Synopsis

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Development of Non-edible Vegetable Oil based Polymers and their Applications

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By:

Vikashkumar Manojbhai Ganvit

Under the Supervision of

Dr.Rakesh K. Sharma

सत्यं शिवं सुन्दरम्

Applied Chemistry Department
Faculty of Technology and Engineering
The Maharaja Sayajirao University of Baroda,
Vadodara-390001, Gujarat, India

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Development of Non-edible Vegetable Oil based Polymers and their Applications

Vegetable oil (VO) as a renewable resource is an ideal candidate for polyol production to replace petrochemicals because of its vast abundance, high availability, cost-effectiveness, high biodegradability, and nontoxicity.[1, 2] Many VOs have active sites (such as double bonds, ester linkages, hydroxyl, and α-methylene groups), which can be modified by many routes to produce different oleochemicals some modification presented in Figure 1A .[3] VOs are often modified to add hydroxyl groups to their structures. This gives rise to VO as polyols, which are essential for making polyurethane (PUs).[4] The modification of VOs through various reaction processes have been known. On the contrary, food crisis issues often limit the utilization of edible VOs in industrial applications worldwide shown in Figure 1B. However, many reports have shown the synthesis of polyols from different VOs such as cottonseed, canola, castor, cashew nut, jatropha, linseed, mahua, nahar, neem, soybean, and tobacco seed oils and their frequent use in the production of PUs.[5, 6]

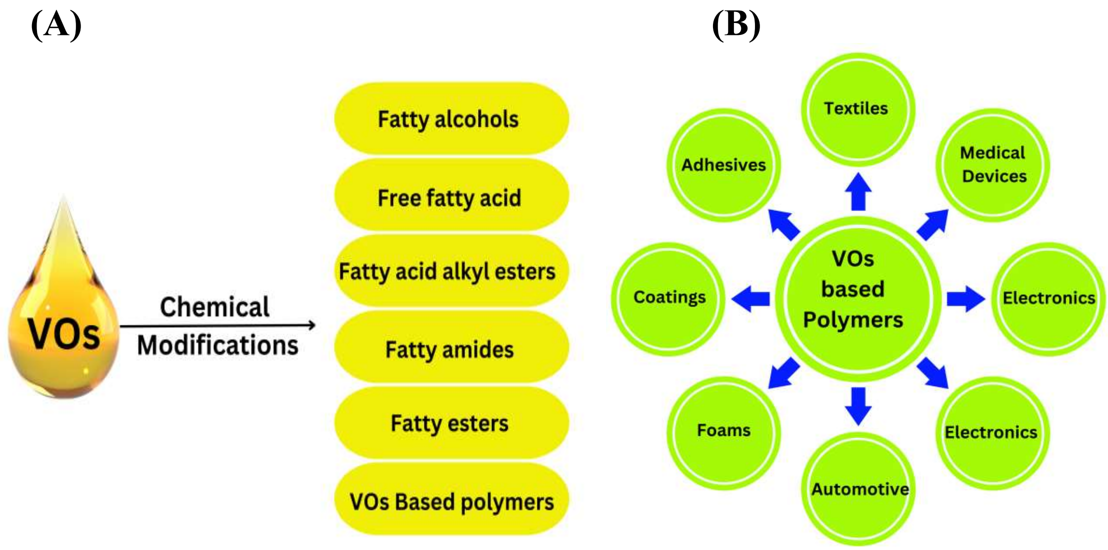

Figure 1: (A) Modifications of vegetable oils and (B) Uses of VOs based polymers

The utilization of non-edible VOs to obtain value-added products reduces the consumption of edible VOs, which is the demand of today's chemical industries. Therefore, the search and assessment of the indigenous non-edible VOs is a promising approach in polymer synthesis.[7] Non-edible VO is often used for the development of PUs, alkyds, and epoxy polymers (Figure 2). Non-edible VO and their physicochemical characteristics are listed in Table 1.

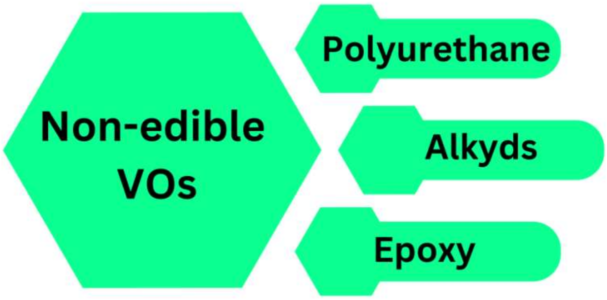

Figure 2: Non edible VOs based Polymers

Table 1: Non-edible VOs and its physicochemical characteristics

Non-edible VOs	Saponification Value (mg KOH/g)	Iodine Value (g of I_2/100 g)	Acid Value (mg KOH/g)	Hydroxyl Value (mg KOH/g)
Castor oil	185	82	0.2	165
Linseed oil	160	181	8.3	-
Neem seed oil	260	89.3	14.3	-
Karanja oil	182	89.9	11.5	-
Mahua oil	187	62.4	0.4	-
Jatropha oil	100	95	2	-

Out of these important polymers, the polyurethane (PU) is prepared from petroleum-based polyols and diisocyanates conventionally which have many disadvantages to human beings and the environment. Recent trends in PU development are the gradual replacement of petroleum-based resources by renewable and sustainable materials for its production. The dependence or consumption of fossil resources can reduce a large extent by replacing it with a biobased one. The growing demand for PU is still increasing as it can be fabricated into different products such as rigid and flexible foams, adhesives and sealants, elastomers, and coatings by the judicious addition of the monomers viz., polyols and diisocyanates. These monomers can be successfully synthesized from renewable feedstocks for instance carbohydrates[8], lignin[9], non-edible VOs[10], and starch[11]. But the major share of PU comprises polyol and the recent studies mainly focus on non-edible VO derived renewable polyols to produce PU[12]. It substantially reduces environmental pollution and carbon footprints. Moreover, it is biodegradable and non-toxic.[13] Amongst the various types of non-edible VO, castor oil (CO), and mahua oil (MO) are the best candidates for the synthesis of PU polymers.

CO is obtained from the seeds of the plant known as *Ricinus communis L.*, and it is believed to have its origins in various areas, including Africa, Asia, India, and China.[14] CO contains ~90% of the unsaturated fatty acid ricinoleic acid, and this great amount of ricinoleic acid gives CO uniqueness among other vegetable oils.[15] There has been a continual interest in CO as a renewable raw material in the chemical and polymer industries. In addition to the ester linkage and double bond present in ricinoleic acid, the presence of the hydroxyl group allows for versatile chemical modifications, making castor oil a suitable raw material for the polymer industry.[16]

CO and its derivatives, such as ricinoleic acid, have been used to prepare PUs directly or after modifications. The CO-based PUs display good mechanical properties, comparable to those of petrochemical PUs and show applications as wood adhesives, flexible foams and hard elastomers. Also CO reacts with diisocyanate and DMPA to give pre-polymer which further reacts with various diamines and water to produce waterborne polyurea-urethane (WPUUs) polymers.[17]

The mahua tree is found in the tropical region of India, where it does not require much attention. It is a nontraditional plant, also known as the Indian butter tree, as it solidifies at room temperature.[18] The MO is obtained from the seeds of mahua. MO has the appearance of a pale yellow color with a pleasant odour and taste. MO seed fruits contain 16.9% protein and 51.5% oil. The fatty acid composition of MO showed the presence of 46.3% (Z)-octadec-9-enoic acid and 17.9% cis, cis9,12-octadecadienoic acid as the prime unsaturated and 17.8% hexadecanoic acid and 14.0% octadecanoic acid as the main saturated fatty acids. We know about the chemistry of MO, the best way to use it has been to make biodiesel. But researchers also want to use these sources to make a variety of useful polymers.[7]

To understand the importance of non-edible VO based polymer, the present research is aimed at developing and well-characterizing polymers (specifically polyurethane (PU), and waterborne polyurethane (WPU)) using CO and MO as polyols and diisocyanate as a curing agents for various useful applications such as antimicrobial properties, coating, and packaging materials.

The developed PU and WPU polymers in the present work have been evaluated for their antimicrobial as well as coating applications.

In order to examine CO- and MO-based PU and WPU polymers, a range of sophisticated characterization techniques were employed. Some of these were spectral, like FTIR, UV-Visible, and UV-Fluorescence spectroscopy; thermal, such as DSC, TGA, and DTA; chemical; XPS; scattering, such as DLS, Zeta, and versatile XRD; and EDX spectroscopy. In the present work, the SEM and AFM methods are also utilized for surface analysis. Not only that, the synthesized PU polymers were also well evaluated for antimicrobial activity, coating, fastness, chemical resistance, storage stability, and flame retardancy properties.

In order to meet all objectives of the present work, the contents of the thesis are summarized into seven chapters.

Chapter 1: General Introduction

The present chapter covers the introduction of vegetable oils (VOs) and their role in the development of a variety of polymers. The chapter also mainly focuses on non-edible VOs, such as mahua oil (MO) and castor oil (CO), for PU polymer synthesis. The relevant research outputs in the area of the present work have been provided.

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

In this chapter, the extraction of two non-edible CO and MOs from their oil-bearing materials, like seeds or fruits, has been provided with all the necessary steps. The physicochemical properties of extracted non-edible VOs, including saponification value, acid value, iodine value, specific gravity, and chemical composition, have been discussed.

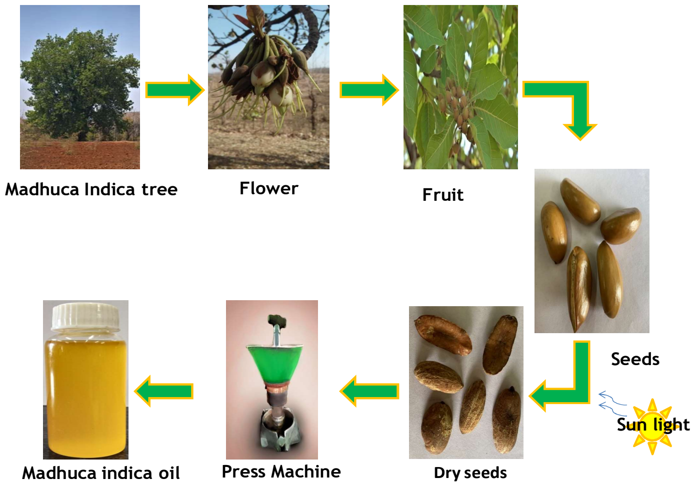

Figure 3: Pathway of the extraction of MO from agricultural resources.

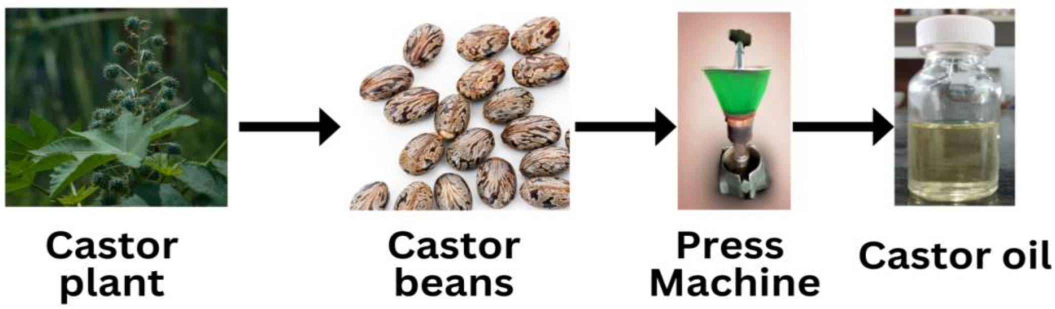

Figure 4: Pathway of the extraction of CO from agricultural resources

Chapter 3: Development of polyurethane (urethane-modified polyester amide) polymers using mahua oil and castor oil

In this chapter, the development of urethane-modified polyesteramide (UmPEA) films using mahua (MO) and castor (CO) oils, as renewable resources. MO and diethanolamine were reacted to form mahua fatty amide (MFA), which was further reacted with itaconic acid to prepare polyesteramide. In order to synthesize the UmPEA polymeric films, different proportions of polyesteramide and CO as polyols were reacted with isophorone diisocyanate. The developed UmPEA films have been evaluated and found excellent chemical resistance against water, acid, alkali, salt, and organic solvents. The thermal stability of the UmPEA films was investigated through TGA and DSC analyses, and their Tg values are between 69.1°C and 56.1°C for UmPEA films, which indicated that a higher content of CO enhances the Tg, and it was also found that the films were highly stable. The measured activation energy (Ea) values [224 kJ mol^{-1} (Tp1) and 226 kJ mol^{-1} (Tp2)] indicate that the CO enhances the thermal stability of the films due to better cross-linking density occurring through the high hydroxyl groups of CO as the polyol. The results of this chapter demonstrate that the newly developed UmPEA films can be potent coating materials.

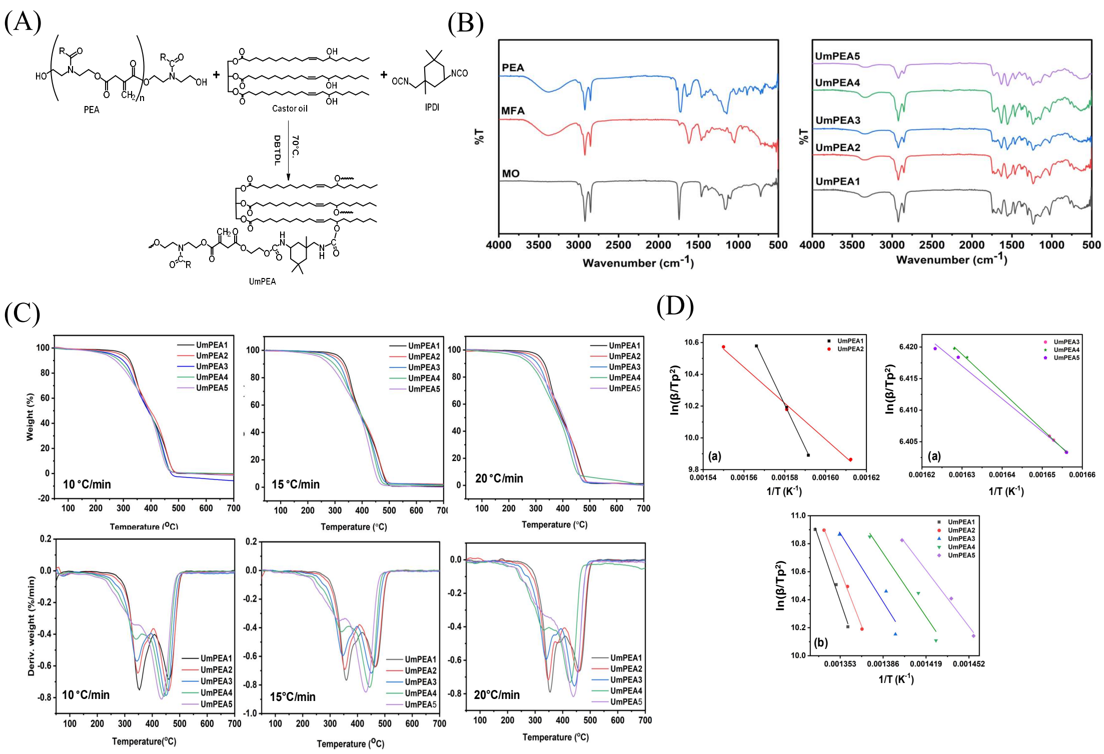

Figure 5: (A) Synthesis of Urethane-modified Polyurethanes, (B) ATR-FTIR of MO, MFA, PEA and Urethane-modified Polyurethanes, (C) TGA and DTA graphs of UmPEA films, (D) Kissinger plot of UmPEA films at two different stages of the degradation :(a) Tp_1 and (b) Tp_2.

Chapter 4: Development of waterborne polyurethane polymers using castor oil

In this chapter, the synthesis of newer waterborne polyurethane polymers (WPUCs) using bio-resources such as castor oil as a polyol and curcumin as a chain extender have been presented. Different mole ratios of curcumin in the synthesis of WPUC polymers were explored and characterized through DLS, Zeta, and ATR-FTIR. The WPUC dispersions had particles ranging in nano-size from 80.1 nm to 48.2 nm, and their zeta potentials were between -61.7 mV and -52.2 mV, which indicated the better stability of the dispersions. The ATR-FTIR of WPUC clearly confirmed the successful insertion of curcumin into the PU polymeric chain. The WPUCs have been coated on polyester/cotton (PE/C) blend fabric through dip coating technique and showed a better improvement in colorfastness properties, reduced air permeability, increased bending modulus, significantly improved abrasion resistance and an increment in tensile property were also evaluated for antibacterial property observed showed a bacterial inhibition rate of 83.12–99.9999% ($p < 0.001$) compared with blank fabric against *E. coli, P. aeruginosa, S. aureus,* and *B. cereus* as inherent properties of curcumin. The antibacterial effects were found to be better with a higher amount of curcumin incorporated in the polymer chain of WPUC. Overall, this chapter provides valuable insights for the possible textile applications of synthesized WPUCs for any blend of fabrics.

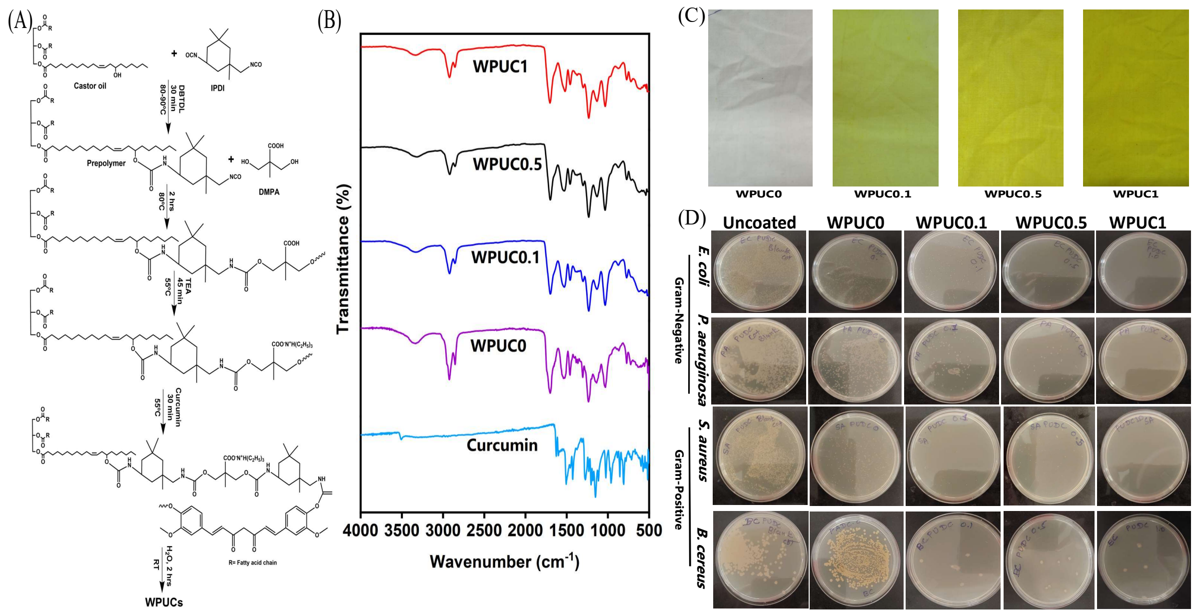

Figure 6: (A) Synthesis of WPUCs Polymer, (B) ATR FTIR of WPUC0 to WPUC1 and curcumin, (C) Coated and uncoated PE/C blend fabric with WPUCs, (D) Antibacterial activity of coated and uncoated PE/C blend fabric

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

In this chapter, a series of waterborne polyurethane-urea dispersions (PUUs) using CO as bioresource have been reported. Diamine was employed as a chain extender to investigate the role of counteraction on the properties of PUUs and their corresponding synthesized cured films. The developed PUU dispersion was characterized by particle size analysis, electrolytic stability, and storage stability. The cured film these developed WPUUs were characterized by FT-IR (ATR), TGA, DSC, SEM, and UTM (universal testing machine). It was found that the waterborne PUU with increasing counteraction of diamine exhibits a smaller particle size and good storage stability, while the corresponding cured film possesses good thermal stability, mechanical strength, and acceptable surface properties. This chapter demonstrates the WPUUs developed here will be potent for coating application.

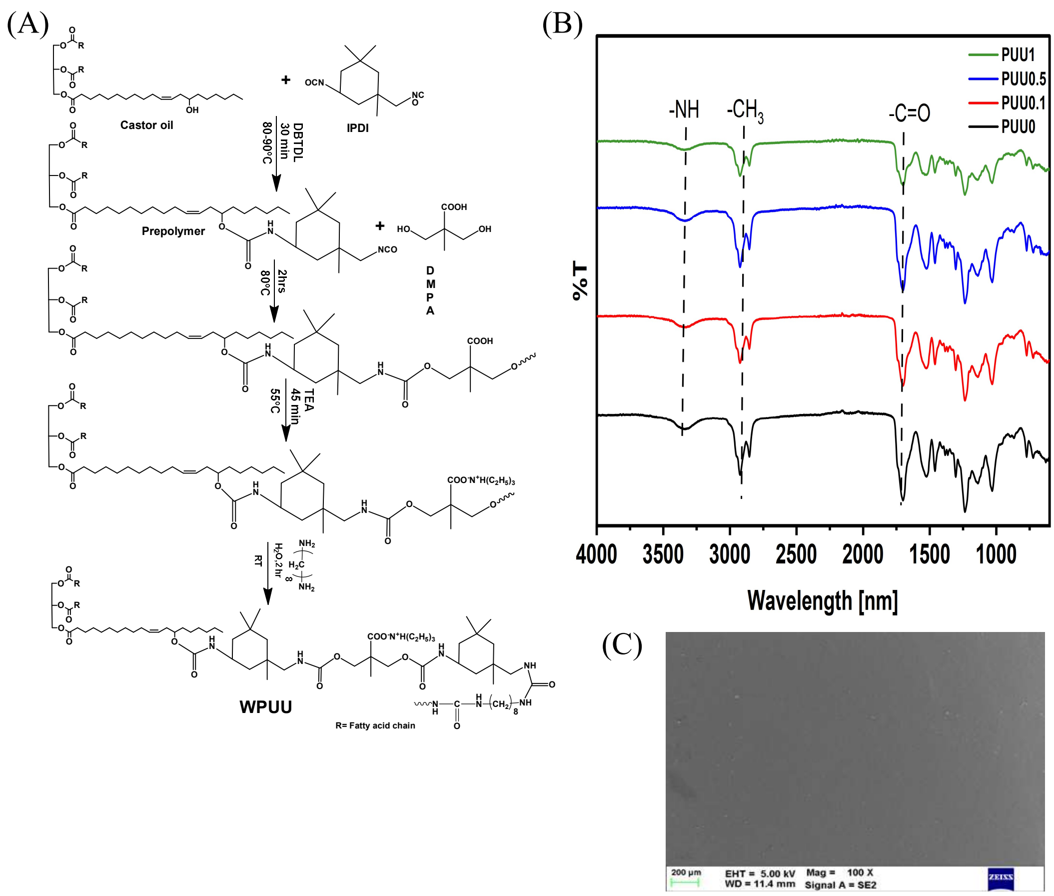

Figure 7: (A) Synthesis of WPUUs from Castor oil, (B) ATR-FTIR of WPUUs films, (C) SEM image of WPUU1

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

In this chapter, the various CO based PU composite films like polyurethane (PU), polyurethane/SiO_2 (PU-SiO_2), polyurethane/curcumin (PU-Cur), and polyurethane/SiO_2/curcumin (PU-SiO_2-Cur) have been explored. The composite PU-Cur and PU-SiO_2-Cur were prepared through the swell-encapsulation-shrink method. All composite samples are characterized for structure, degree of swelling, thermal properties, optical properties, leaching behaviour, photoluminescence, surface morphology, hydrophobicity, chemical content and antibacterial activity. DSC results have revealed that there have been slight shifts in the Tg in order to increase the PU with the addition of nano-SiO_2 and encapsulation of curcumin. The developed composites have shown very strong photoluminescence. The antibacterial properties of a synthesized nanocomposite were tested against *S. aureus* and *E. coli* using the colony-counting method. As per the findings, the nanocomposite films PU-Cur and PU-SiO_2-Cur containing curcumin showed very promising antibacterial activity. Finally, this chapter provides the use of PU composite films as effective antibacterial materials for use in the packaging process.

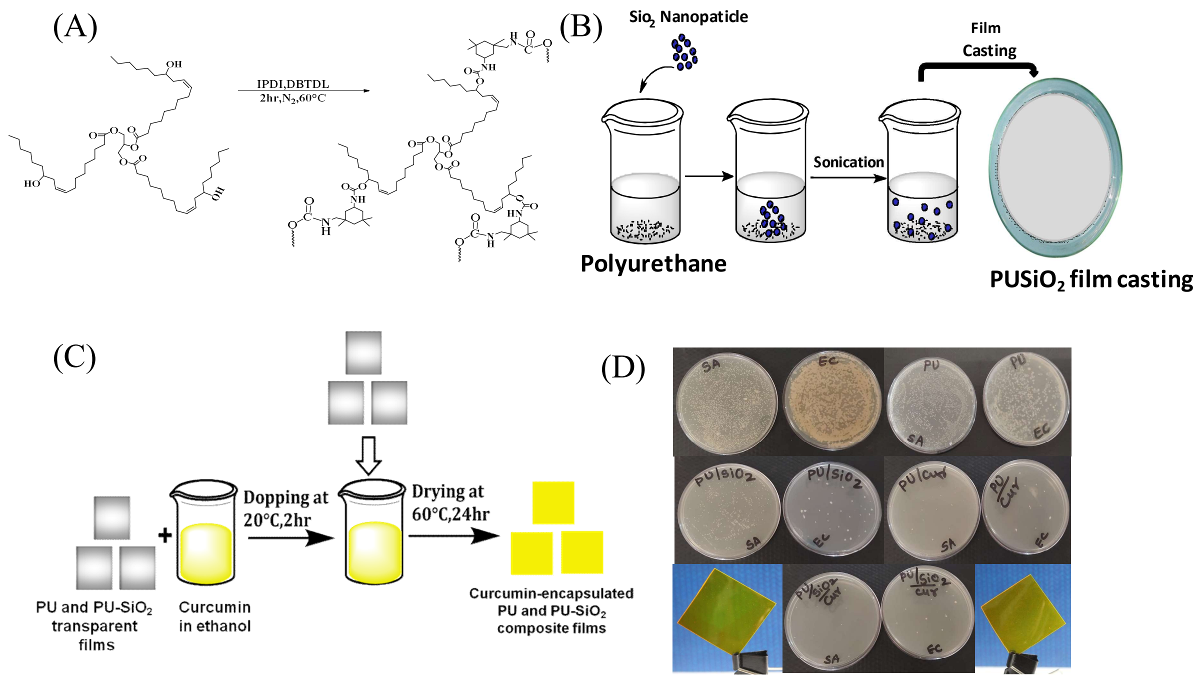

Figure 8: (A) synthesis of CO based polyurethane (B) Rout of synthesis of PU-SiO_2 (C) Development of PU-Cur and PU-SiO_2-Cur (D) Antibacterial activity and curcumin encapsulated films PU-Cur (Right) and PU-SiO_2-Cur (Left)

Chapter 7: Summary and Conclusions

The thesis ends with a summary of all the reported work and general conclusions drawn from the investigations.

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❖ List of the Research Publications

Under the Thesis work

1. **Ganvit VM**, Sharma RK. Recent developments of Madhuca indica (Mahua) oil-based polymers: A mini review. Polymers from Renewable Resources. 2022 ,13, 55-70.
2. **Ganvit VM**, Patel V, Patel M, Dharva A, Sharma RK. Synthesis, physicochemical and thermal properties of urethane-modified polyesteramide films using mahua and castor oil as sustainable resources. Journal of Applied Polymer Science. 2023, e54872.
3. **Ganvit VM**, Bhandari PD, Kunjadiya A, Mansuri J, Bambhaniya SB, Mandot AA, Sharma RK Synthesis and Characterization of Waterborne Polyurethane Dispersions using Castor oil and Curcumin as Sustainable Resources for Antibacterial Coating Applications. Journal of Applied Polymer Science (Under review)

Other than the Thesis work

1. Bambhaniya SB, Mandot AA, **Ganvit VM**, Sharma RK. Biomass derived coating material against petrochemical based polymer for architectural fabric. Man made Textile in India. 2023, 8, 274-279.

❖ List of the Papers presented in the conferences/ Seminars/ Workshops/ Online Webinar

Conferences

1. Incorporation of Rice husk ash-derived Silica nanoparticles in Castor oil- based Polyurethanes: Thermal and Mechanical Properties.

   Vikash M. Ganvit, Mehul Patel and Rakesh K. Sharma at International Seminar on Advanced Materials and Applications-2022 (ISAMA-2022), Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara (18th July, 2022) (Oral).

2. Investigations Structural, Thermal and Antibacterial Properties of Castor oil-based Polyurethane/Curcumin Nanocomposite Films.

   Vikash M. Ganvit, Mehul Patel, Anju Kunjadya, Rakesh K. Sharma at National Conference on Material and Chemical Sciences-2023 (MEMCS-2023) Parul University, Vadodara (6-7th January) (**Poster- Second Prize**).

3. Synthesis and Characterization of Urethane-modified Polyesteramide Films using Mahua and Castor oil as Bioresources: Exploring Physicochemical and Thermal Properties.

   Vikash M. Ganvit, Mehual Patel, and Rakesh K. Sharma at National Conference on Emerging Technologies in Chemistry & their Applications-2023 (NCETCA-23) Government College , Shirohi, Rajasthan (19-20th October 2023) (Poster).

Online Conference Attended

1. One day online seminar on 'adsorption and Adsorbed : theory and applications' organize by department of chemistry, MANIT- Bhopal, University of St. Andrew-Scotland (UK) and DCRUST- Mathura on 8th March 2021.
2. Virtual international conference on multifunctional advanced materials (VICMAM-2021)' organized by Department of Chemistry, JVM's Degree College in collaboration with Association of Chemistry Teachers (ACT) on 9-10th August, 2021.

Workshop and Webinars

1. Webinar on Recycling of Plastic Waste to Plastic Composites Products organized by Asian polymer association on 10th April, 2021.

2. Webinar on polymer characterization by analytical pyrolysis technology organized by research & innovations webinars on 30th April 2021.
3. National level one week Faculty Development Program on Research methodology by Kamla Nehru Mahavidhyalaya, Nagpur, on 26th June to 1st may, 2021.
4. Three day national online FDP on ICT tools for effective teaching learning organize by IQAC, Kamla Nehru Mahavidhyalaya, Nagpur, on 8-10th June, 2021.
5. Webinar on polymer for gas separation membranes: where are we now? Organized by research & innovations webinars on 12th August 2021.
6. National webinar on recent advances in chemistry organized by the department of chemistry & IQAC, Govt. G.N.A. PG College, Bhatapara, Chhattisgarh on 26th August 2021.
7. One week training program on "Synergistic training program utilizing the scientific and technology infrastructure (STUTI)" at NIT Jalandhar, Panjab on 6-12th February 2023.

Signature of Candidate

(Vikash M. Ganvit)

Endorsement of Supervisor;
Synopsis is approved by me

Dr. Rakesh K. Sharma
Guide

Head
Applied Chemistry Department

Dean
Faculty of Technology and Engineering