CHAPTER 1

General Introduction

1.1. Resources for polymer development

The high demand for petroleum-derived materials has led to the reduction of natural petroleum reserves. It is already estimated that a serious shortage in crude oil and significant increase in its costs will be noticed as early as 2040.[1] Approximately 10–12% of crude oil is currently used in the production of polymers.[2,3] Polymers derived from petroleum exhibit a diverse range of desirable physical properties, including durability, lightweight, and resistance to corrosion and chemicals. Also, petroleum-based polymers find extensive applications across various sectors, from packaging to construction materials[4,5] and medical devices.[6] Unfortunately, petroleum-based polymers do not easily decompose and continue to remain almost untouched for centuries.[7] Concerns over environmental impact, coupled with the shortage of petroleum supplies, have spurred considerable interest among industrialists and researchers in exploring alternative options to petroleum-based polymers.[8]

Nowadays, the utilization of renewable resources for polymer development has garnered attention from researchers and scientists as an alternative to petroleum resources.[7,9] There are many reasons for promotion of renewable sources, including their abundant availability, reliable regeneration, and eco-friendly nature.[10] Additionally, petroleum sources come with certain disadvantages such as finite availability, rising prices, and supply uncertainties, which further promote the use of renewable sources.[11] Renewable sources can be defined as those that can be replenished by nature after a certain interval of time. **Figure 1.1. s**hows the renewable resources available for the possible use in the polymers and material development.

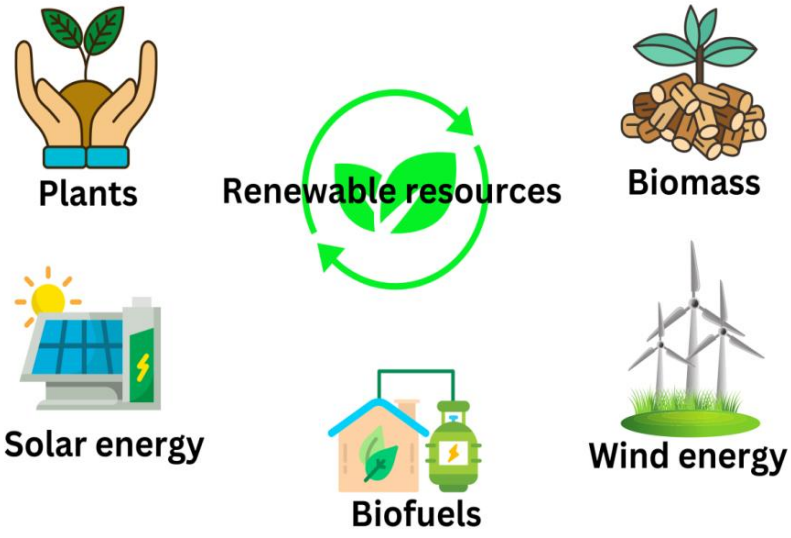


Figure 1.1. Renewable resources for materials development

Non-renewable resources, also known as conventional resources, cannot be regenerated by nature within a short period of time, and there is concern about the depletion of their current reservoir after consumption, as it may take thousands of years for them to form as discussed for petroleum resources.[12,13] The non-renewable resources is shown in the **Figure 1.2**.

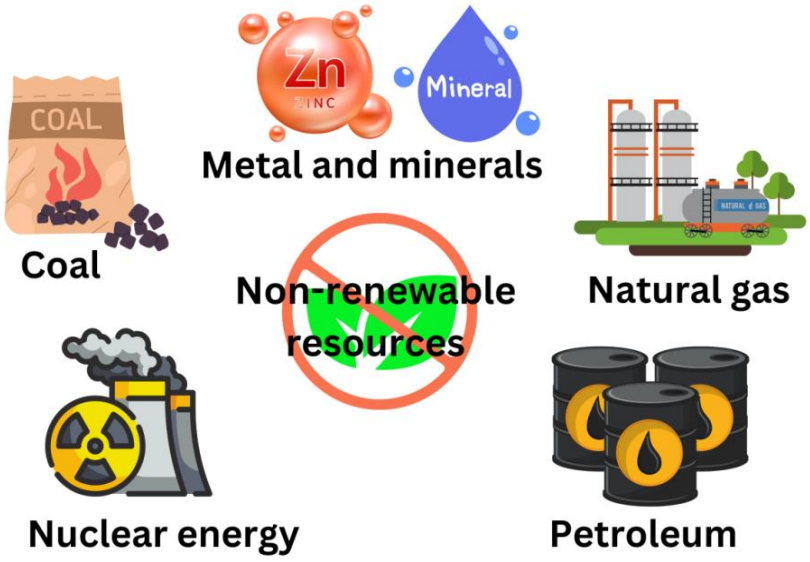


Figure 1.2. Non-renewable resources for materials development

While petroleum-based products and their technology for producing monomers for polymer synthesis are well-established, they face various socio-environmental issues. This has prompted researchers to develop intermediates using renewable resources as a replacement for petroleum.[14,15] Thus, nowadays major technologies for polymer synthesis are increasingly oriented towards greener synthesis, utilizing renewable sources. These synthesis take into account economic viability, environmental friendliness, low emission of hazardous pollutants, and the challenges associated with petroleum sources.[16]

Amongst the renewable resources, the biomass/agricultural feedstocks is referred as very important because of abundant availability and only 7% of it used by mankind. Examples of agricultural feedstocks include cellulose, proteins, starch, polysaccharides, sugars, natural fibers, and glycerol esters derived from vegetable oils (VOs) or fats.[17]

The most preferred renewable sources in polymer synthesis are vegetable oils (VOs), cellulose, and natural fibers. These materials hold the potential to serve as green monomers or intermediates and have garnered significant attention in the development of polymeric materials.[18] VOs have garnered significant attention from researchers for resin preparation. This is due to their abundant availability, potential variants, cost comparability with

petroleum, and functionality suitable for modifications.[19] Furthermore, the biodegradability of VOs made them crucial feedstock for polymers intended for use in environmental, social, and energy-related applications. This helps reduce issues surrounding waste disposal and the depletion of non-renewable resources.[20]

The applications of such polymers include composites, coatings, elastomers, foams, and more. In the area of coatings, several researchers have directed their attention towards developing polymeric coatings based on renewable sources, both in laboratory and industrial scale.[21] For this purpose, numerous routes have been explored, including alkyds, polyurethanes (PUs), polyesters, phenols, silicates, acrylics, epoxies, and more.[12]

1.2. Vegetable oils (VOs): *Renewable source for polymer development*

VOs are regarded as a vital category of renewable resources within the chemical and polymer industries. VOs play a significant role in the production of monomers, polymers, and fine chemicals.

VOs are triglycerides formed from glycerol and long-chain fatty acids (FAs), as depicted in the accompanying **Figure 1.3**. FAs constitute 94-96% of the total mass of a triglyceride molecule.[22] Typically, the chain length of FAs ranges from 14 to 22 carbons, with C16 and C18 being the most prevalent, and may contain 0 to 3 double bonds per chain.[22–24]

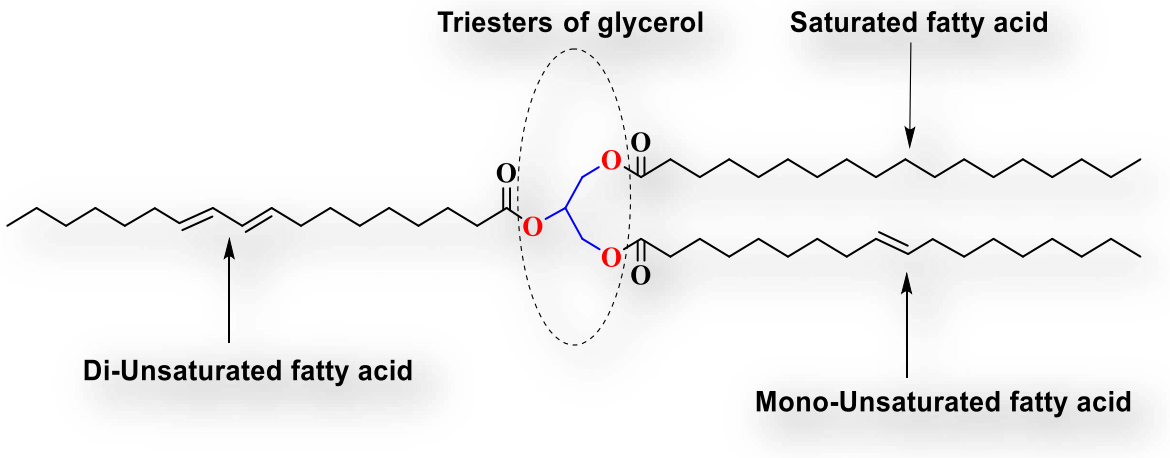


Figure 1.3. General molecular structure of VO

Although over 1000 FAs have been identified, only about 20 are found in quite good amounts in VOs.[25,26] The composition of FAs in VO varies depending on factors such as the plant species, crop, season, and cultivation conditions.[27]

Table 1.1 provides a list of the most prevalent FAs found in VO compositions and their molecular structures are displayed in **Figure.1.4**.

Table 1.1. List of the common FAs

Common name	IUPAC name	C:BD	Formula
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$
Stearic acid	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$
Lignoceric acid	Tetracosanoic acid	24:0	$C_{24}H_{48}O_2$
Behenic acid	Docosanoic acid	22:0	$C_{22}H_{44}O_2$
Arachidic acid	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$
Oleic acid	cis-9-Octadecenoic acid	18:1	$C_{18}H_{34}O_2$
Palmitoleic acid	cis-9-Hexadecenoic acid	16:1	$C_{16}H_{30}O_2$
Linolenic acid	cis,cis,cis-9,12,15-Octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$
Linoleic acid	cis,cis-9,12-Octadecadienoic acid	18:2	$C_{18}H_{32}O_2$
α-Eleostearic acid	cis,trans,trans -9,11,13-Octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$
Erucic acid	cis-13-Docosenoic acid	22:1	$C_{22}H_{42}O_2$
Ricinoleic acid	12-Hydroxy-cis-9-octadecenoic acid	18:1	$C_{18}H_{34}O_3$
Vernolic acid	12,13-Epoxy-cis-9-octadecenoic acid	18:1	$C_{18}H_{32}O_3$
Licanic acid	4-Oxo-cis,trans,trans-,11,13-octadecatrienoic acid	18:3	$C_{18}H_{28}O_3$

*C: *Indicates the no. of C atoms* and DB: *The no. of double bonds in the FA chain*

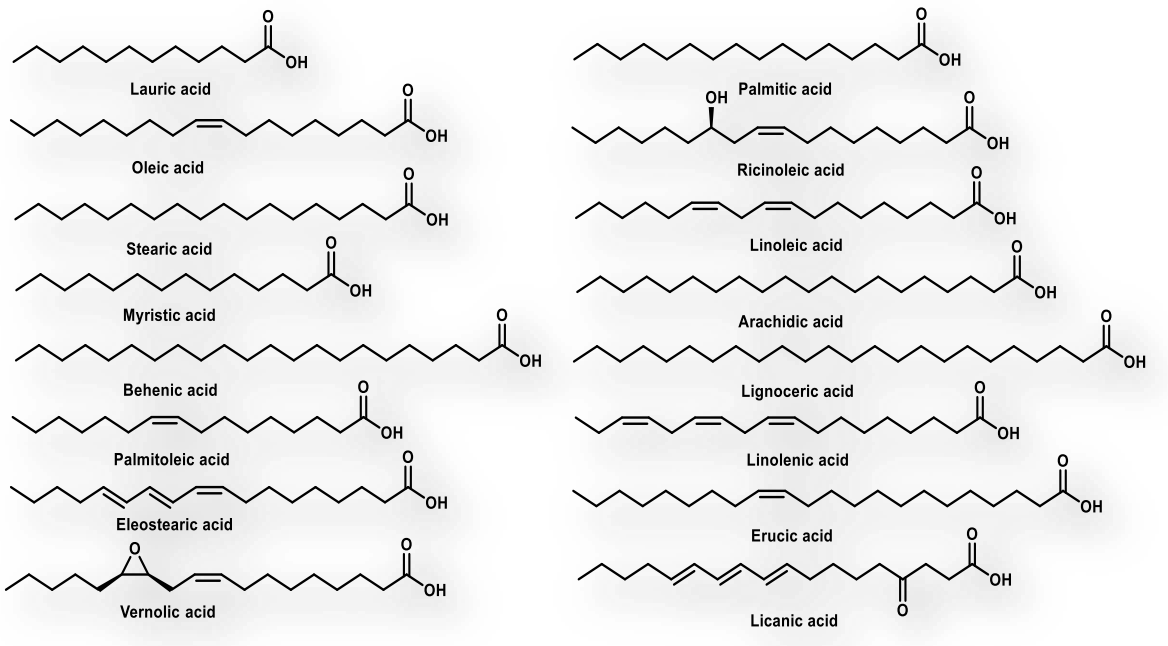


Figure 1.4. Molecular structures of various FAs

Many FAs exhibit saturation likes lauric, myristic, palmitic, stearic, arachidic, behenic, and lignoceric acid, while some (e.g. oleic and erucic acids) demonstrate monounsaturated characteristics, and others polyunsaturated (e.g. linoleic and linolenic acid). Typically, in the VOs, the cis isomers of FAs are found (as observed in oleic and linoleic acid) mostly, although small quantities of trans isomers (α-eleostearic and licanic acids) may also be present. Moreover, the majority of double bonds in FAs are non-conjugated, resembling the configuration of linoleic and linolenic acids, whereas a select few exhibit conjugation, as found in eleostearic and licanic acid. Finally, some oils contain FAs with additional functional groups alongwith their chains, such as ricinoleic, vernolic, and licanic acid, featuring hydroxyl, epoxy, and carbonyl groups, respectively.[25,28,29]

Dependent upon the necessity in the ecosystem, VOs can be classified as edible oils (EVOs) (which can be used in food) and non-edible oils (NEVOs) (which cannot be used in food). Due to the presence of harmful gradients, NEVOs are not safe for human consumption. Examples of EVOs and NEVOs are shown in the **Figure 1.5**.

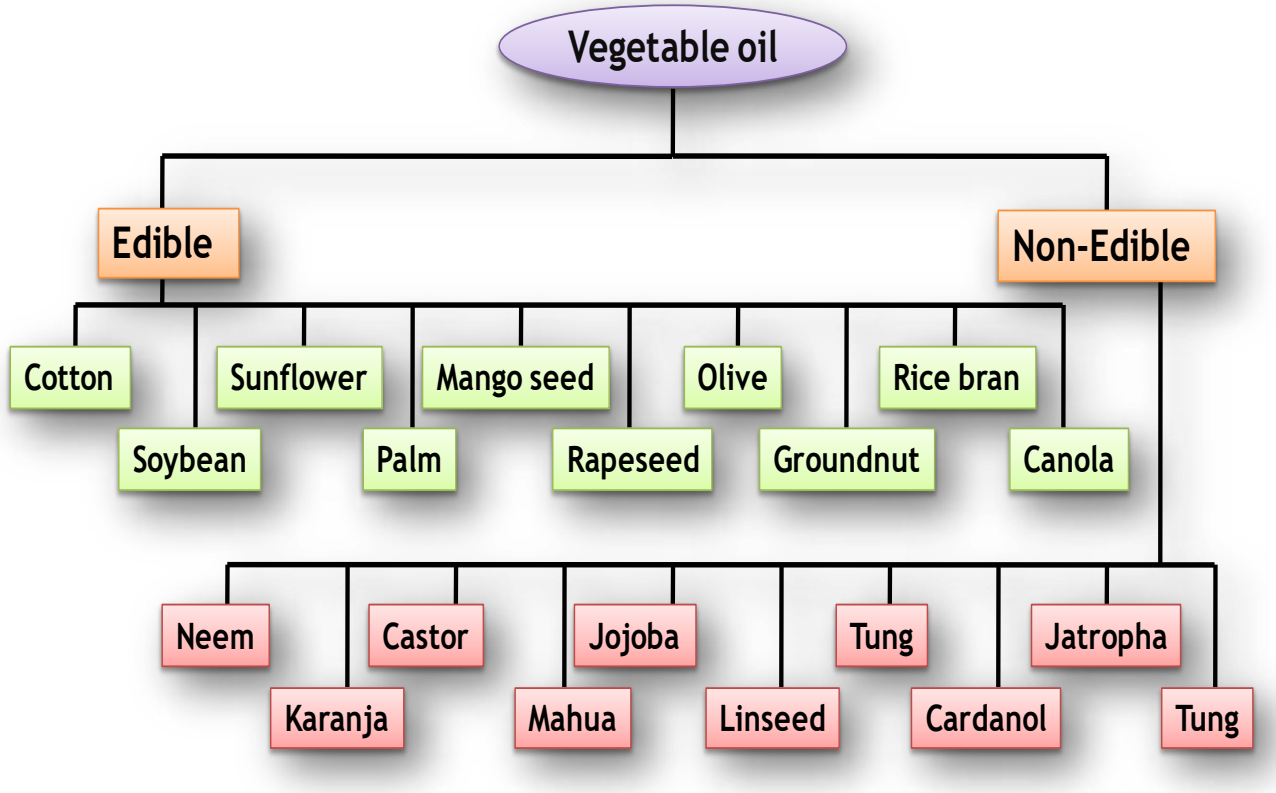


Figure 1.5. Examples of edible and non-edible VOs

1.2.1. Non-edible VOs (NEVOs) : *Important sources for polymer development*

NEVOs such as those from castor seeds, neem, karanja, polanga, rubber, jatropha, linseed, Mahua, cashew nut shell and nahar seeds have already been proven to transform into value-added materials.[30] The process of preparing polyols (one of the monomer) from NEVOs is very similar to that from EVOs, utilizing various pathways as illustrated in **Figure 1.6.**

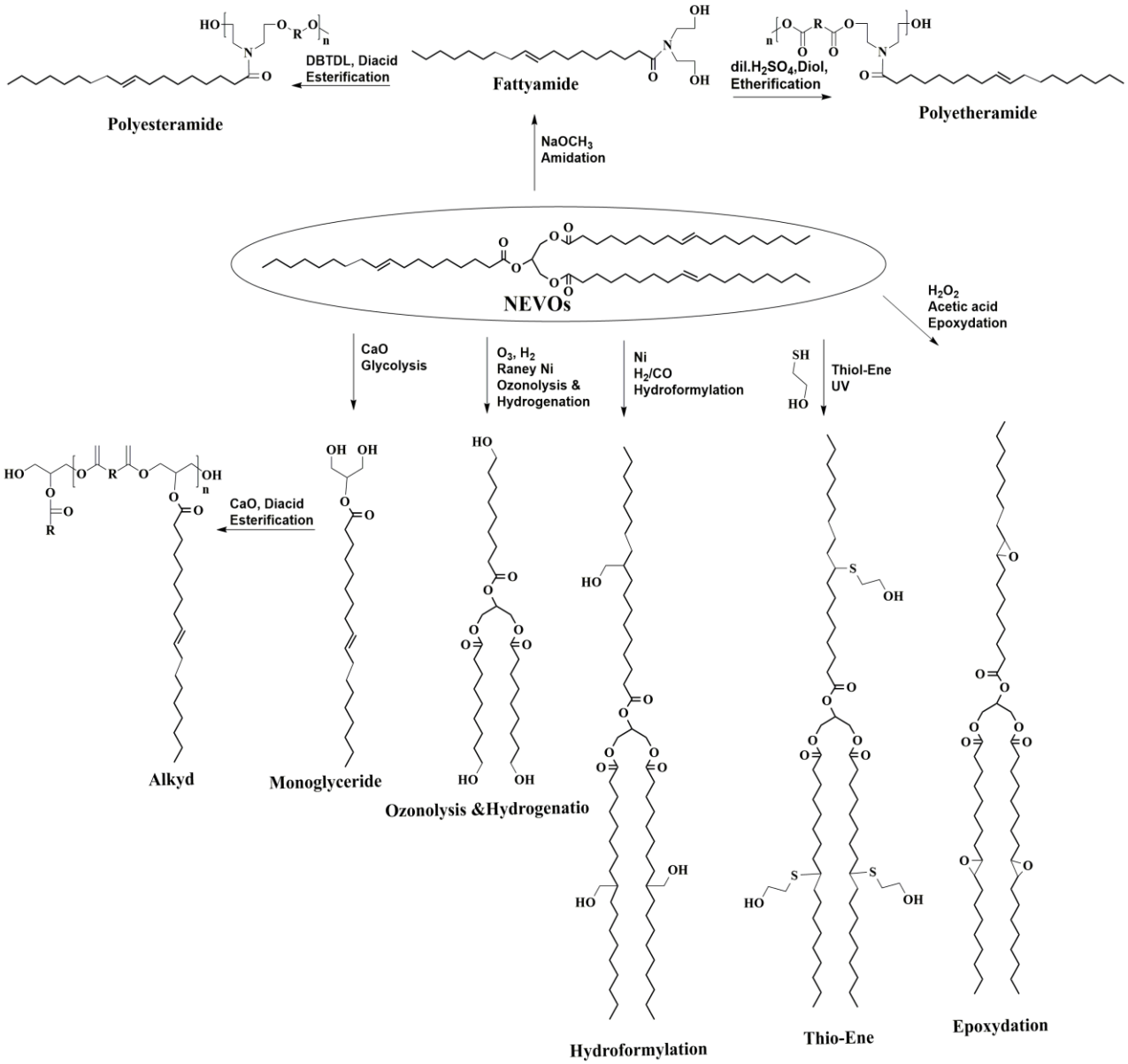


Figure 1.6. Preparation of different polyols from NEVOs

NEVOs are used to prepare polymeric binders for coating, flooring materials and various resin-based applications. These oils have also been widely used in the preparation of inks, lubricants, diluents, agrochemicals, plasticizers, coatings, smart materials, food, composite materials and so on.[31–33] The availability of NEVOs as the raw materials are easy

as their sources (agricultural feedstocks) have flexibility of planting in non-agricultural lands with little fertility, cultivated in very low rainfall/dry zones as well as higher rainy/wet zones, do not contest with already available agricultural resources.[34] It can be utilised in additional chemical processes or burnt to generate heat and power, can repair degraded lands, reduce CO_2 emissions and have strong resistance to disease and insect pests. The main benefits of NEVOs are the natural portability of their liquid, being easily available, renewable, high heat content, low sulphur composition, residual aromatic content and being biofreindly.

Amongst many NEVOs, the rich source of castor oil (CO) and mahua oil (MO) in India is now being used by polymer chemists for the development of various materials and may be the future choice of renewable sources as precursors for polymer synthesis and development.

1.3. Castor oil (CO) : *NEVO source*

CO originates from the seeds of the plant scientifically known as Ricinus communis L. (Shown in **Figure 1.7(a)**), with its believed origins spanning various regions such as Africa, Asia, India, and China.[35,36] It has historically been employed for medicinal purposes as a purgative. Owing to its characteristics such as high viscosity, excellent lubricating properties, stability across temperatures, and its resistance to dissolution in aliphatic petroleum solvents and fuels, CO is utilized as a fluid for various applications.[37–39] CO contains approximately 90% unsaturated FA, primarily ricinoleic acid. This significant concentration of ricinoleic acid distinguishes CO from other NEVOs, giving it a unique characteristic.[40,41] The high ricinoleic acid content (due to presence of unsaturation and hydroxyl groups) makes it versatile for applications in the chemical industry.[42]

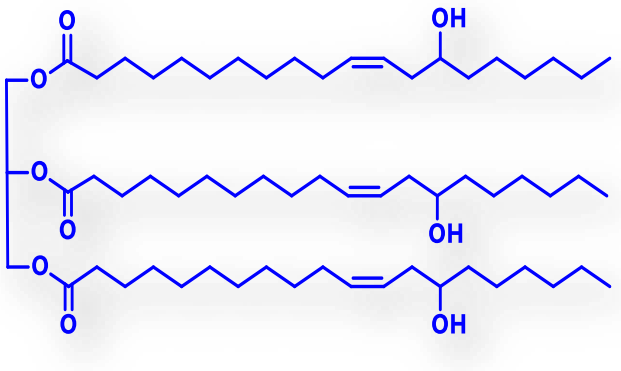


Figure 1.7. (a) Real image of castor plant and **(b)** Chemical structure of CO

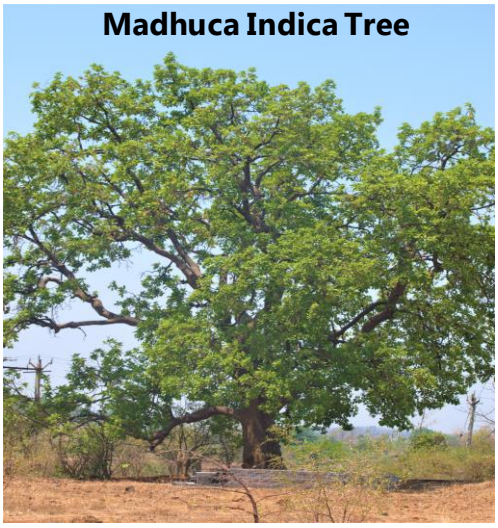
In addition to the ester linkage and double bond found in ricinoleic acid **(Figure 1.7(b))**, the hydroxyl group allows for versatile chemical modifications, making CO a suitable raw material for the chemical industry.[43,44] The ester linkage enables reactions like alcoholysis, hydrolysis, and esterification, while the double bond allows for chemical modifications through processes such as hydrogenation, epoxidation, and halogenation. The hydroxyl group facilitates dehydration, increasing the degree of unsaturation in CO (shown in **Table 1.2**).[45,46]

Table 1.2. Possible modifications in CO for various material developments

	Name of reaction	**Added Reactant**	**Product**
Ester linkage	Reduction	Na reduction	Alcohols
	Halogenation	$SOCl_2$	Fatty acid halogens
	Amidation	Alkyl amines, alkanoamines, etc.	Amine salts, amides
	Alcoholysis	Glycerols,glycols, pentaerythritol etc.	Mono-and diglycerides, monoglycols etc
	Saponification	Alkalies, alkalies plus metallic salts	Soluble soaps, insoluble soaps
	Esterification	Monohydrixc Alcohols	Esters
	Hydrolysis	Acids, enzymes or Twitchcell reagent catalyst	Fatty acids, glycerol
Double bond	Oxidation, Polymerization	Heat, oxygen, crosslink agent	Polymerized oils
	Hydrogenation	Hydorgen(moderate pressure)	Hydroxystearates
	Epoxidation	Hydrogen peroxide	Epoxidized oils
	Halogenation	Cl_2,Br_2, I_2	Halogenated oils
	Addition reaction	S, maleic acid	Polymerized oils
	Sulfonation	H_2SO_4	Sulfonated oils
Hydroxyl group	Dehydration, Hydrolysis, distillation	Catalyst (plus heat)	Dehydrated castor oil, Octadecadienoic acid
	Caustic fusion	NaOH	Sebacic acid, capryl alcohol
	Pyrolysis	High heat	Undecylenic acid, heptaldehyde
	Halogenation	PCl_5, $POCI_3$	Halogenated castor oils
	Alkoxylation	Ethylene and/or propylene oxide	Alkoxylated castor oils
	Esterification	Acetic-, phosphoric-,maleic-, phthalic anhydrides	Alkyl and alkyl aryl esters, phosphate esters
	Sulfation	H_2SO_4	Sulfated castor oil (Turkey red oil)
	Urethane reactions	Isocyanates	Urethane polymers

1.4. Mahua oil (MO): *NEVO source*

The Mahua/Madhuca indica tree is found in the tropical region of India, where it does not require much attention. **Figure 1.8** shows the picture of the Mahua tree and the detailed specifications of the plant. It is known as the Indian butter tree, as it solidifies at room temperature. The MO is obtained from the seeds of Madhuca indica.[34] Mahua seed contains some elements, such as carbon, calcium, nitrogen, magnesium, phosphorus, and sodium.[47]



Plant Category of Madhuca Indica	
Kingdom	Plantae
Subkingdom	Tracheobionta
Superdivision	Spermatophyta
Division	Magnoliaphyta
Class	Magnoliopsida
Subclass	Dilleniidae
Order	Ericales
Family	Sapotaceae
Genus	Madhuca
Species	Madhuca longifolia (Madhuca Indica)

Figure 1.8. Real image of Mahua tree and its detail categorization.

As per the Trifed, Institute of Ministry of Tribal Affairs, India, "MO has moisturising properties, which are used in skin diseases, rheumatism, and headaches. It is a laxative and is used to treat constipation, piles, and hemorrhoids, as well as an emetic. In addition, it was employed as an illuminant and hair fixer by native tribes.[48] MO has the appearance of a pale yellow colour with a pleasant odour and taste. Major compositions of MO contain saturated FAs (strearic and pamitic acids) and unsaturated FAs (linoleic and oleic acids). Last morethan decades, MO has been largely sourced in production of biodiesel due to high acid value and so suitable for transesterification processes. As biodiesel production is a long, multistep, and costly process, the MO is now being utilized for the development of polymers as renewable sources.

1.5. Polyurethanes (PUs): *Versatile class of polymers*

PU is a versatile polymer as it can vary from thermoplastic to thermosetting material. A polyaddition reaction between organic isocyanates and polyols is used for the industrial production of PUs.[49] An environmental- friendly way to produce PU can be achieved using biobased diols and diisocyanates or using nonisocyanate chemistries.[50] Several types of PUs can be obtained by varying the compositions of isocyanates and polyols. PU offers excellent

properties and very simple for processing. Therefore, a variety of PU products such as low and high density foams, flexible and rigid elastomers, fibers, adhesives, emulsions, etc. can be developed. Other features of PUs include its light weight, good impact strength, chemical and environmental resistance.[51] The basic chemistry of PU is represented in **Figure 1.9.**

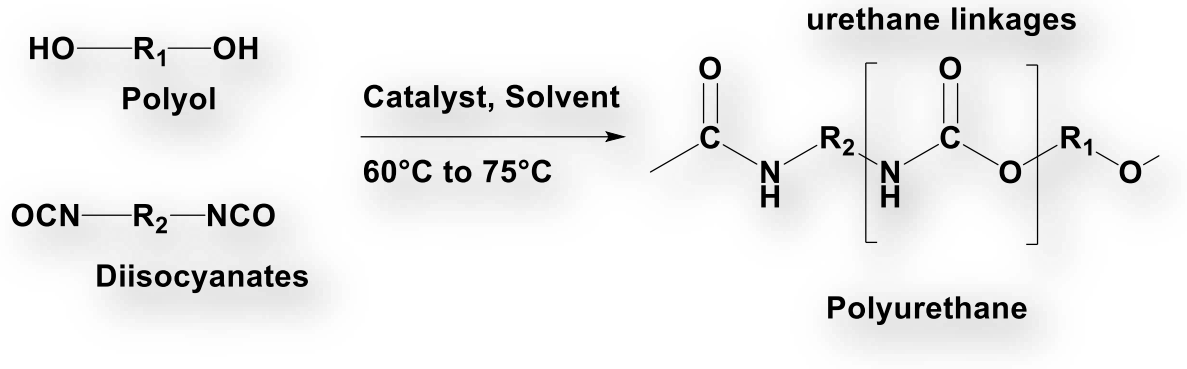


Figure 1.9. General preparation of PU

1.5.1. Waterborne polyurethane polymers (WPUs)

WPUs have a PU backbone that is dispersed in water rather than in organic solvents, as seen in solvent-based PUs. Many organic solvents, such as toluene, formaldehyde, and xylene are classified as volatile organic compounds (VOCs). Due to recent environmental concerns, the use of organic solvents in PU dispersions has been reduced. WPUs offer several advantages over conventional PU, including high tensile strength, high abrasion resistance, high flexibility, good adhesion ability, and good low-temperature resistance.[52] WPUs are utilized in a wide range of applications, including antibacterial coatings, flame-retardant coatings, anticorrosive coatings, self-healing coatings, automotive coatings, adhesives, and biomedical applications.[53] Despite the variations in the end products and applications of each type of PU, the fundamental chemistry for synthesizing the PU linkage remains consistent.

1.5.2. Chemistry of WPUs

The WPU reaction involves forming a urethane linkage using two functional monomers [a polyol (contain -OH groups) and a diisocyanate (having NCO groups) compound] in the presence of metal catalysts like DBTDL,[54] zinc or bismuth-based catalysts, dibutyltin dichloride, dimethylethanolamine (DMEA), or amine catalysts such as dimethyl cyclohexylamine (DMCHA), triethylenediamine (TEDA), and 1,4-diazabicyclo[2.2.2]octane (DABCO). Not only catalysts accelerate the process, but measurements have proven that autocatalysis carried out by the initially formed urethane bonds also accelerates the

reaction.[55] The polyol functions as a soft segment, giving flexibility to the PU, while the diisocyanate compound makes a hard segment, imparting toughness to the PU chain.

Over the last 60 years, significant technological advancements in the WPU field have been highly emphasized and reported. The production of PU emulsion by Dietrich and his colleagues at the Bayer(AG) lab marked a significant revolution in WPU dispersion technology. This milestone by Dietrich and his team motivated researchers to dedicate themselves to further investigation and innovation in this domain.[56,57] The WPU dispersion is a biphasic system, where particles in the discontinuous phase (PU) are dispersed within the liquid (continuous) phase. The high surface energy of the particles, which are typically about 20–200 nm in size, creates a strong driving force for film formation as the water evaporates. Particle size and their degree of distribution are the primary factors influencing the dispersion system and the stability of the emulsion.[58,59] The stability of the emulsion is also influenced by coalescence, where larger droplets form and reduce the total surface area, and by flocculation, where particles accumulate without creating new ones. These instability factors in such dispersions have been thoroughly studied.[60]

WPU synthesis encompasses both chemical and colloidal elements, meaning the final material's properties are influenced by these factors. The physico-mechanical properties of the polymer are determined by factors such as component mixing, addition rate, reaction conditions, slight temperature variations, pH, and shear force during WPU preparation.[61]

To emulsify, disperse, or dissolve hydrophobic (water-repellent) PU, it is necessary to modify its structure with an appropriate protective colloid, external emulsifier, or through structural modification. Protective colloids and external emulsifiers, however, have drawbacks: they need strong shear forces to disperse the polymer, leading to coarse particles and poor stability. Thus, the most largely used method is structurally modifying hydrophobic PU with introducing hydrophilic terminals in the PU network, aiding in an aqueous dispersion. This is generally achieved through one of two processes: tailoring the PU matrix with suitable hydrophilic groups or adding a selective surfactant. The older method, where ionic groups are introduced to act as internal emulsifiers, results as a PU ionomer.[56,62,63]

The hydrophilic component is essentially incorporated as ionic groups (sulfonate, carboxylate, or quaternary ammonium salt) or nonionic groups poly(ethylene oxide) of the di-hydroxyl group. For example, dimethylolpropionic acid (DMPA) is attached to the polymer as an internal emulsifier. The carboxylic ion in DMPA is hydrophilic and acts as both an anionic center and an internal emulsifier in the polymer matrix.[62,64]

The suitable base group is then employed to neutralize these pendant acid groups. This dispersion process ensures better dispersion stability and provides three primary benefits to the PU: enhancing water and solvent-resistance properties, improving barrier properties due to suitable particle size while retaining hydrophilicity, and imparting a suitable networking structure. The WPUs can be synthesized using the acetone process,[65] prepolymer-mixing process,[66] ketamine/ketazine process,[67] or a hot melt dispersion process.[63] The acetone and prepolymer mixing processes are commonly used in the PU industry for the preparation of adhesives and coatings, respectively.[21,57]

The prepolymer emulsification method is commonly used in moisture-cure coatings. It typically involves reacting suitable diols or polyols (such as polyethers, polyesters, or bio-based polyols) with diisocyanates or polyisocyanates in an excess molar ratio, along with an internal emulsifier, neutralizer, and water to create an –NCO terminated prepolymer.[56] The final step involves dispersing the prepolymer in an aqueous media by phase inversion, as presented in **Figure 1.10.** Diols containing an ionic group or a nonionic group function as internal emulsifiers. These internal emulsifiers or surfactants play a crucial role in stabilizing the dispersion in an aqueous medium.[68] In both the methods, the internal emulsifier is a part of PU chain.

Depending on the type of ionic species present in the internal emulsifier, a minimal amount of counter ions is required to form a stable dispersion. The evaluation of WPU film properties depends on the hard and soft segments contributed by the polyol and diisocyanate in the PU backbone, respectively. The hard segments (HS) are primarily provided by the diisocyanate, while the polyol part contributes the soft segments (SS) to the PU matrix. As illustrated in **Figure 1.11**, the structure of the PU consists of SS (polyol) and HS (urethane). Overall, the soft and hard domains play a crucial part in evaluating the end-use properties and uses of the material.

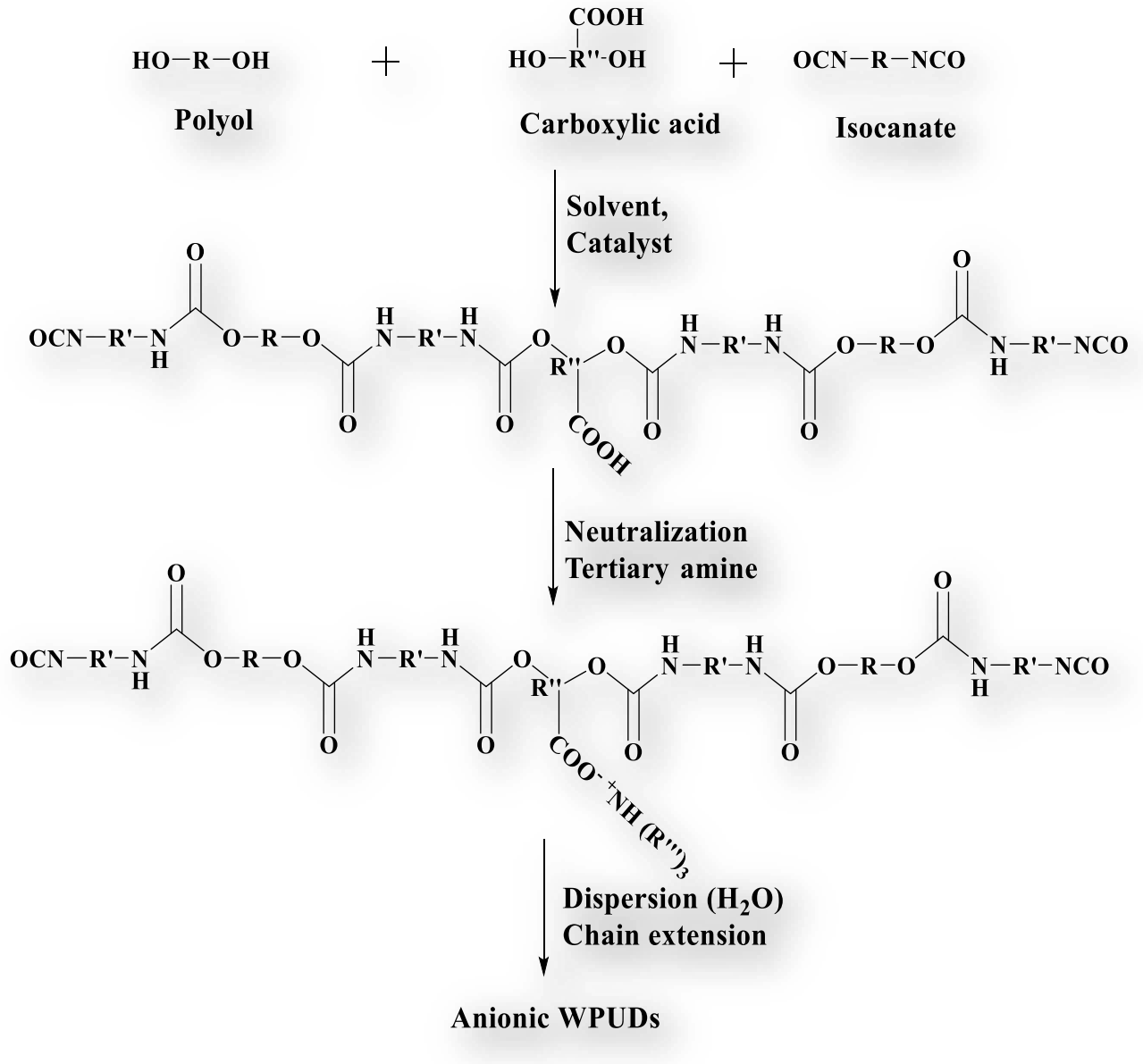


Figure 1.10. Synthetic route of WPUDs

Structurally, diisocyanate segments derived from aromatic groups have a greater impact on the end properties of PU than those from aliphatic groups. Additionally, due to their stereoelectronic configuration, the isocyanate groups in the primary and secondary groups of isophorone diisocyanate (IPDI) exhibit different reactivities. Similarly, the reactivity of toluene diisocyanate (TDI) differs between its 2,6 and 2,4 isomers, with the 2,6 isomer being more reactive and thus contributing more to the hard segment. Furthermore, the –NCO groups at ortho positions are 12% high reactive than those at para positions because of steric hindrance created in the structure.[66]

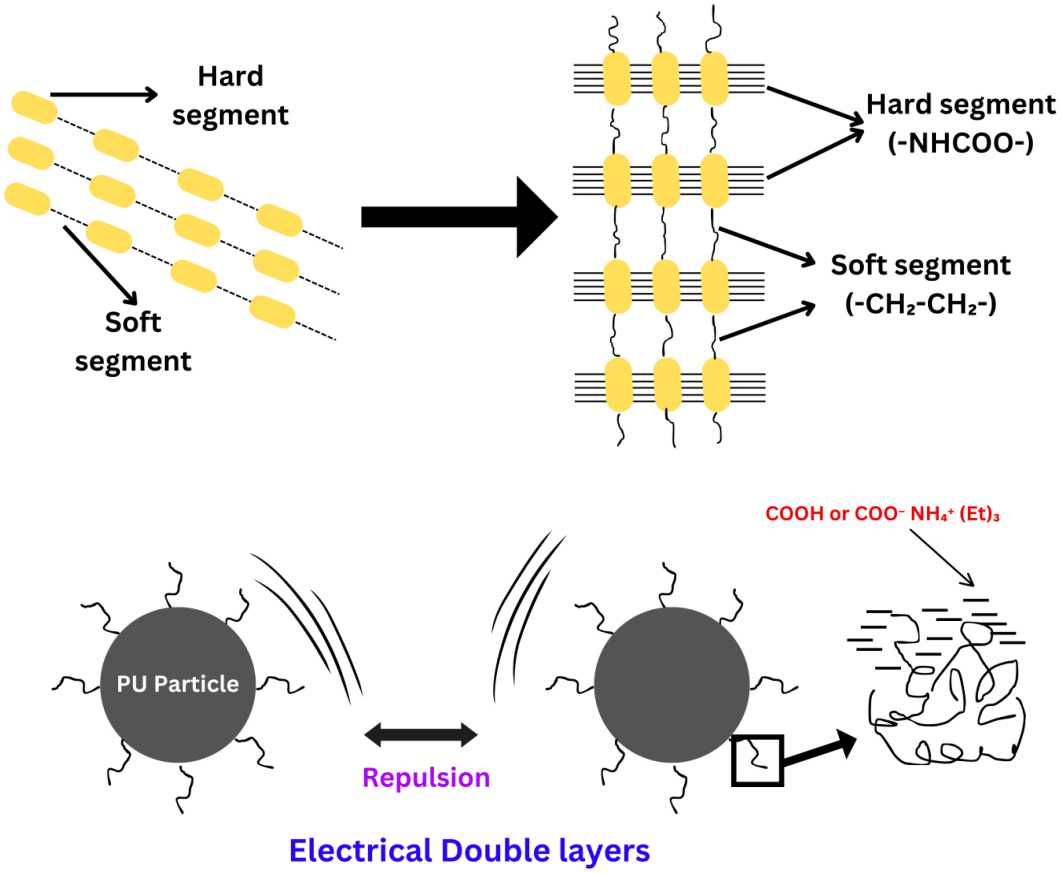


Figure 1.11. Schematic presentation of different segments and interaction of WPUs.

1.6. CO-based PUs and WPUs

CO is usually applied to prepare polyols due to its hydroxyl groups.[69] CO reacts with different isocynates to prepare PU having urethane linkages (–NHCOO–) in the main chain. This polymerization is catalyzed by 3° amines with very low steric hindrance, such as triethylenediamine (TEA) and N,N-dimethyl cyclohexylamine (DMCHA), and certain tin, lead, and mercury compounds like stannous octoate(tin 2-ethylhexanoate). **Figure 1.12** presents the possible route of PU synthesis where CO reacts with different kinds of di- or polyisocyanates in the presence of catalysts at a temperature of 60°-75°C.

PU-based coatings derived from CO-based polyols have demonstrated good anticorrosive ability due to the long aliphatic FA ester chains of oils and the hydrophobicity of the constituent triglycerides, further enhancing their physic-chemical properties. Yi Su et al.[70] developed 1-thioglycerol modified CO-based PU using solvent-free thiol-olefin click reaction. The resulting cross-linked PUs, prepared without solvents or catalysts, exhibited high tensile strength (~83 MPa) and Tg (~124 °C), surpassing other VOs-based PUs. These PUs also demonstrated excellent coating and optical properties, superior to those from unmodified CO. P. Saha et al.[71] synthesized biobased PUs using CO

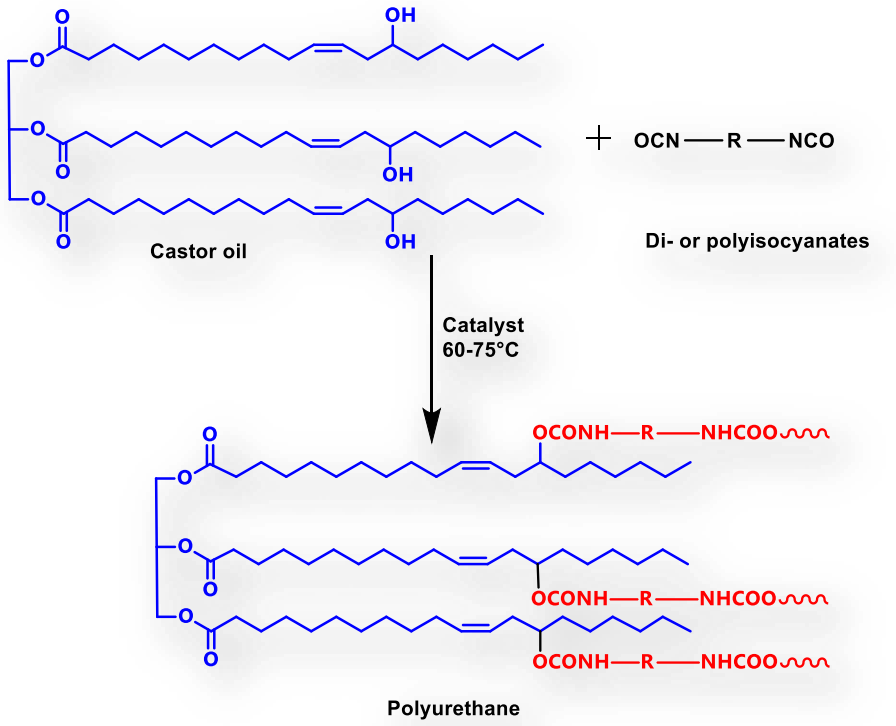


Figure 1.12. Synthesis of CO-based PU

and poly(3-hydroxybutyrate) diol (PHBD) using hexamethylene diisocyanate (HMDI) as a crosslinking agent. PHBDs were produced via transesterification of bacterial PHB with ethylene glycol by varying reaction times. Increasing PHBD content significantly improved tensile strength by 300% compared to neat CO-based PU, with short-chain PHBD providing higher tensile strength than long-chain PHBD. Using PPG, phosphorus, phthalic anhydride, and isophorone diisocyanate (IPDI), V.K. Mishra et al.[72] prepared polyether ester urethane (PEEU). Bio-based PU from CO (CPU) was blended with PEEU to create polymer blends (PBs). Thermal degradation studies indicated a 30–40% decrease in degradation rate for PBs. Limiting oxygen index (LOI) values of PBs decreased by 2–3%. Mechanical tests revealed that breaking elongation of PBs increased by 50–90%, while tensile strength decreased by 3–5 MPa. Gel content in PBs increased by 10–20%. Hydrolytic stability and contact angle improved with higher CPU ratios, and soil burial tests showed reduced bacterial attack on PBs with higher CPU content. K.M.S. Meera et al.[73] have developed bio-renewable nanocomposite CO-based PU–silica films using CO, and 1,6-hexamethylene diisocyanate (HMDI). Silica nanoparticles improved the thermal stability of PU films, raising activation energy values during degradation. Results indicated interfacial interactions between silica nanoparticles and the PU hard segment, lowering melting temperature. Optical transmittance decreased with more silica content due to scattering, while storage modulus increased by up

to 24% for PU-5AMS. M. A. Alaa et al.[74] performed the comparative study of PPG based PUs and mixture of CO and PPG-based PUs. The presence of large CO content in PUs resulted in greater oxidative thermal stability. Mechanical properties, an increase in elongation at break was also observed, while tensile strength decreased compared to pure PUs. CO and PPG-based PUs showed a ~21% improvement in elongation at break and a ~35% decrease in tensile strength in comparative stress–strain studies with pure PUs. M. L. Chaudhary et al.[75] developed CO-based PU adhesives with excellent bonding strength. The bonding strength of CO-based PU adhesives was enhanced by introducing chain extenders such as N, N-bis (2-hydroxyethyl) thiophene-2,5-dicarboxamide (ETP) and N, N-bis(2-hydroxyethyl)-terephthalamide (ETAM), increasing the strength to 7.22 MPa and 9.68 MPa, respectively. Tests showed bonding strengths of 9.68 MPa on oak wood and 6.73 MPa on stainless steel for the 5.0 wt% ETAM-based PU adhesive. Noncovalent bonds between the PU molecular chain and the substrate surface contributed to the strong bonding.

Besides CO, the other primary VOs are challenging to use directly for WPUs preparation due to the absence of active hydroxyl groups. CO can directly react with isocyanates to form urethane bonds without any prior modification (shown in **Figure 1.13**).

The uniform distribution of hydroxyl groups on the CO chain allows for the synthesis of WPU with a high degree of crosslinking, resulting in superior mechanical properties and thermal stability. CO-based WPUs can be directly utilized in the production of PU adhesives, coatings, and foam plastics, and it can also be modified for other uses.[76,77]

Victoria et al.[78] studies on synthesis of WPUs using CO, IPDI, and tartaric acid (TA) as emulsifiers. They studied the WPU synthesis without TA and developed WPU films with flexible, thermally stable, improved mechanical strength, water and chemical resistance properties. W.B. Lim et al.[79] developed series of WPUs using the polycaprolactone diol and CO through polyaddition reaction. The developed WPUs shows enough enhancements in tensile strength and Young's modulus. The quaternary ammonium groups in the CO-based WPUs was grafted by Y. Zhong et al.[80] Gelatin was then added with various concentrations of WPUs to create PU composite films. As the WPUs concentration increased, the mechanical properties, thermal stability, permeability of water and oxygen of PU composite films improved significantly. Additionally, the composite films exhibited a strong inhibitory effect on E. coli and S. aureus due to the presence of the quaternary ammonium compound.

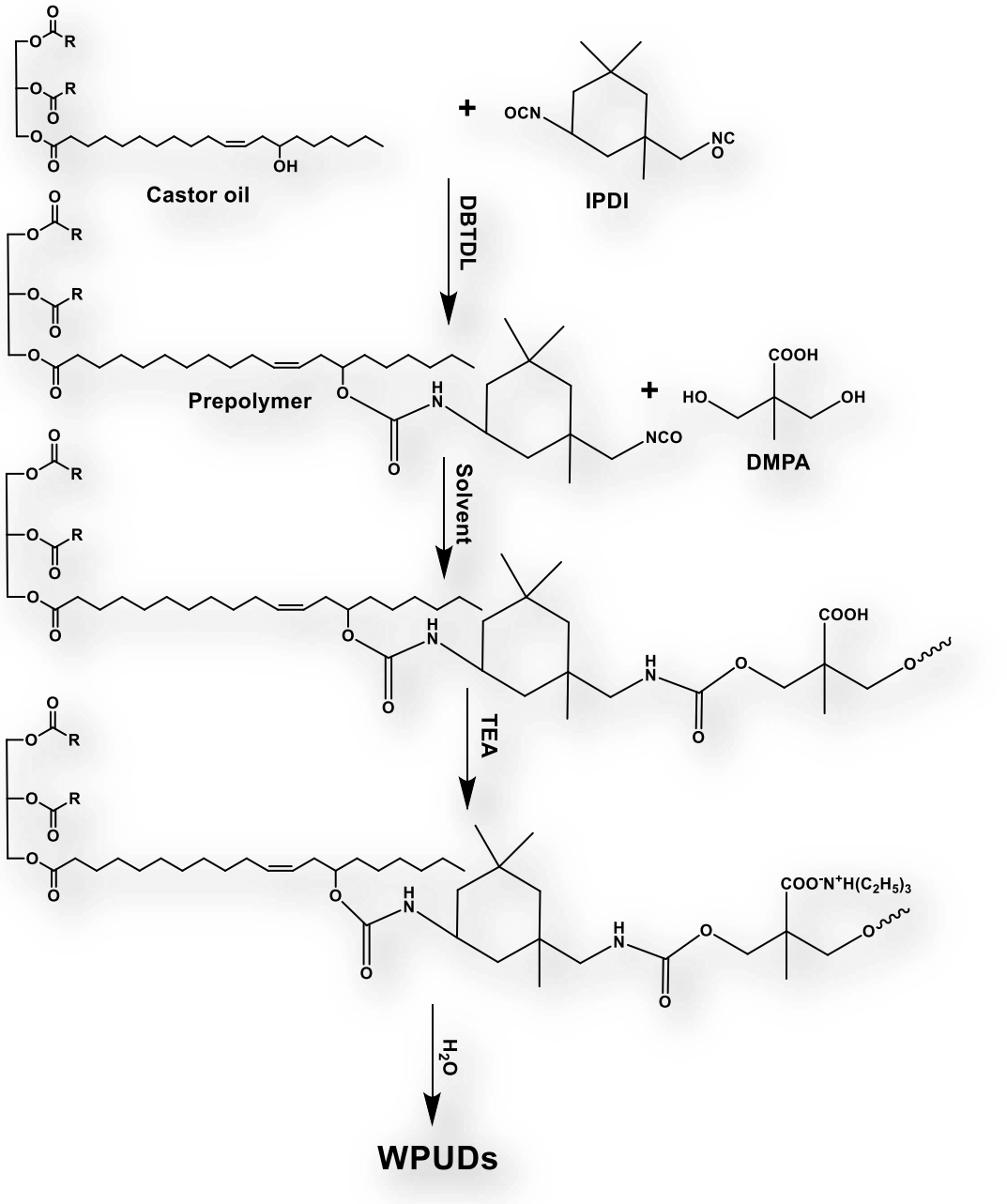


Figure 1.13 Synthesis of WPU dispersion from CO

J. Zhang et al.[81] also synthesized CO-glycerol-based WPU. Upto 50% glycerol (Gly) in the polyol mixture showed significantly improvement in the bio-based PU properties. The tensile strength reached 30 MPa, Young's modulus 333 MPa, elongation at break over 26% with the 82°C Tg and 6H pencil hardness. This study highlighted the potential of Gly to enhance the performance of bio-based WPUs. R. Shen et al.[82] developed modified anionic CO-based WPUs using CO, isosorbide (IS), and L-tyrosine derived cyclic dipeptide (L-CD). The modified WPUs showed improved performance, with tensile strength up to 29.56 MPa and toughness at 20.12 MJ/m³. The Tg ranged from 5.93°C to 57.23°C. Additionally, the

modified CO-based WPUs demonstrated enhanced anticorrosion properties on 45# steel, attributed to their robust, hydrophobic nature. Not only that the antibacterial WPU-based shielding nanocomposites synthesized by Y. Zhan et al.[83] are crucial for combating electromagnetic interference (EMI) pollution and antibiotic resistance. They synthesized composites using carbon nanotubes (CNTs) and an antibacterial surfactant (CTAB) mixed with CO-based WPU via ultrasonic-assisted solution mixing and freeze-drying. The presence of CTAB ensures uniform CNT dispersion at 24.3 wt%, resulting in high electrical conductivity (635.8 S/m), thermal conductivity (0.308 W/(m·K)), and exceptional shielding effectiveness (88.81 dB), with a specific SE of 997.4 dB/cm. These composites also show enhanced antibacterial properties, making them ideal for portable and wearable smart electronics, showcasing a new approach for ecofriendly, multifunctional polymer composites.

Hence, PUs and WPUs development using the CO as polyols are promising for their potent applications in variety of industrial and household material preparation. **Figure 1.14** shows the applications of CO-based PUs and WPUs.

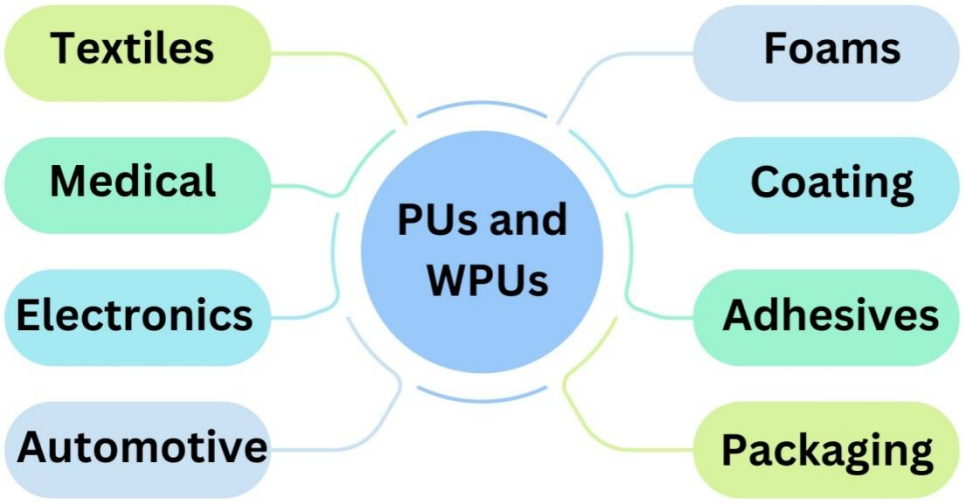


Figure 1.14. Application of PUs and WPUs

1.7. Mahua oil (MO)-based PUs and WPUs

MO as a renewable source for the development of various polymers has already been reported. **Figure 1.15** shows the synthetic routes of various MO-based polymers that are synthesised using MO as a basic raw material.

PU contains different functional groups, likewise urethane, amide, ester, vinyls, acrylics, double bonds, and others.[84,85] In general, MO was used as a raw material for the manufacture of MO-based fatty amide (MFA) by a base-catalyzed aminolysis reaction. The synthesised MFA was transformed into the polyetheramide (PEA) polyols by a step growth

reaction with bisphenol-A or bisphenol derivatives (seen in **Figure 1.15**). PEA polyols react with different isocyanates like aliphatic and aromatic to produce MO-based PU.[86,87]

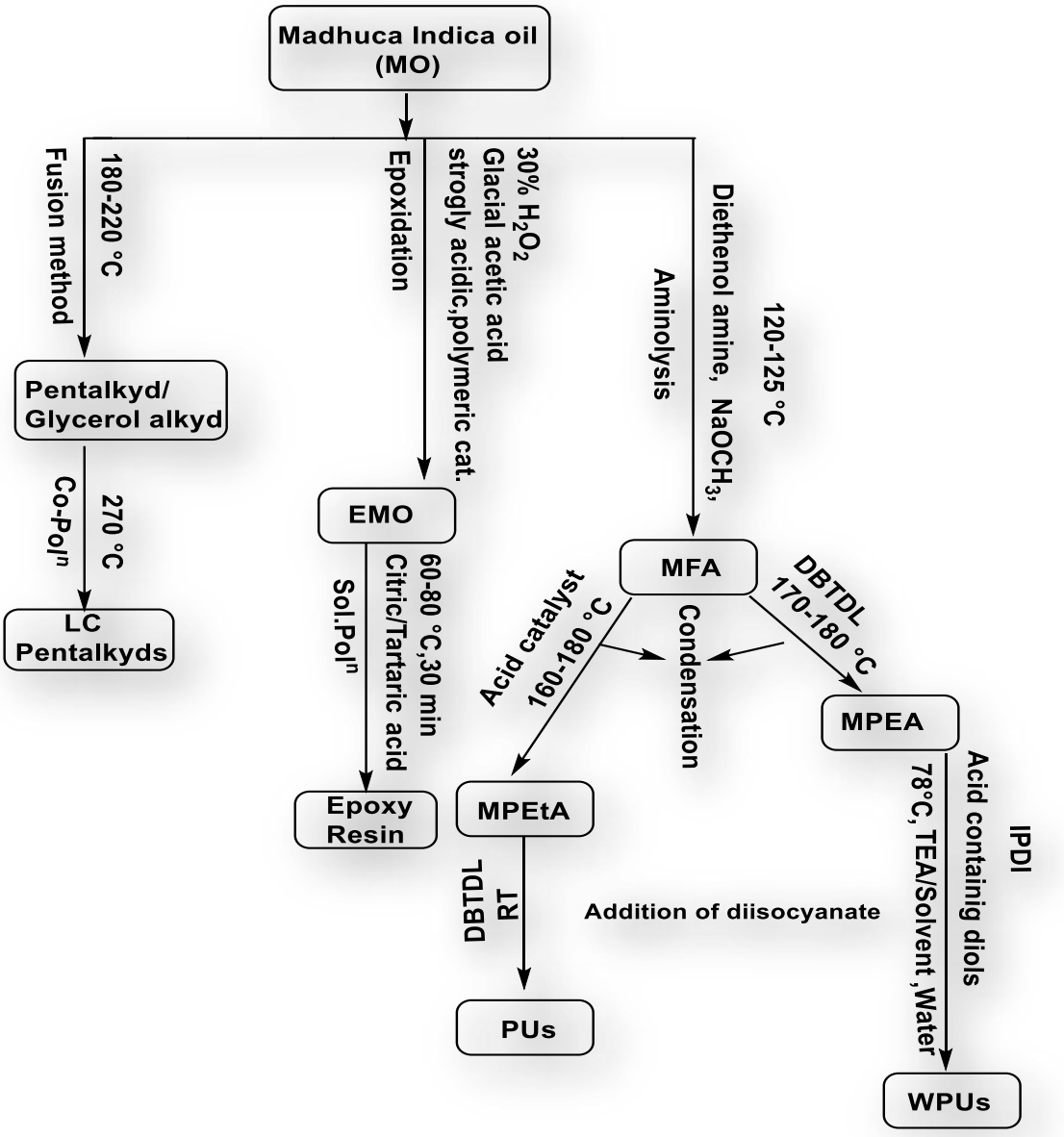


Figure 1.15. Various routes to synthesize MO-based polymers

The preparation of the PU using the MO is shown in **Figure 1.16**. Raychura, A. et al.[87] synthesised a MO-based PU polymer that could be reacted with isocynates and a polyetheramide polyol made with the MFA and the diglycidyl ether of bisphenol-A (DGEBA).

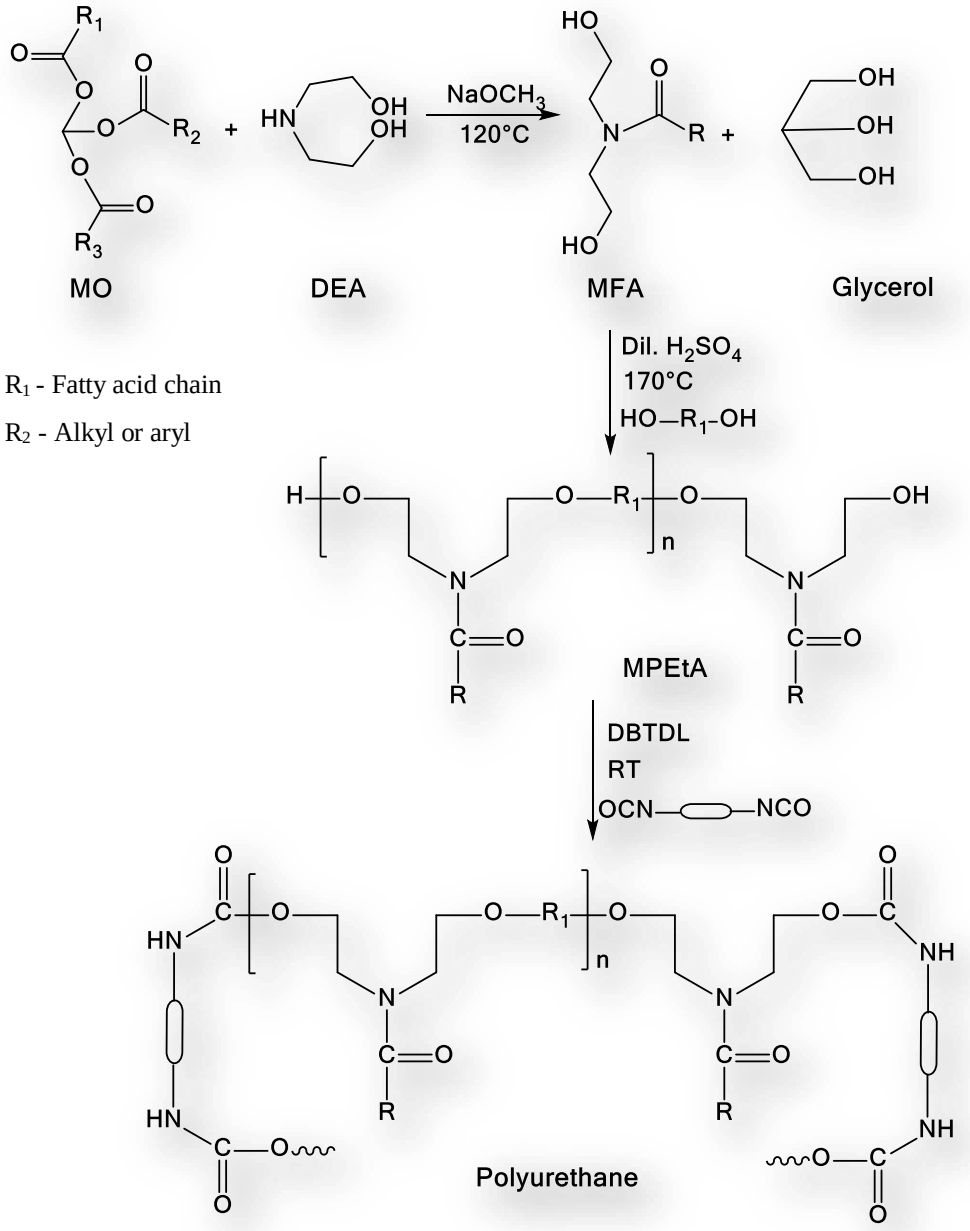


Figure 1.16. Preparation of PU using MO as a polyols

The developed PU was applied to the wood substrate as a protective coating and was noted to have 100% adhesion to the wood surface and showed better hardness and thermal stability similar to those of other VO-based PUs. These PUs had no discernible fungicidal or microbicidal effects on microbial or fungal strains.[88] The PU coating on metal plating provides a protective measure against oxygen, which reduces the rate of corrosion by reducing the presence of oxygen, H+ ions, and water on metal surfaces.[89,90] Due to polar urethane and ether parts, the PU coating resulted in excellent chemical resistance and outstanding mar resistance reported by Pawar, M. et al..[91] Not only that, the outstanding

flexibility is granted by the ether linkages and polar urethane as well as the lengthy MFA chains, which also enhance adhesion to the substrate. As a result, MO-based PUs has exceptional potential in coating binder formulations. Yemul O.S. et al.[92] reported that polyesteramides are polymers that are used to create PU dispersions and coatings considered MO-based WPUs. They used dicarboxylic acid, which is a sustainable and natural resource. The synthesised MO-based WPU dispersion has almost identical coating properties to that of a synthetic polyester diol-based PU dispersion coating. However, due to the presence of a triglyceride structure that is more favourable to hydrolysis than petroleum source-based PU, the MO-based PU films showed quite low thermal stability.

As for the overall inputs, as a novel and valuable feedstock, MO may be a promising renewable source for the synthesis of various PU and WPU polymers with superior properties and applications in coatings.

To understand the importance of NEVO based polymer, the present research was aimed at developing and well-characterizing PU and WPU polymers using CO and MO as polyols and diisocyanate as a curing agents for various useful applications such as antimicrobial activity, coating, and packaging.

The developed PUs and WPUs have been evaluated for their antimicrobial as well as coating applications.

In order to examine CO and MO-based PU polymers, the following sophisticated characterization techniques were employed.

Spectral techniques:

Attenuated total reflectance-fourier transform infrared (ATR-FTIR),

Proton nuclear magnetic resonance (^{1}H NMR),

Ultraviolet–visible (UV-Visible), and

Ultraviolet-Fluorescence (UV-Fluorescence) spectroscopy;

Thermal techniques:

Differential scanning calorimetry (DSC),

Thermogravimetric analysis (TGA), and

Derivative thermogravimetry (DTG);

Chemical techniques:

X-ray photoelectron spectroscopy (XPS);

Scattering techniques:

Dynamic light scattering (DLS),

Zeta potential,

X-ray diffraction (XRD); and

Energy-dispersive X-ray (EDX) spectroscopy.

Optical techniques:

Scanning electron microscopy (SEM), and

Atomic force microscopy (AFM) method for surface analysis.

The synthesized PU polymers were evaluated in a series of studies, including antimicrobial activity, coating, fastness, chemical resistance, thermal stability and storage stability.

1.8. References

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