability, and mechanical strength,

which suggests promising application of these environmentally friendly WPUU materials, particularly in the area of decorative and protective coating.

Chapter 6: Development of polyurethane polymer composite films using castor oil

In this chapter, we successfully synthesized CO-based polyurethane (PU), PU-Silica (PUS), PU-Curcumin (PUC), and PU-Silica-Curcumin (PUSC) composite films using bio-based resources such as CO, rice husk-derived silica nanoparticles (SiO_2NPs), and curcumin for potential applications in the food and packaging industries.

SiO_2NPs have several important characteristics. They are extremely small, with an average size of 54.2 nm, which ensures they are suitable for applications requiring nanoscale precision. Their structure is amorphous, meaning they lack a crystalline form, as shown by a broad XRD peak at 22.8°. SiO_2NPs are composed of 45.87% silicon and 53.14% oxygen, as confirmed by EDX analysis, ensuring their purity and reliability. ATR-FTIR spectra verified the formation of urethane linkages and the successful incorporation of SiO_2 and curcumin. The films exhibited low swelling degrees in organic solvents, with PUC showing the lowest swelling due to higher crosslink density. AFM analysis showed uniformly distributed curcumin and reduced surface roughness, with root mean square (RMS) values of 2.64 nm for PUC and 6.88 nm for PUSC. XPS analysis highlighted the increased oxygen content in curcumin-incorporated films, confirming the integration of functional groups. No curcumin leaching was detected, ensuring safety for applications involving liquid media. Optical analysis confirmed enhanced absorption properties, with a characteristic peak at 424 nm due to curcumin. Thermal analysis showed that the glass transition temperature (Tg) increased from 54°C in PU to 62°C in PUSC, indicating improved thermal stability. TGA demonstrated enhanced thermal degradation resistance, with three distinct degradation stages and the highest stability observed in PUSC. The films also exhibited enhanced wettability. The contact angle decreased from 78° for PU to 68° for PUSC, reflecting increased hydrophilicity. Surface energy calculations showed a rise from 87.94 mJ/m^2 for PU to 100.07 mJ/m^2 for PUSC. Antibacterial tests demonstrated significant activity, with a bacterial growth reduction of over 99% against both Gram-positive and Gram-negative bacteria.

These findings highlight the potential of developing eco-friendly polyurethane coating films with potent antimicrobial properties, leveraging sustainable bio-based resources for advanced applications in the food and packaging sectors.

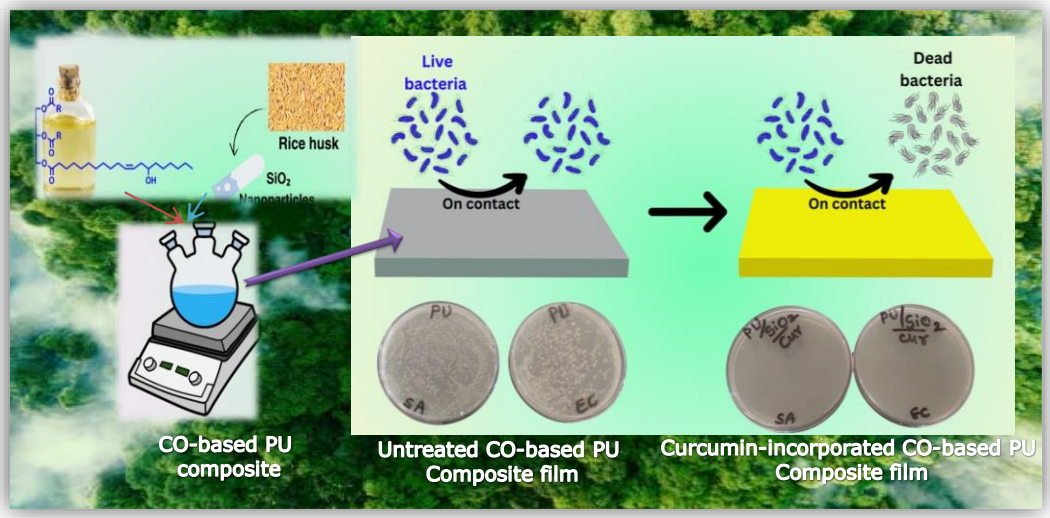

Figure 7.4: Graphical representation of synthesized PU composite used as antibacterial material

Overall, this thesis demonstrates the synthesis of various polymers, including UmPEA using MO and CO, WPUC with CO and curcumin, WPUU with CO and OA, and PU composites incorporating CO, SiO_2NPs, and curcumin. The focus of the research was on the synthesis of VO-based polymers, particularly PU and WPU, using CO and MO as primary renewable polyols. CO was employed as an unmodified source for direct reaction with isocyanates, while MO underwent chemical modification to form suitable polyols for polymerization. The CO-based PU polymers exhibited excellent antimicrobial and coating properties, while the MO-based PU polymers demonstrated promising thermal and mechanical stability, making them ideal for protective coatings.

These VO-based PU polymers were evaluated for their potential applications in antimicrobial activity, packaging, and eco-friendly coatings, highlighting their potential for sustainable material development.