



Recent Advances in Polyurethane Coatings and Adhesives Derived from Vegetable Oil-Based Polyols

Dhiraj S. Kaikade¹ · Anagha S. Sabnis¹

Accepted: 3 May 2023 / Published online: 18 May 2023

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2023

Abstract

Sustainability and renewability are the terms that concern most researchers today. In the world of paints and adhesives, polyurethane (PU) is a popular material due to the enormous possibilities in the choice of raw materials. The scientific community today is more focused on adopting water-based and low-solvent or solvent-free technologies instead of traditional solvent-based routes in the synthesis of PUs. Adopting more ecological routes is a step towards achieving the goal of sustainable and renewable development. The use of bio-derived monomers not only contributes to the goal of sustainable development but also eliminates the uncertainty of price, availability and environmental hazards associated with traditional petroleum-derived monomers. Among the biologically derived resources, vegetable oils are the most promising and most studied raw materials in the PU industry due to their abundance, inherent biodegradability, non-toxicity and low price. Since primitive times they had traditionally been used for coatings and adhesive applications. Today, the full field use of vegetable oil-based monomers or polymers as raw material is an excellent effort for a sustainable future in the world of coatings and adhesives worldwide. The review highlights recent advances in vegetable oil-based polyols as an environmentally friendly material for PU coating and adhesive applications.

Keywords Vegetable oil · Polyurethane · Coatings · Adhesives · Polyol · Seed oil · Sustainable

Introduction

Since invented by Otto Bayer in 1937, polyurethane (PU) has become an interesting material due to its versatility. Due to its high mechanical strength, excellent wear resistance and chemical resistance, PU quickly became an industrially important material. Traditionally, PUs are synthesized by reacting the hydroxyl groups of polyols with isocyanates. General reaction of isocyanate and hydroxyl is shown in Fig. 1.

The term versatility is particularly applicable to PUs as it involves a good range of reactants. However, isocyanate has various reactions with active hydrogen-containing materials such as reaction with hydroxyl group produces urethane bond, amine group produces urea bond, urethane group

produces allophanate bond, and urea produces biuret bond. Figure 2. Shows various reactions of isocyanates.

Today, PUs are emerging as new components of polymer materials with applications such as foams, insulating materials, plastics, composites, films, sealants, coatings, inks, adhesives, thermocurable and thermoplastic elastomers to fibers etc. [1–4]. The outstanding success of PU has led it into multifold growth. According to a recent report, the global PU market is projected to grow at a compound annual growth rate (CAGR) of 7.5% to US \$ 92 billion by 2025 [5]. The PU coatings and adhesives market was valued at US \$ 16.8 billion and US \$ 7 billion in 2019 [6, 7]. This market is expected to grow to US \$ 30.5 billion and US \$ 9.1 billion by 2027, respectively [8, 9]. Industrial production of PU began in 1940s, but was heavily influenced by World War II, the PU material was used as replacement of rubber [10, 11].

Today, a variety of materials are PU coated to improve their appearance and durability. PU coatings exhibit properties such as excellent wear resistance, cold resistance, toughness, chemical resistance, corrosion resistance with a wide range of mechanical strength. PU coatings are widely used in automotive industry due to their high exterior gloss,

✉ Anagha S. Sabnis
as.sabnis@ictmumbai.edu.in

¹ Department of Polymer & Surface Engg., Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400019, India

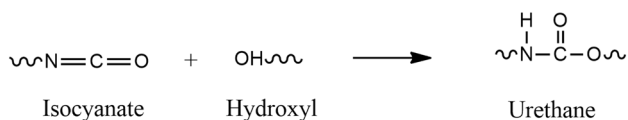


Fig. 1 Isocyanate and Hydroxyl reaction

improved color stability, improved scratches and corrosion resistance. These coatings can also be used for industrial maintenance. Various PU coatings are used in construction, and spray coatings are applied to concrete columns, steel beams, and building floors to reduce maintenance costs and increase resistance to environmental impacts. PU adhesives were first used in truck hoods and then became very important for bonding numerous substrates such as glass, wood and plastic [12].

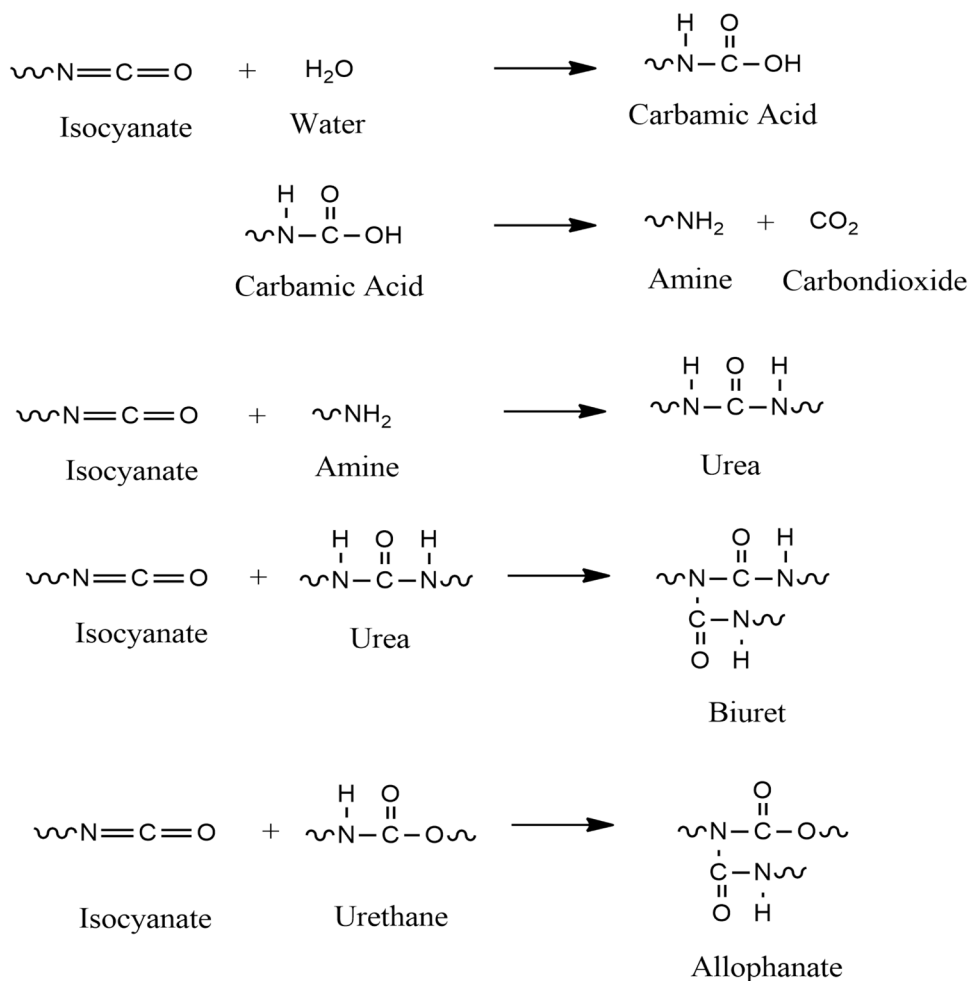
The wide range of uses for PUs are due to the variety of raw material choices [13]. The problem related to PU is its volatile organic compounds (VOC) content due to traditional solvent-borne synthesis. These solvent-based PUs are slowly replaced by waterborne polyurethanes (WPU) in past decades as WPU have many advantages, such as ecofriendly

non-toxic, non-flammable, non-polluting, low viscosity at high molecular weight, good applicability and low cost. This makes it one of the most rapidly developing and active branches of PU chemistry and technology [14, 15].

Recently, PU has been attracting attention due to environmental laws such as pollution caused by the use of substances containing VOCs and hazardous air pollutants (HAP). The treatment and application of these solvent-based PUs also causes side effects such as evaporation of organic solvents that increase atmospheric VOC and HAP levels [14]. Most of these ingredients are also carcinogenic. Various governments and environmental protection agencies have made progress to ban and eliminate the use of such ingredients. As a result, there is a research shift towards the use of environmentally friendly materials, unleashing the potential of natural raw materials for the use of PU [1].

The polyols used so far in the PU industry are mainly derived from petrochemical products. Bio-based materials are of great interest in the competition to replace petroleum-based materials. Of the bio-based materials, vegetable oil-based products are the best choice due to their low toxicity, high purity, low cost and easy availability. These

Fig. 2 Various reactions of Isocyanates



oils contains triglycerides with 8–18 linear carbon chains. Triglycerides can be monounsaturated, polyunsaturated, saturated depending on the type of plant and the climatic conditions [2, 16, 17]. Figure 3. Shows general structure of triglyceride molecule.

Researchers are actively engaged in the discovery and formulation of new strategies for using natural resources to achieve the goals of reducing raw material costs, developing environmentally friendly formulations, promoting accelerate post-service degradation and add value to the generated waste. This review describes recent advances in vegetable oil-based polyol for PU coatings and adhesive changes and their applications. It also includes the role of vegetable oil-based polyols in controlling the properties of these coatings and adhesives.

Vegetable Oil Polyols

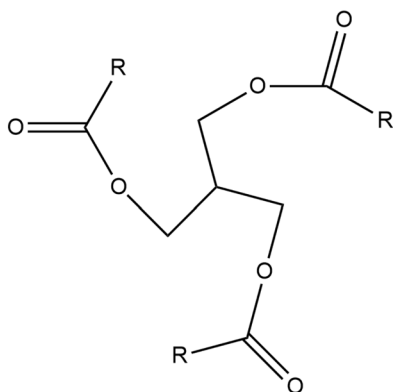
Vegetable oils constitute a broad class of sustainable resources and are one of the most important components in producing polymeric materials. They are triesters of glycerol and fatty acids (saturated and unsaturated) [18]. Vegetable oil is mainly composed of triglyceride (93–98% by weight) as the main component and a small amount of diglyceride and monoglyceride. They have unique film-forming property due to the presence of unsaturation and are therefore very useful for coating. Traditionally, vegetable oil-based PUs have been made with castor oil and suitable diisocyanates.

Castor oil and Lesquerella oil have naturally occurring hydroxyl groups in the triglyceride structure, which makes them natural vegetable polyols that can be used with or without modification. Castor oil is an inexpensive source of secondary hydroxyl group-containing polyol. It is a triglyceride of fatty acids with 85–89% ricinoleic acid. *Lesquerella fendleri* (Brassicaceae) is a genus that contains 95–100 species. Among them, *L. fendleri* (Gray) can grow over wide geographical ranges which includes different types of soils, temperatures, and elevations. The

composition of this oil is around 60% of lesquerolic acid (14-hydroxycis-11-eicosenoic acid), and 3% to 5% of auricollic acid (14-hydroxy11,17-eicosadienoic acid) [19, 20]. Other vegetable oils such as linseed [21], soybean [2], canola [22], rapeseed [23], jatropha [24], rice bran [22], cottonseed [25] etc. offer more versatility for polyol production. Triglyceride is mainly made up of the fatty acids such as saturated ones including stearic (C18:0) and palmitic (C16:0) and unsaturated includes linoleic (C18:2), oleic (C18:1) and linolenic (C18:3). As stated above the composition of a vegetable oil depends upon the soil, seed, climatic type and conditions. To use vegetable oil-based fatty acids for PU applications, the unsaturation present is modified to yield hydroxyl groups. The methods are epoxidation of carbon–carbon double bonds followed by ring-opening of epoxide, hydroformylation, hydrolysis, ozonolysis, transesterification, thiol-ene coupling. All the mentioned routes are schematically presented in Fig. 4. These methods transform an inexpensive, readily available, renewable feedstock into a valuable monomer. Table 1 shows the comparison of the above-stated methods [22, 26].

Factors such as OH functionality, dangling chains and primary or secondary hydroxyl groups etc., directly affect the properties of vegetable oil-based PUs. The functionality of isocyanates and polyols can directly affect the formation of crosslinks in the PU. As the crosslink density increases, the tensile properties of the PU are expected to increase and vice versa. Some properties, such as the network structure, mechanical and thermal properties of the PU system, depend primarily on the crosslink density [29]. From another point of view, the addition of flexible groups such as plasticizers reduces the above-mentioned properties. The presence of dangling chains increases the free moving chains, aids in plasticizing activity, and reduces the, tensile strength, and hardness of the PU. Another important factor is intermolecular forces between polymer chains, the intermolecular forces (attractions) are hydrogen bonding, permanent dipole, London dispersion

Fig. 3 General structure of triglyceride



R: Aliphatic carbon chain with carbon chain length generally from C8–C18

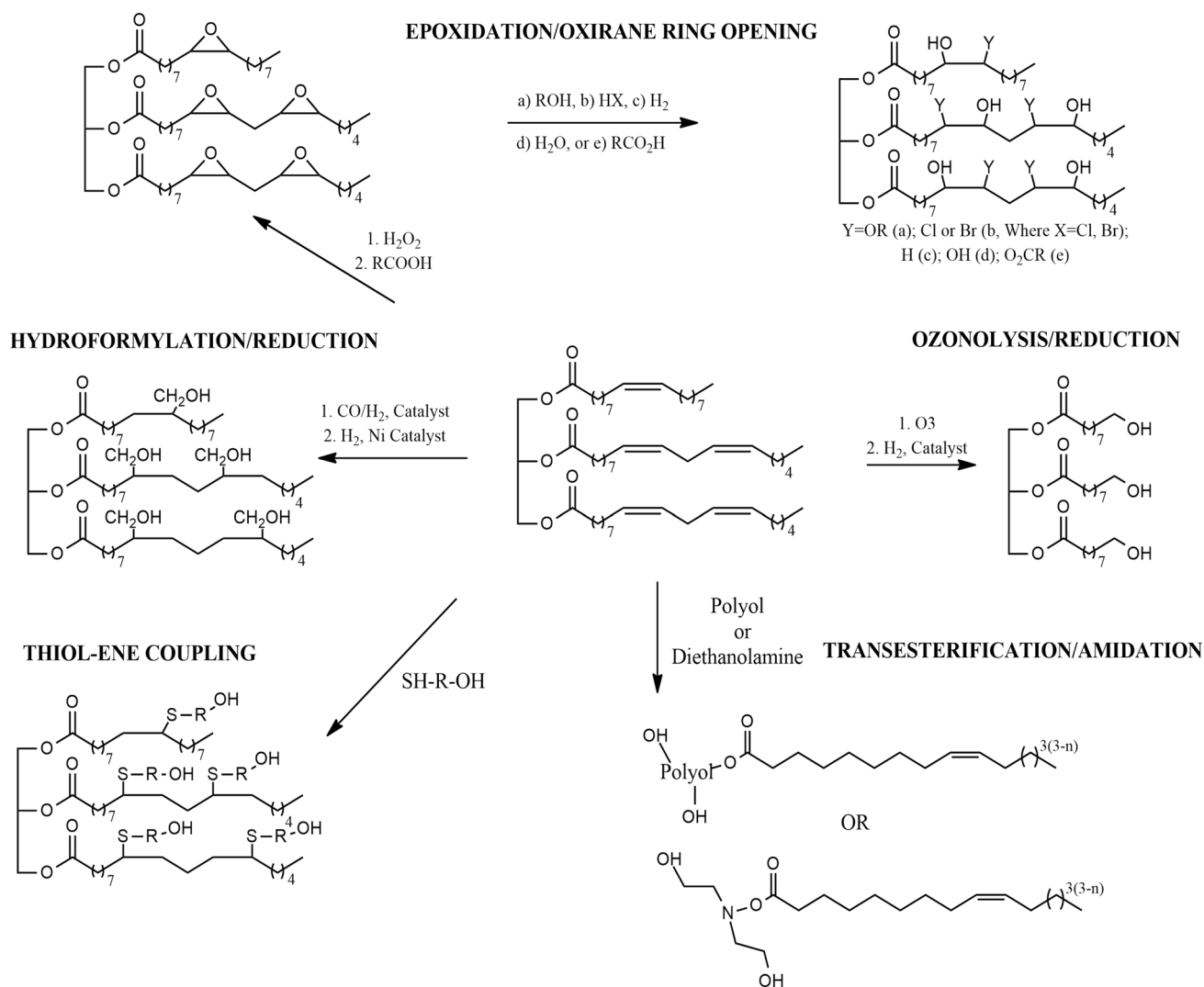


Fig. 4 Various routes to convert vegetable oil into polyols [4, 27, 28]

Table 1 Comparison of different methods for vegetable oil-based polyols

Reaction Route	Epoxidation	Transesterification/Amidation	Hydroformylation	Ozonolysis	Thiol-ene Coupling
Number of steps	2	1	2	2	1
Primary or Secondary hydroxyl	Secondary, tunable	Primary and terminal	Primary, tunable	Primary and terminal	Primary, tunable
Dangling Chains	Yes	Yes	Yes	No	Yes
Functionality	3–4	2–2.5	> 4	Maximum 3	> 2
OH number (mg KOH/g)	150–200	250–300	> 200	200–300	200–250
MW (g/mol)	900–1100	350–450	900–1100	500–700	1070–1440
Viscosity	High	Low	Medium	Low	Medium
Catalysis	Cheap	Cheap	Expensive	Cheap	Cheap
Reaction Temperature (°C)	50–190	120–220	approx. 120	RT	RT

forces, ionic bond interactions and Van der Waals forces. They are together expressed as cohesive energy density (CED). Higher CED value leads to superior mechanical properties [30–32].

Advances in Conventional Solvent-Based PU Coating

The presence of long aliphatic fatty acid chains in vegetable oils, often in combination with commercially available resins, acts as a solvent or reactive diluent for the coating. They form an inherent part of the final material by participating in the chemical reactions that occur during drying, curing, or cross-linking. Researchers have also focused on using low or minimal solvent content in solvent-based coatings to overcome VOC pollutions and to carry out reactions with ease. Akram et al. made boron-containing PU coating by using castor oil for corrosion protection using the minimum amount of solvent. The solvent was used in PU synthesis to minimize the effects of high viscosity and complexity. They have successfully synthesized a PU-boron coating with excellent physical, mechanical and chemical resistance to alkalis, acids, tap water and xylene, and also the thermal stability was up to 220 °C [33]

In another attempt, after successful material synthesis, the author removed all solvents by evaporation. In the synthesis of polyorthotoluidine (POT) dispersed castor oil PU rust-proof nanocomposite coating, a rotary evaporator was used to remove the solvent [34]. The minimum possible methyl ethyl ketone (MEK) solvent was also used to prepare the TDI solution. This TDI solution was then used in the synthesis of soybean oil-based silica nanocomposite coatings. The resulting coating showed improved anticorrosion ability. The strong bond between the $-O-Si-O$ bond and the organic polymer network has improved various properties such as physico-mechanical, hydrophobic and corrosion resistance [35]. The use of green solvents such as dipentene is an eco-friendly approach in developing sustainable products. In one study by Kulkarni et. al, dipentene was used as a solvent and

oleic acid was used as a ring-opening agent for epoxidized soybean oil to increase green content in PU coatings. The oleic acid-containing PU was showed a faster-curing rate and higher thermal stability [36].

UV curable coatings are now termed as next generation coatings. It is one of the most efficient techniques to rapidly synthesize highly crosslinked polymer networks with advantage of “5E” (Efficient, Energy Saving, Economical, Enabling, and Environmentally friendly). These coatings not only reduce VOCs but also speed up production processes [37–39]. Figure 5 depicts general scheme of UV curable coatings. These coatings are generally solventless but often minimal quantity of solvent is added to ease the reaction but Yang et al. had made a truly solvent less coating by replacing the solvents with active diluents. This improvement led to the following advantages. First was the reduction in viscosity of the reaction system. Second, the post-processing was omitted, the utilization rate of raw materials was close to 100%. Third, the reactive diluent can be UV cured, so improvement in the curing properties was observed [38].

Solvent-Based PU Hybrid Coatings

Hybrid systems are the combinations of two or more different types of polymers. The resultant polymer may have organic-organic bonding or organic-inorganic bonding. It is a well-known fact that properties which can be provided by inorganic bonding cannot be provided by organic bonding. Various systems of PU combined with acrylics, epoxies, silanes etc. are available. Out of these the most focused is silane incorporation in PU coatings [40, 41].

It is also well known that castor oil contains ricinoleic acid which is a hydroxyl-containing fatty acid in its triglyceride structure. This is the main reason it is exhaustively modified as PU for various applications. PU coatings made from aromatic petroleum sources tend to be brittle, but those obtained from vegetable oil-based polyols have inherent flexibility due to the long aliphatic fatty triester chains. Many researchers have focused on this characteristics of vegetable oil as it reduces mechanical strength. It is improved

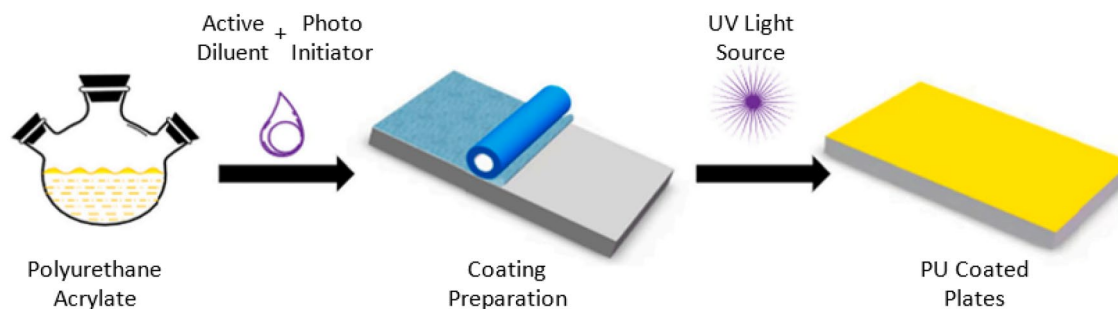


Fig. 5 General Scheme of UV-Curable Film [38]

by adding an inorganic element to the main structure as a reinforcing material. Properties are highly dependent on structure, type of nano reinforcing material, nature and type of alkyl group, solvent, concentration of catalyst, pH and temperature. Hong et al. incorporated silicon in soybean oil polyol, can be seen in Fig. 6. The polyol was made by the thiol-ene route having an average of two hydroxyl groups per mole. (3-mercaptopropyl)trimethoxysilane (MTS) was used to introduce silane functionality in the polyol. PU coatings were made by keeping the NCO: OH ratio 1.2: 1. The incorporation of rigid silane functional group fundamentally increased cross-linking degree which increased the gloss and hardness of coatings. The electric current density was 1.32×10^{-7} for silane polyol based PU coatings, which was lowest as compared to other PU coatings [42].

Tetraethoxy orthosilane (TEOS) formed silanol after hydrolysis and after self-condensation or condensation with OH of polyol formed -O-Si-O- bonding with the main chain of polyol. The increase in silica content effectively increased gloss, but other properties such as scratch hardness were optimum at 0.5 mol TEOS. The major development here was the method of synthesis. The earlier methods were

multistep processes and required more time for curing [40]. An adduct of castor oil and maleic anhydride was reacted with 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) to make acrylated alkoxysilane castor oil (AASCO). It was then reacted with PU/urea-silica hybrids, as seen from Fig. 7. The addition of TMSPMA resulted in increasing T_g and storage modulus due to the Si-O-Si network and cross-linked structures. The hydrophobicity effectively increased with an increasing quantity of TMSPMA, the water contact angle was observed to be 102° with dosing of 0.3 g of TMSPMA. The Si-O-Si linkages also provided a barrier to water and corrosive agents leading to enhance the corrosion protection, results of salt spray test can be seen in Fig. 8 [43].

The organic-inorganic hybrid (OIH) PU coatings of soy oil- monoglyceride (organic precursor) and TEOS (inorganic precursor) showed very much improved physico-mechanical properties. This low VOC coating was prepared by taking a minimal amount of methyl ethyl ketone (MEK). Properties such as scratch hardness was doubled at a dosing of 0.5% and were three times higher than reference only with 2.0% TEOS. Thermal degradation also got improved due to the incorporation Si-O-Si bond in the main chain. The

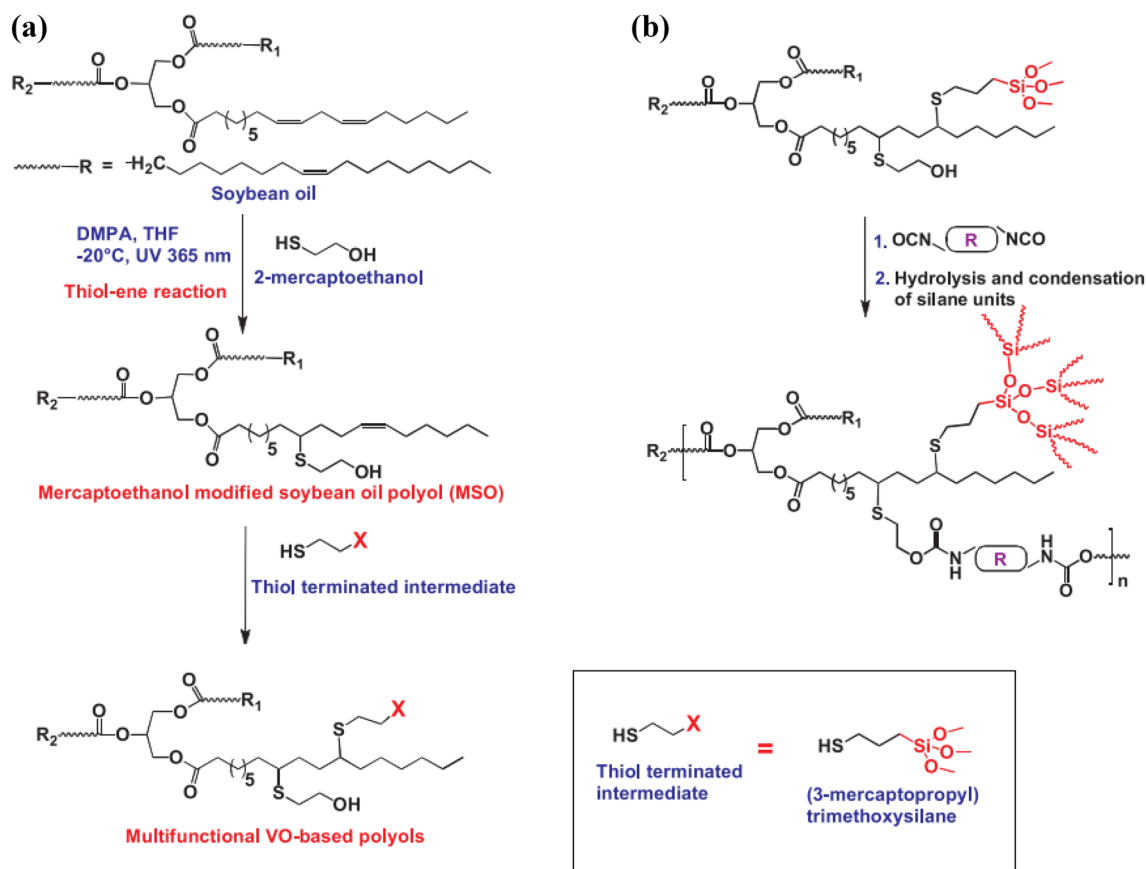


Fig. 6 Reaction scheme for the preparation of functionalized polyols through sequential thiol-ene reactions: **a** first step, the preparation of MSO and second step, the preparation of functionalized polyols containing silane. **b** Preparation of PU coatings [42]

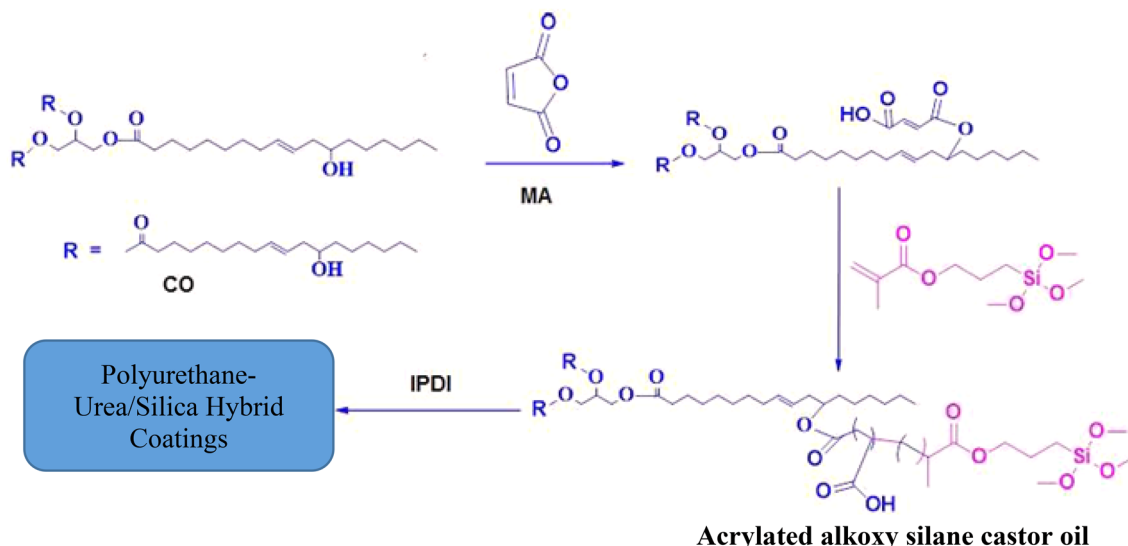
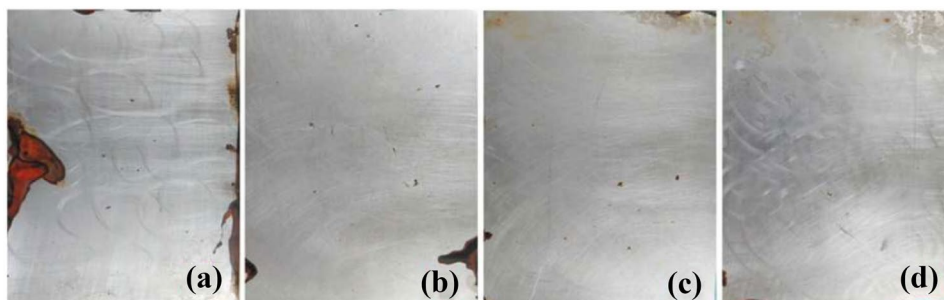


Fig. 7 Synthesis route of Polyurethane-Urea/Silica Hybrid Coatings [43]

Fig. 8 Salt spray images: **a** COPU; **b** AASCOPU-0.05; **c** AASCOPU0.15 and **d** AAS-COPU-0.3 [43]



effect of TEOS in anticorrosive coatings was evaluated by Electrochemical Impedance Spectroscopy (EIS), the superior corrosion protective property was found to be with 2% TEOS coats. This is due to the formation of optimum cross-linked hydrophobic nanostructured surface morphology of the coating ($-\text{O}-\text{Si}-\text{O}-$), which repels the water and aqueous corrosive ions [35]. A simple oxidation reaction can also introduce hydroxyl groups in vegetable oil. Bianchi et al. made soybean oil-based polyol by air oxidation at a constant flow rate of air at $120\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ for 24 or 48 h. The PU-Urea hybrid was made by using (3-aminopropyl) trimethoxysilane (APTMS) which acts as a network former in the organic–inorganic material. A two-step reaction was carried out by first adding APTMS and polyol and subsequently MDI at room temperature. To carry out final polymerization, the reaction mass was first heated to $60\text{ }^{\circ}\text{C}$ for 12 h after which it was heated at $160\text{ }^{\circ}\text{C}$ for 1 h for thermal hydrolysis and condensation of silanol groups. The system without APTMS was a single-phase film but when APTMS was added, a double phase started to appear in the system. Particle sizes observed were between 5 and $10\text{ }\mu\text{m}$, and it was more spherical for films produced with oil oxidized for

48 h. The observed spheres were silicone rich and this was due to the difference in the reaction rates. The urea group formation was higher than the urethane group formation hence more segregation of uncondensed silanol and urea which not only increased the hydrophilic character but also lowered anticorrosive property [44].

A polyesteramide polyol was prepared using cottonseed oil-based fatty acid amide which was synthesized by amidation of cottonseed oil and subsequent reaction with a series of dicarboxylic acids which have natural sources such as sebacic acid, succinic acid, tartaric acid, maleic acid and azelaic acid. They also used suberic and phthalic acids in the reaction. This methodology increased bio-based content up to 81% in the overall product. The gloss value of azelaic acid was found to be highest due to the presence of more ($-\text{CH}_2-$) linkages [45]. A similar attempt was done to make PU coatings from bio sourced itaconic acid based polyesteramide [29, 46]. A dual crosslink polymer network (DCPN) was prepared by using castor oil, castor oil epoxy (ECO), ricinoleic acid epoxy (RAE) with TDI. The reaction of TDI with the epoxy ring produced oxazolidinone ring in the chain and the reaction of TDI with hydroxyl groups

produced urethane linkages. Together this system was called DCPN and gave an overlapping combination of two or more cross-linked polymers i.e., polyurethane & polyoxazolidinone (POXDN), as seen from Fig. 9. The tensile strengths were 0.26 MPa, 12.47 MPa, 22.87 MPa for CO/TDI, RAE/TDI and ECO/TDI systems respectively.

The factors such as rigid bridge–ring chemical structure and a higher cross-linking density jointly control mechanical properties. The shore hardness and storage modulus were found to be highest for the ECO/TDI system [47].

The fatty acid amide of *Azadirachta indica* Juss oil showed anticorrosive performance. The inclusion of nitrogen would increase the performance so that fatty acid amide was modified with piperazine. Piperazine modified PU coatings had more soft segments which increased mar, impact

and chemical resistance [48]. A dramatic increase in thermo-mechanical properties was observed in PU-imide made from *N*-(2-hydroxyethyl)-maleimide (HEMI), castor oil and eleostearic acid diethanol amide (EADEA) of tung oil. A possible Diels–Alder adduct forms between EADEA and HEMI can be seen from Fig. 10. which increased rigidity in the overall structure. Keeping in mind the structure–property relationships, the rigidity was increased directly with the amount of EADEA and HEMI.

It caused the increase in crosslinking density as well which is a major factor affecting thermal properties such as T_g and storage modulus. The T_g and storage modulus increased linearly with the amount of Diels Alder adduct (DA) of EDEA and HEMI. Tensile strength increased from 1.4 MPa for 0% DA to 48.2 MPa for 60% DA whereas the

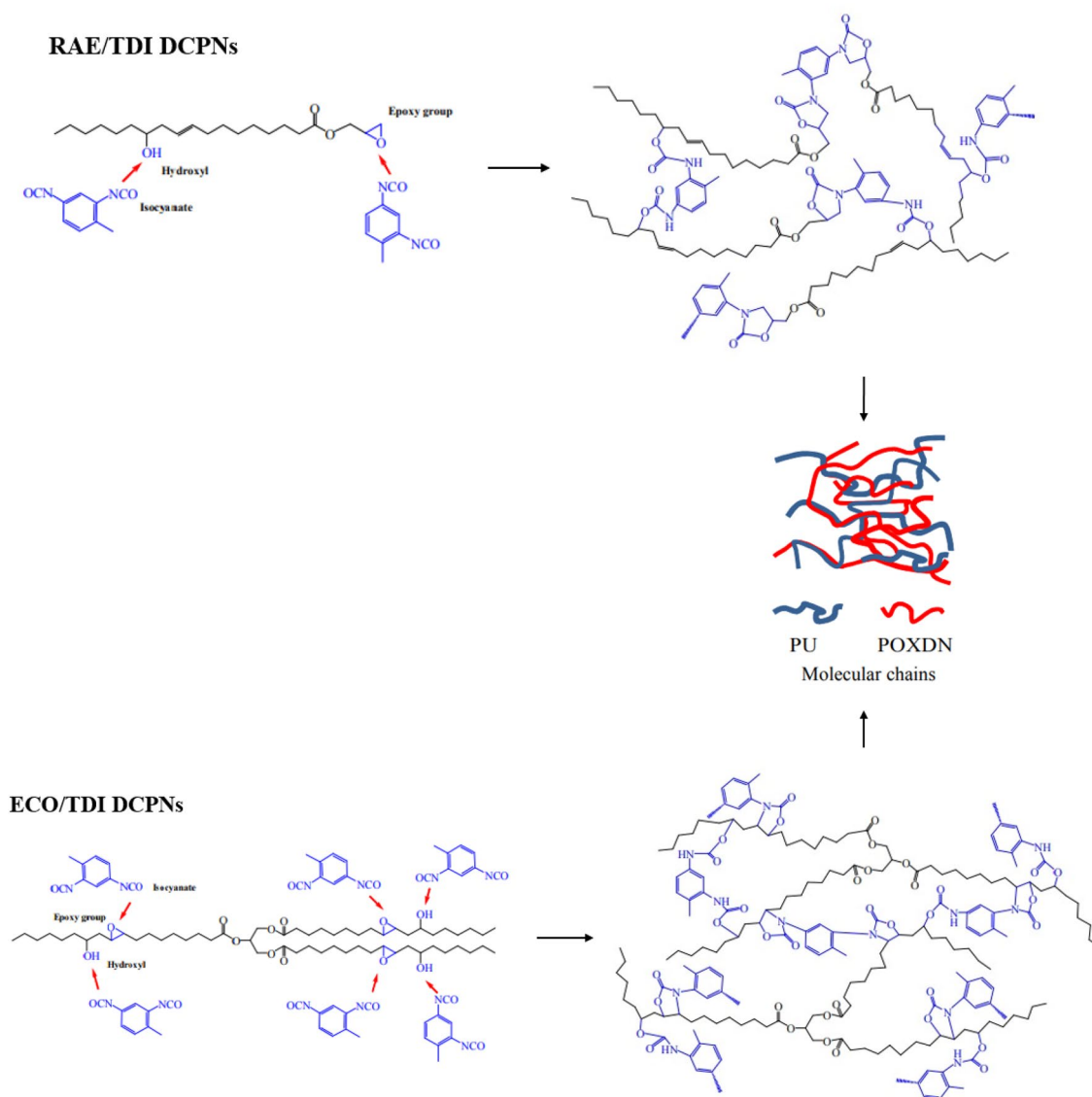
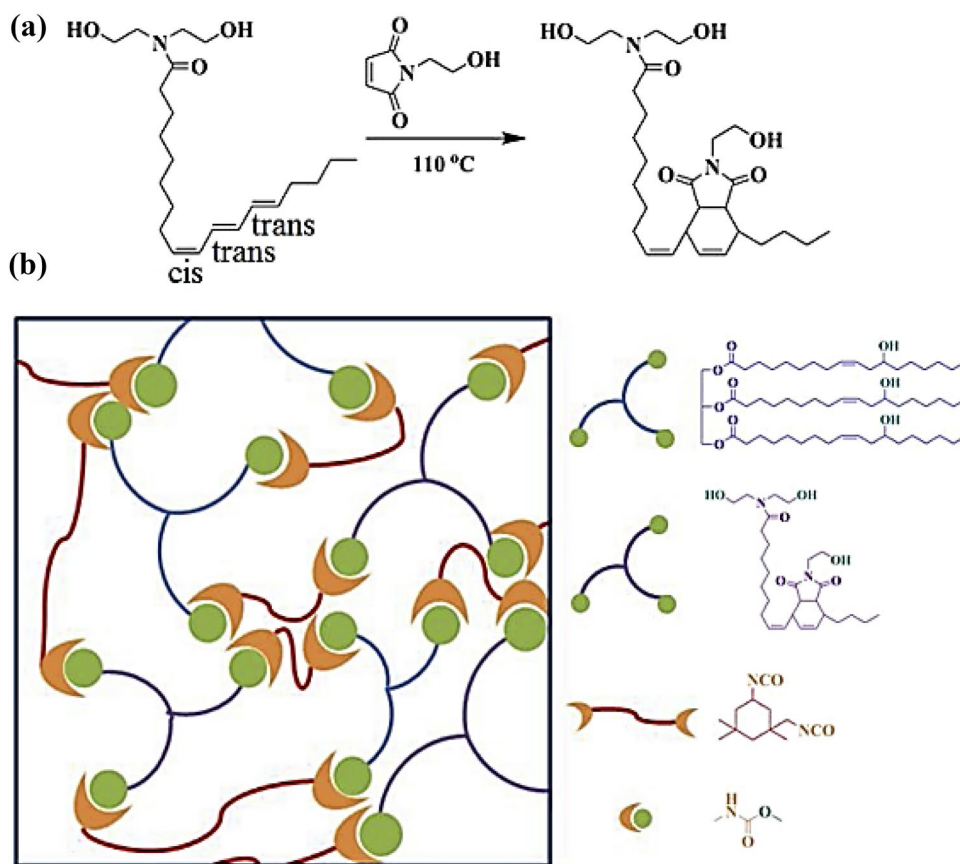


Fig. 9 Reacting mechanism of prepared RAE and ECO based DCPNs [47]

Fig. 10 a Diels–Alder adduct from EADEA and HEMI, b possible network structure of polyurethanes with EADEA and HEMI [49]



glass transition temperature increased from $-13.9\text{ }^{\circ}\text{C}$ for 0% DA to $74.1\text{ }^{\circ}\text{C}$ for 60% DA [49].

Solvent-Based PU Nanocomposite Coatings

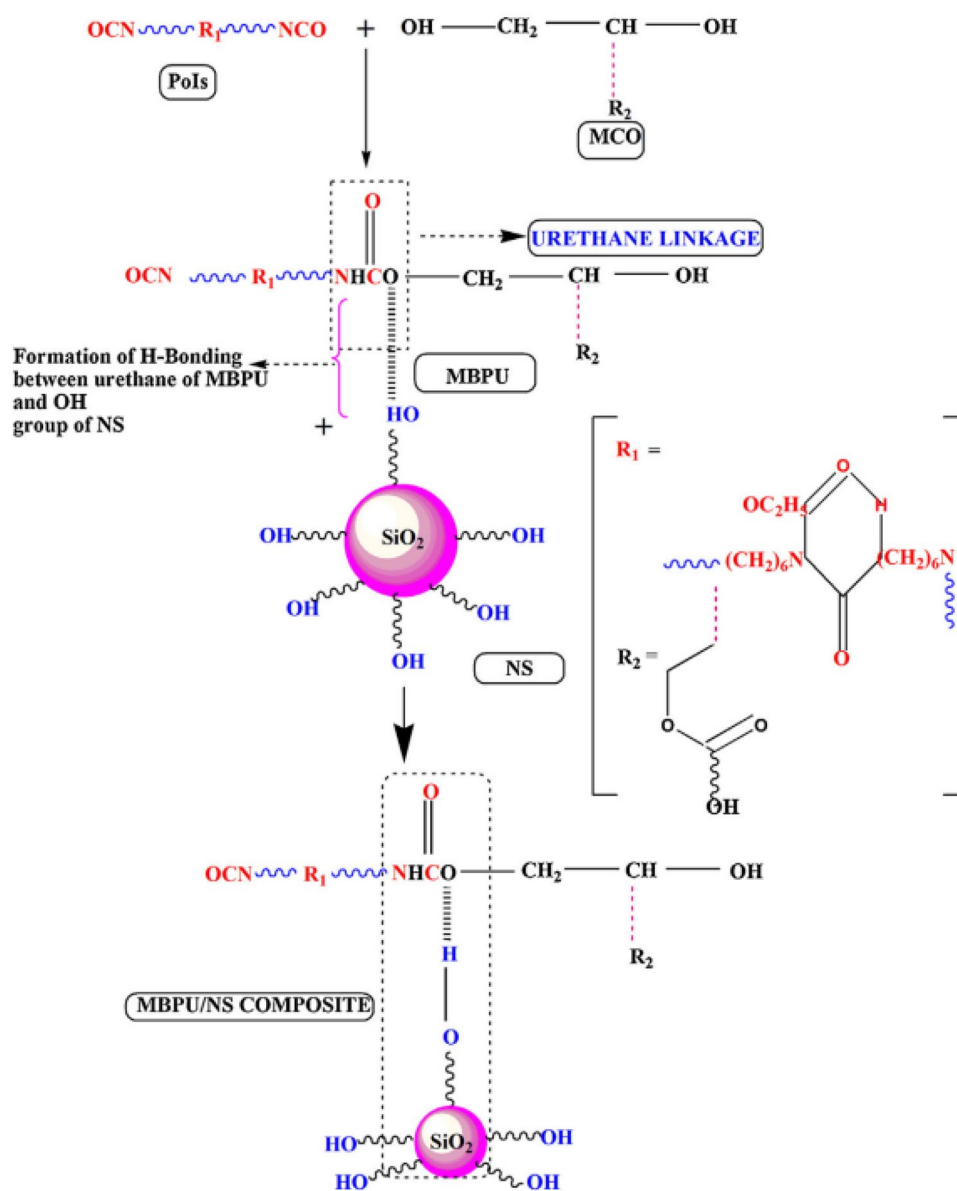
Nanocomposite coatings consist of nanoscale filler in the dispersed state. Various studies have been done on the performance and properties of PU containing nanofillers such as exfoliated clay, carbon nanotubes, carbon nanofibers, exfoliated graphite, natural fibrous nanoclay (attapulgite, ATT), cellulose nanocrystals etc. Various other nanosized fillers like TiO_2 , ZnO , Al_2O_3 , silica and clay also have been reported to improve the performance characteristic of PU coatings. Nano silica has been found to pass on excellent mechanical, chemical and optical properties owing to the strong bonding. Overall coating performance characteristics such as water resistance, ageing resistance, transparency and finish of coating were improved significantly due to network structure formed in PU/nanosilica (NS) composite [50–54]. PU/NS composite coating was also made by using palm oil-based isocyanate and transesterified castor oil, as seen in Fig. 11. The PU referred as MBPU. The NS particles were first dehydrated by keeping in a hot air oven for 12 h at $80\text{ }^{\circ}\text{C}$. After that, about 2.5% of NS particles were ultrasonicated in palm oil isocyanates (PoIs) to promote homogenization

and dispersion. The adhesive strength of PoI based coatings was comparable to petroleum-based isocyanates due to the molecular structure of PoIs. The PU networks were highly crosslinked without any steric hindrance, the NS containing coats were also faster curing as compared to PU coats without NS. This was due to the interaction between both silanol groups on the NS surface and urethane via hydrogen-bonding resulted in faster cross-linking within a short period. NS incorporation resulted in increased gloss, taber resistance as well as improved chemical resistance [50].

Amine modified silica nanoparticles were made by adding TEOS in solution of ammonia and ethanol and subsequently adding 3-aminopropyltrimethoxysilane dropwise. These nanoparticles were added in PU of castor oil and HDI in a dropwise manner to make castor oil PU–silica nanocomposites. In this system, the presence of amine-modified silica groups increased agglomeration on the surface which increased hydrophilicity and decreased water contact angle. Tensile properties of PU-based castor oil/silica nanocomposite also improved and were nearly doubled than that of the control sample with only 1% AMS content, due to transfer of load from the polymer matrix to inorganic silica [55].

Among the nanomaterials, TiO_2 has a great potential in semiconductors, fuel cells, self-cleaning and anti-fog glass coats, antibacterial surfaces, chemical sensors and

Fig. 11 Probable H-bonding linkage between the OH group in NS and urethane group in MBPU [50]



photocatalysis. TiO_2 nanoparticles-induced PU coatings were prepared by using sunflower oil-based fatty acid amides. It showed optimum performance at a maximum of 2% dosing. Pencil hardness, scratch hardness, curing time were much superior to the coatings without nanoparticles also, anticorrosive performance was higher for high TiO_2 containing coating in aqueous, NaCl and HCl mediums [56]. A new approach towards anticorrosion coatings was made by dispersing nanostructured polyorthotoluidine (POT) in castor oil-based PU coatings. Synthesis scheme shown in Fig. 12. The increase in the dosing of POT led to an increase in scratch hardness, impact resistance and curing rate. POT is conducting polymer and no doubt the increasing amount of POT in castor oil-based PU led to an increase in the conductivity. The anticorrosion performance was extremely

good as compared to the past works by Mobin et al. They used poly(aniline-co-o-toluidine) and poly-(pyrrole-co-o-toluidine) to coat steel plates. The corrosion rate under 0.1 M HCl was 5.02 and 4.11 mpy respectively. The POT containing nanocomposite coatings showed corrosion rate of 5.2×10^{-3} , 4.2×10^{-3} and 3.7×10^{-3} mpy for 0.25, 0.5 and 1.0 wt percent of POT respectively [34].

Advances in Solvent-Based PU Applications

Urea is the most used fertilizer in crop productions but the use of nitrogen reduces efficiency when more amount of urea is added. It affects groundwater and surface water in a negative way. It also affects the atmosphere through the leaching, runoff and volatilization of nitrogen. Polymer

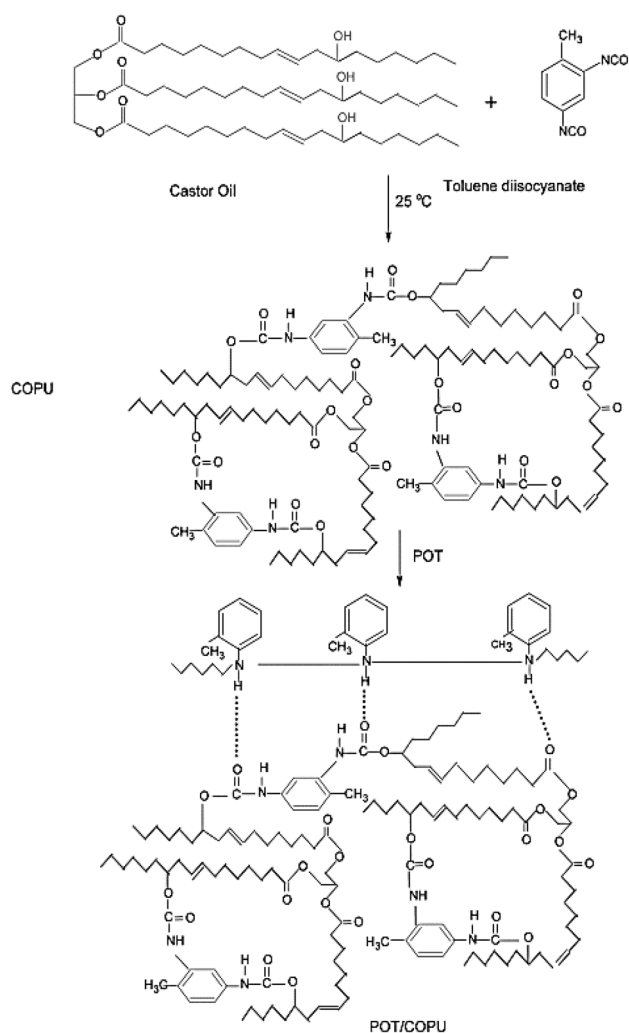


Fig. 12 The synthesis scheme of castor oil PU (COPU) and POT/COPU composite [34]

coated sustained release urea (CRU) is a proven technique to solve the problem of low nitrogen utilization in plants and reduce their environmental impact. CRUs also save labor costs and time compared to multiple applications throughout the growth period. High doses of soluble fertilizer are needed to meet the nutritional requirements of plants [57]. One component castor oil-based PU prepolymer was coated on urea granules by rotation coating, schematic representation can be seen in Fig. 13. A smooth and compact coating shell is needed to hinder the water from entering the core which was resulted from a lower OH/NCO ratio. Initial nutrient release was affected by the basic structure of PU. Reactivity due to aromaticity was the dominating factor as it controls the crosslinking density. This finding was also supported in PU made by castor oil with higher OH number as it directly increased crosslinking density. Nutrient release rate in 24 h was found higher for isophorone diisocyanate (IPDI) based PU than TDI and polymeric methylene

diphenyl diisocyanate (PMDI) systems respectively. It was also due to the hydrophobicity of coatings. The PU from PMDI blocked the discharge of dissolved nutrients from fertilizer to a higher level. Hence proper control over crosslinking density by OH number of polyol and reactivity provided by isocyanates were the controlling factors to synthesize slow-release fertilizers with the nitrogen release longevity from 20 to 140 days [58]. Figure 14 shows schematic of the synthesis of castor oil based PUs.

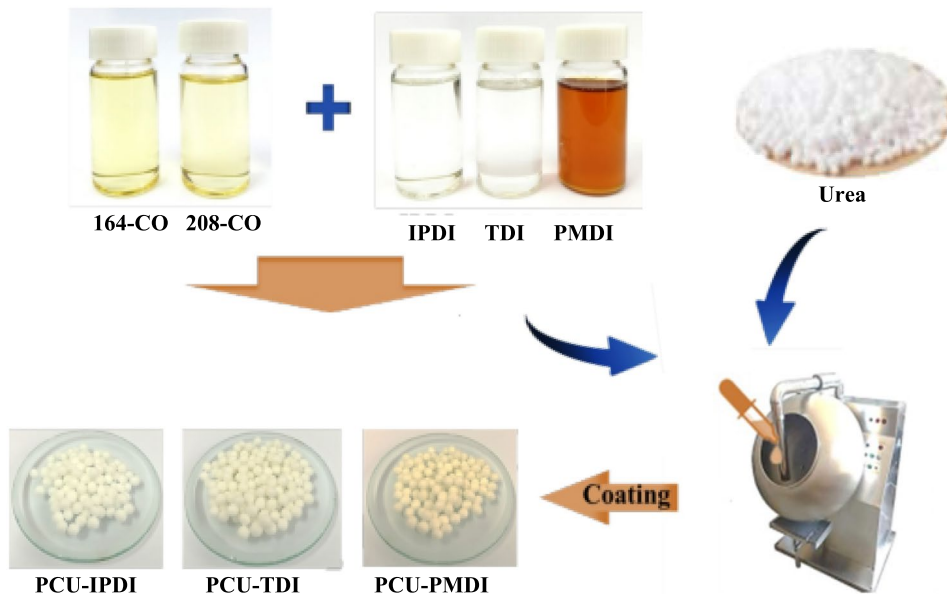
In phosphate fertilizers, the amount of iron and aluminum-based compounds are high, which reduces the overall efficiency of phosphate fertilizers. To overcome the issue, castor oil-based PU was used to coat the diammonium phosphate (DAP). The rate of release of fertilizer was inversely related to the coating percentage. Hence higher was the percentage of coating slower was release rate of fertilizer. Materials with 3.0, 4.5, 6.0, 7.5 wt% of polymer content showed significant delays in phosphorus release, with 80% release reaching in 50 h, 75 h, 240 h, 375 h respectively. The release rate is also dependent on coating thickness as it governs solubilization and diffusion of the sample in medium [59].

An omniphobic coating was made by using epoxidized soybean oil and castor oil-based polyol in separate studies. The coating was a hybrid of monocarbinol terminated polydimethylsiloxane (PDMS-OH) and PU network. PDMS-OH acted as covalently introduced de-wetting agent to enable the coating with omniphobic dewetting properties [60, 61]. A wood coating was prepared using peanut oil-based fatty amide and hexamethylene diisocyanates biuret. In a separate batch, a commercially available hardener was added and both PU coats were applied on wood panels. The gloss and the hydrophobic properties were observed to be excellent as compared to the commercially available PU systems [62]. In another attempt, mahua oil-based polyetheramide polyol was prepared. At first, mahua oil fatty amide was prepared and it was reacted with diglycedyl ether of bisphenol A to get polyetheramide polyol. PU wood coatings were prepared from this polyetheramide polyol with aromatic and aliphatic isocyanates, as seen in Fig. 15. The aliphatic diisocyanate based PU showed a slightly higher water contact angle and water absorption than aromatic diisocyanate based PU, water contact angle is shown in Fig. 15. The hydrophobic nature of the PUs prepared were mainly due to the two reasons: first, high crosslinked structure of the PUs prepared and second the hydrophobic nature of the mahua oil and diglycidyl ether of bisphenol A (DGEBA) [63].

Advances in Water-Based PU Coating

Waterborne PU dispersions are prepared by addition of water in PU ionomers containing a very small amount of solvent. Hydrophilic groups are introduced in the main

Fig. 13 Preparation process of the coated urea with castor oil based polyurethanes [58]



or side chain to make the salt of polymer. This enables the dispersibility of polymer in water. The ionomers are anionic and cationic types amongst which dimethylol propionic acid (DMPA) and N-methyl diethanolamine (MDEA) are mostly used ionomers respectively [15, 64]. The residual unsaturation of polyols plays an important role in mechanical property. Toughness and break strength of the coatings increases as the unsaturation increase. The overall composition and distribution of fatty acids in triglyceride plays a vital role in determining the properties. Properties improved with homogenous distribution [65]. The increase in hydroxyl groups from emulsifiers or polyol/castor oil increases the transparency of PU dispersions (PUD). It creates a pool of hydrophilic groups and enables the hydrophobic hard and soft segments of PU to disperse in water and also reduces the particle size of PUD. Another fact is with the increase in hard segment content, the mechanical properties such as tensile strength, Young's modulus and thermal properties such as glass transition temperature also increase. This is due to increase and improvement in hydrogen bonding and crosslinking density [22, 66–68]. The stability of dispersion can be determined by particle size and zeta potential. Smaller particle size and the high absolute value of zeta potential denotes more stable dispersion. Zeta potential is the particle charge at the edge of the layer and the surrounding solvent. The higher value suggests the particles tend to repel each other resulting in better stability [24]. Also, researchers are currently focused on alternate synthetic methods to generate not just solvent-free products, but also totally solvent-free synthesis processes.

Water-Based PU Hybrid Coatings

Hybrid waterborne PU is the area of intensive research for coatings, sealants, and adhesive applications. Hybrid water-based polyurethane (WPU) has a broad range of options for selecting raw materials. Properties of hybrid WPU can also be improved by physical methods like grafting with another raw material also sometimes by blending and mixing. In a novel attempt made by Saetung et al. used Hydroxy telechelic natural rubber (HTNR) and Hydroxyl rubber seed oil (HRSO) in a 50:50 mol ratio. Simultaneously butyl acrylate/methyl metha acrylate (BA/MMA) was added in water and poured after neutralization to check the effect of grafting on PU but on higher addition of BA/MMA, the particle size increased. This happens due to an increase in interparticle interactions, including van der Waals and hydrophobic interactions and hydrogen bonding leading to agglomeration. The elasticity was reduced after the addition of BA/MMA [69]. Refer Fig. 16 for schematic representation.

In soybean oil-based dispersion the addition of hard monomers such as MMA and styrene with the increase in quantity from 25 wt% to 50 wt%, resulted in decrease in gloss. This is majorly due to the phase separation of PUDs and hard segments. Possible reasons are a thermodynamic incompatibility between aromatic and aliphatic segments as well as mobility of segments and roughness of the surface. In particular, the addition of hard monomers up to 35% improves the tensile strength and Young's modulus a little bit but not the percentage of elongation [70].

Just like acrylates, other important polymers were copolymerized to get PUDs with advanced properties. Such

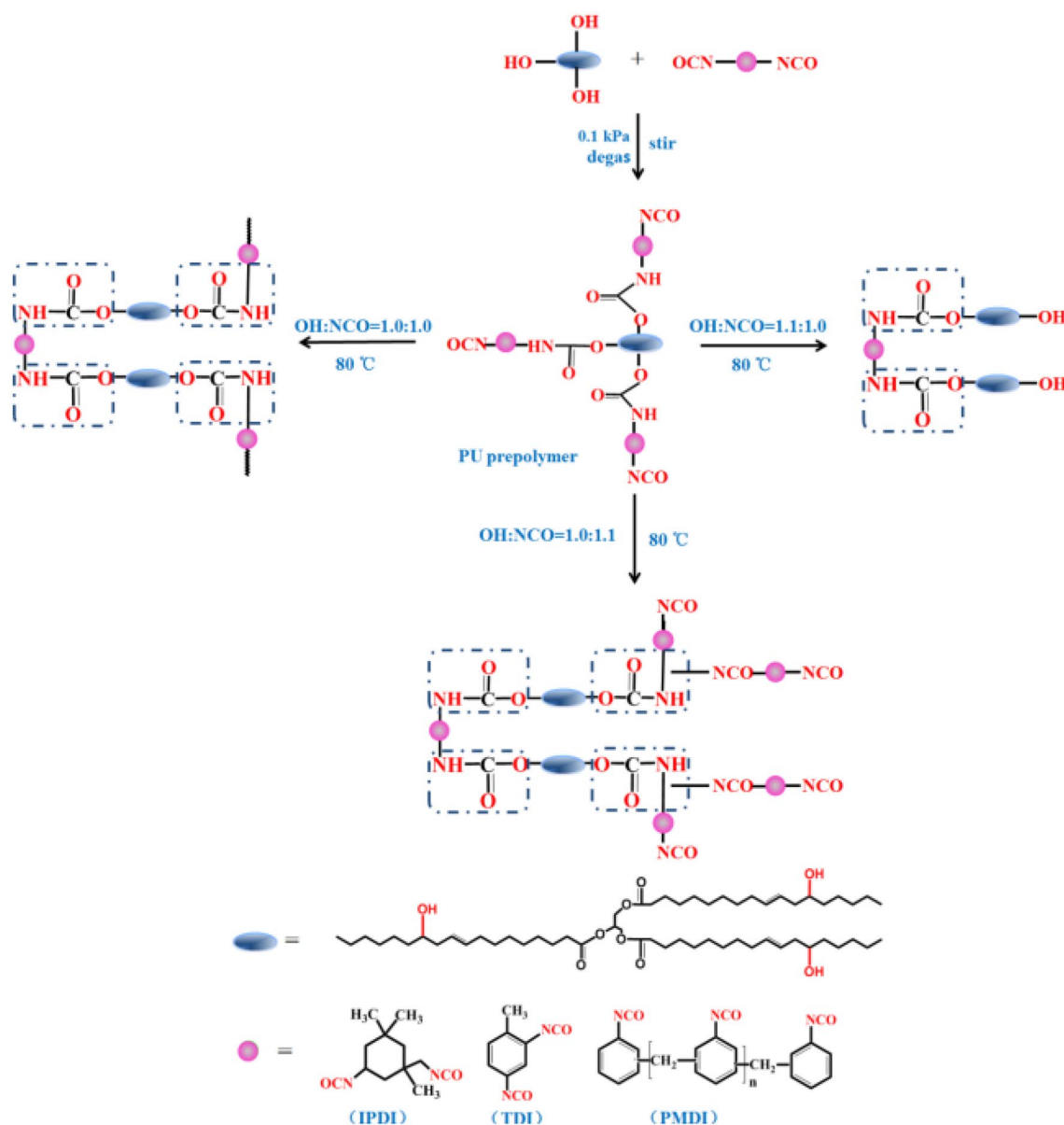


Fig. 14 Representative schematic of the synthesis of castor oil based PUs with different OH/NCO molar ratios [58]

high-performance polymers are polyamides, especially aromatic polyamides. They maintain their structural integrity even at high temperatures. A polyamide of bis(4-aminophenyl)sulfone and terephthaloyl chloride was introduced before the neutralization step in castor oil-based prepolymer of varying weight percentages of 1, 3, 5. The addition of polyamide undoubtedly increased the thermal stability of PUD with delay in degradation temperature, also T_g of PUD was increased with an increase in weight percentage of polyamide [71]. A hybrid material based on linseed oil monoglyceride and IPDI with aminopropyltrimethoxysilane (APTMS) was made. APTMS was used as a network modifier. The introduction of siloxane network in PU increased

storage stability, thermal and mechanical properties and hydrolysis resistance [72]. In one study organic montmorillonite (O-MMT) was dispersed in castor oil-based PUD. The water resistance of coatings decreased at around 10–15% dosage of O-MMT. Due to the presence of silane coupling agents, thermal stability and rigidity of the nanocomposites were enhanced [73]. The addition of sodium alginate (SA) in PUD of castor oil, IPDI and dimethylol butanoic acid (DMBA), improved water resistance with an increase in content from 5 to 20%. Sodium alginate is extracted from brown algae and it is an eco-friendly natural polysaccharide carbohydrate. SA added in the solution form in PUD. SA undoubtedly increased the physical crosslinking which

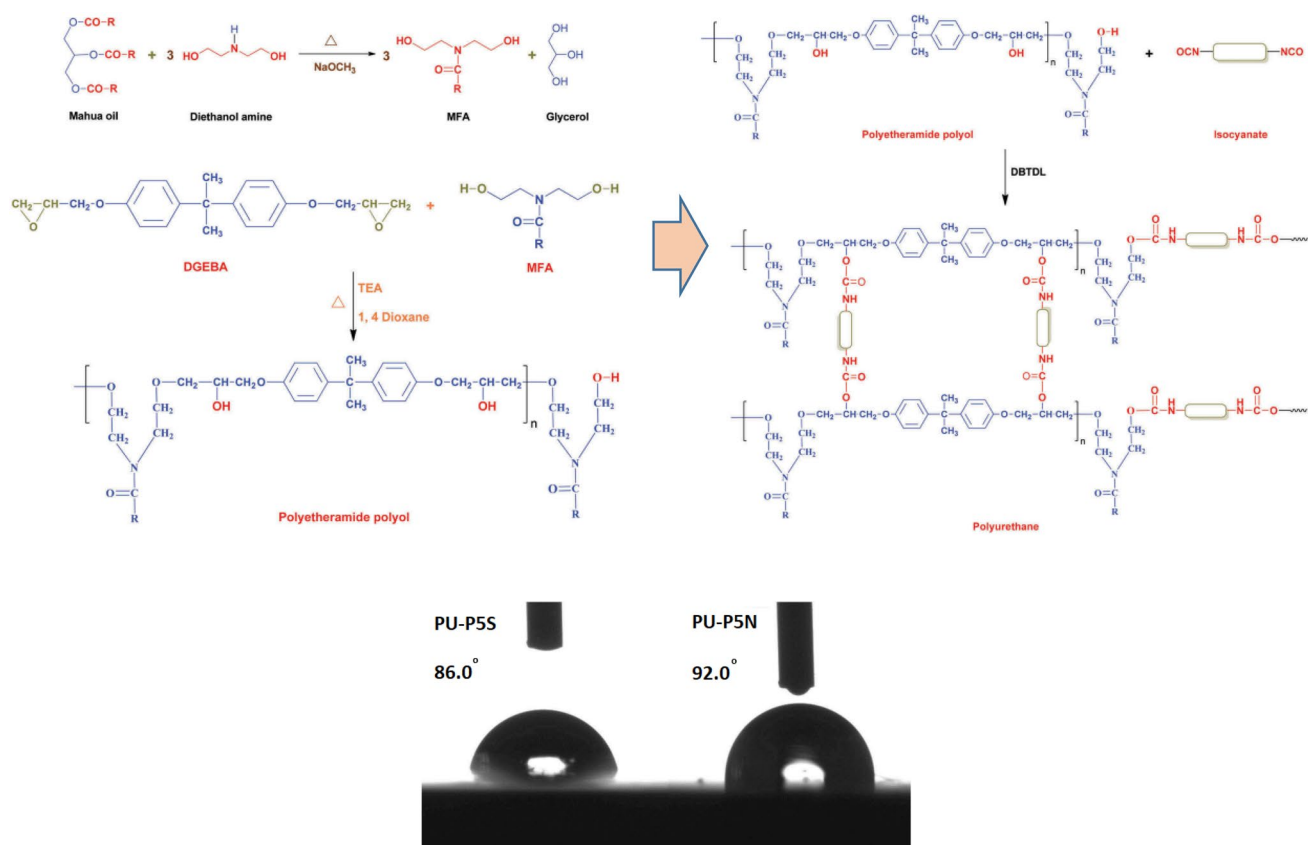


Fig. 15 Schematic representation of polyol & polyurethane synthesis, water contact angle of PU-P5S (PU made by using aromatic isocyanate) and PU-P5N (PU made by using aliphatic isocyanate) [63]

resulted in an increase in storage modulus after calcification. Figure 17 depicts schematic representation of films.

As the SA content increased from 5 to 20 wt. %, storage modulus at 25 °C increased from 147.1 to 522.1 MPa. With increasing content of SA, hydrogen bonding and the formation of interpenetrating networks increased the physical crosslinking density, preventing the chains from sliding to each other which improved the tensile properties such as tensile strength, Young's modulus and decrease in elongation and toughness [74].

Zhang et al. introduced a new approach towards a completely environment-friendly hair styling agent. They used castor oil-based PUD with DMPA, DMBA and acetic acid as an emulsifier. This dispersion was carefully sprayed to tress and then combed for a minimum of 10 times, blow-dried for 90 s. It was then spiral-wrapped around an iron (120 °C) for 10 s. The final lengths were measured after hanging the curled tresses at 25 °C, 75 ± 5% RH environment for 90 min. The hairstyling efficiency i.e., $R_S = (\text{The hair crimp ratio after hanging for 90 min}) \times 100\%$, was higher for a sample having Young's modulus > 50 MPa, elongation at break in the 15–300% range, and moisture uptake < 4%. Low elongation at the break resulted in early breaking of the styling

thin film, resulting in lower hairstyling efficiency, and excessive moisture uptake reduced mechanical characteristics. Another critical measure is the skin irritation test, which was carried out on rabbits for 72 h. The results indicated no evidence of skin irritation, outperforming a commercial hair spray [75]. A castor oil based anticorrosive Waterbased PU was made by incorporating sustainable diols, isosorbide (IS) and L-tyrosine derived cyclic dipeptide (L-CD), as seen in Fig. 18. This improved hydrogen bond density and ultimately resulted in increased tensile strength (TS). The maximum TS was found to be 29.56 MPa. The corrosion inhibition rate (% IE) towards 45# steel was found to be 96.61% [76].

Various green crosslinking agents were also made to increase bio carbon content in the system. Itaconic acid based UV curable crosslinking agent is one of them. It was made by esterification reaction between itaconic acid and hydroxyethyl acetate [77]. The authors also have used various oils to make crosslinking agents. Sapium sebiferum oil was modified by thiol-ene photo-click reaction to yield a polyol. This was then introduced in castor oil based water-based PU. The films made by this system showed excellent water and graffiti resistance [78].

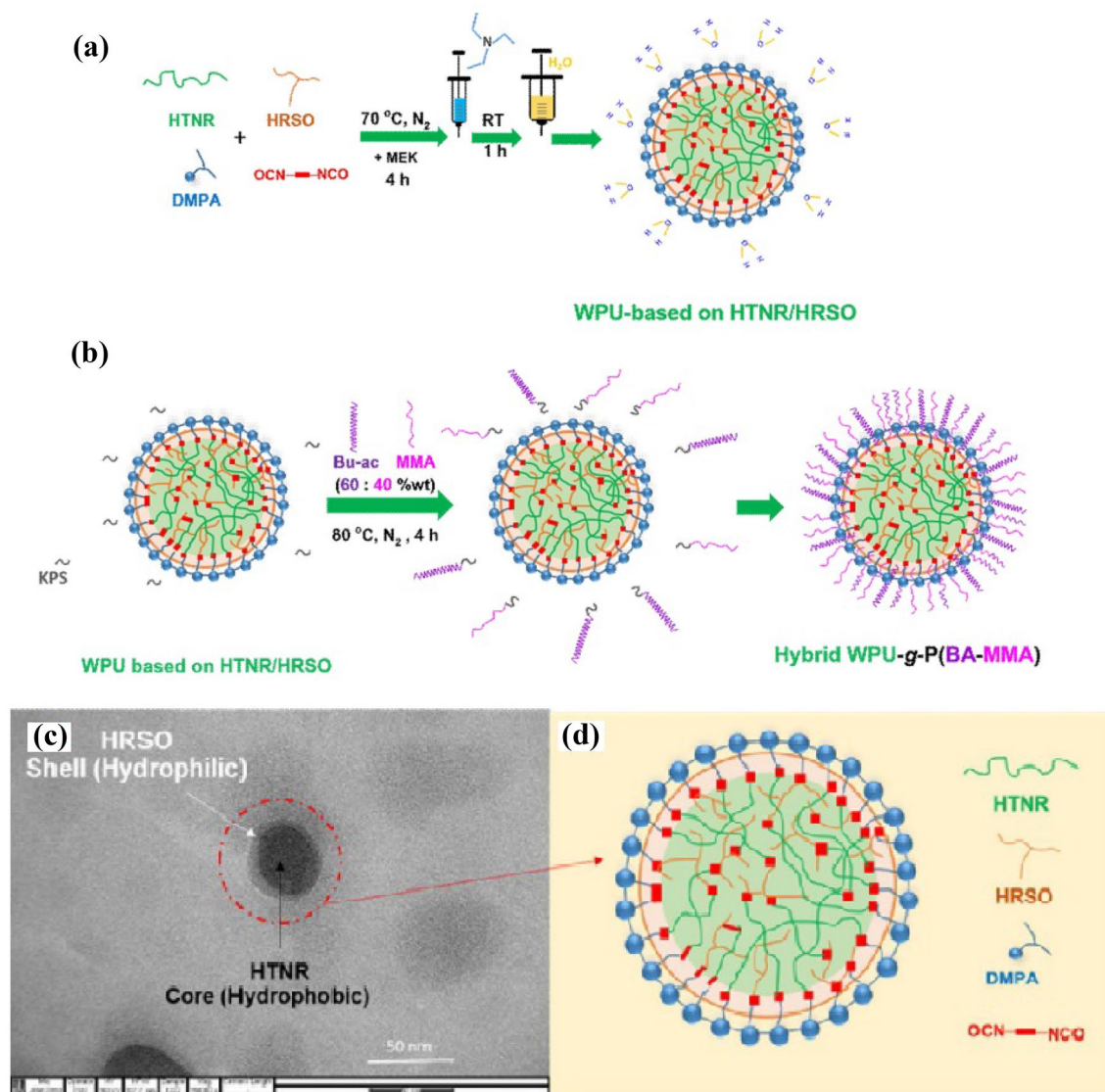


Fig. 16 **a** Synthesis of WPU based on HTNR/HRSO, **b** synthesis of hybrid WPU-g-P(MA/PMMA), **c** TEM image of synthesized WPU based on HTNR/HRSO, and **d** possible model of phase separation in the micellar particle [69]

Water-Based PU Nanocomposite Coatings

The inclusion of nanoparticles such as silica into the polymer matrix enhances performance of the polymer. Various properties such as mechanical, surface and thermal properties can be effectively altered by the addition of nanoparticles in the polymer matrix. A cross-linked castor oil-based PU with 3-aminopropyl trimethoxysilane (APTMS) was made by Gurunathan et.al, to incorporate PU–siloxane structures into the matrix. Such material has good biocompatibility and has positive applications in the medicinal field. Mechanical property such as tensile strength of neat COPU-SiO was 13.4 MPa and increased to 25.9 MPa with incorporation of 5% silica. The interfacial interaction between the silica

filler and the polymer matrix was the key factor in carrying load from the polymer matrix to inorganic silica. The thermal properties improved substantially due to Si–O–Si linkages. These linkages act as mass transfer barrier for volatile compounds and thermal insulator [79]. Three different kinds of nanoclays viz, montmorillonite (MT), attapulgite (AT), and halloysite nanotubes (HT) with platelet-like, rod-like, and tubular structures respectively, were modified with by γ -aminopropyltriethoxysilane (APTES) and then introduced into jatropha oil-based PU matrix via in situ polymerization to make WPU/clay nanocomposites. The hybrids were referred as WPU/SMT, WPU/SAT and WPU/SHT for made with WPU and montmorillonite (MT), attapulgite (AT), and halloysite nanotubes (HT) respectively. These nanoclay

Fig. 17 Schematic representation of composite films [74]

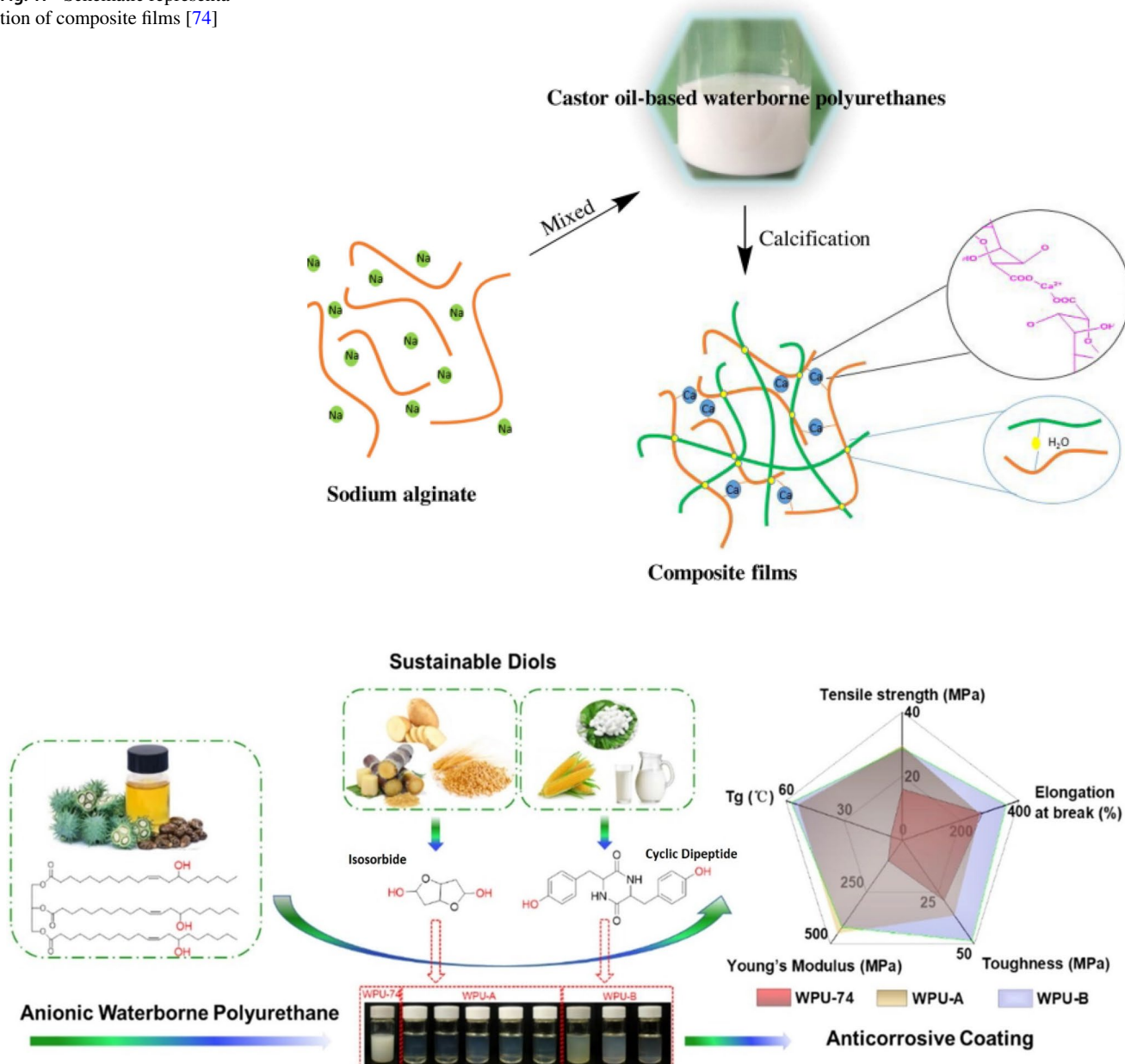


Fig. 18 Schematic representation of water based PU made by incorporating sustainable diols, isosorbide (IS) and L-tyrosine derived cyclic dipeptide (L-CD) and their properties [76]

particles acted as heat insulators and mass transfer barriers, which significantly increased the degradation temperature. Increase in properties was mainly confined to the degree of interaction between nanoclay and the soft, hard segments of PU. The degree of interaction was highest for MT as the layered structure showed the highest surface area and more amino sites for interaction. This improved the bonding and load transfer property and an increase in tensile strength was observed. The 50 wt % weight loss of the WPU and WPU/clay nanocomposite was at temperature 361, 381, 376, and

364 °C for WPU, WPU/SMT, WPU/SAT, and WPU/SHT, respectively. This was mainly due to the barrier phenomenon effect of clay [80].

Advances in Water-Based PU Applications

The type of emulsifier governs the neutralization degree of the PUD. This is because the higher the steric hindrance the lower the reactivity of the COOH group, which produces a thinner electrical double layer around each PUD

particle. This ultimately reduces the electrostatic repulsive forces between the PUD particles, resulting in larger particle size. DMPA and DMBA are the most widely used emulsifiers in anionic PUD, refer Fig. 19. Above said particle size theory holds in this case, PUD made from DMBA had smaller particle size hence tensile strength, Young's modulus, elongation at break, toughness and T_g are higher for DMBA based systems than those from DMPA due to the lower chain mobility of DMBA which is induced by the large side-chain, however the thermal stability and contact angle were lower [81].

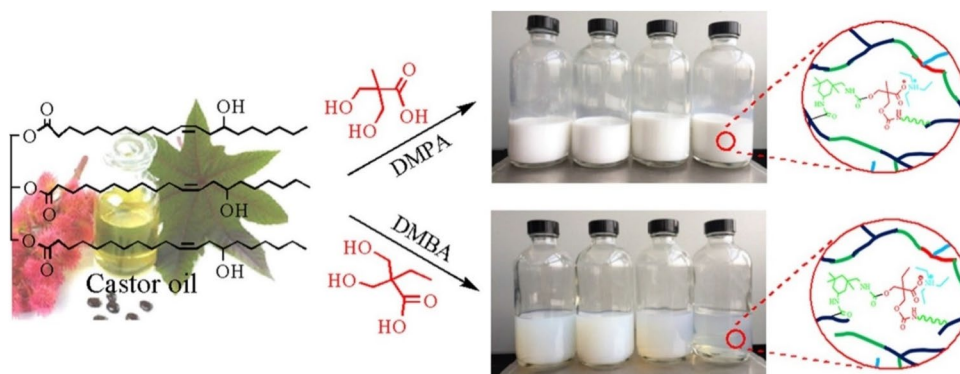
Fatty acid-based emulsifier is a novel approach towards PUD based on completely renewable resources. Fatty acid decreases the hard segment content which ultimately provides more freedom to chain for movement. When one to one replacement of DMPA with fatty acid as an emulsifier was compared, the T_g with DMPA was higher than that of the fatty acid-based dispersion. The OH number also plays a significant role in property determination. One modification was carried out in the above-mentioned case, the whole PUD was made with fatty acid and isocyanates and T_g values obtained were significantly higher. The toughness was lost and PUD became more brittle in nature [21]. There are some disadvantages of DMPA as an internal emulsifier. It increases the film formation time and decreases the compatibility between hard and soft segments. Both the hydroxyl and carboxyl functionality in the triglyceride backbone of the vegetable oil-based polyol is the key to replace DMPA. The maleation of epoxidized-polyol of cottonseed oil was carried out using maleic anhydride. The chain extenders were oxalic, succinic, adipic and sebacic dihydrazides. The minimum particle size was 41 nm and it was observed that as the chain length of the chain extender was increased, the particle diameter got reduced. This was due to the flexible characteristics associated with the molecule with longer alkene groups. These characteristics let more deformation of particles, when shear force was applied. This led to easy breaking of particles in the dispersion process. The reduction in particle size improved storage stability as larger particles enhance the settlement rate of PUDs, but the increase in

alkene groups increased the hydrophobic character of the film. The enhancement in tensile strength and modulus was seen as the alkene groups increased the degree of intermolecular hydrogen bonding which increased the rigidity and toughness of the films. However, it restricted the movement of the polymer segments and the elongation properties had inverse effect [82]. The same methodology was followed to make PU-imide dispersions (PUID) using pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BPOTCDA), 4,4'-hexafluoroisopropylidene-diphthalic anhydride (HFIPDA) to form amide groups. The presence of the C-F bond has low surface energy and thereby giving the highest hydrophobic character to PUID-HFIPDA films. The incorporation of imide groups enhanced the rigidity of polymer chains and hence the tensile strength, fluorine groups increased the rigidity and crystalline nature of the polymer chains thereby giving superior mechanical properties [83].

Dihydroxy fatty acid (DHA) is yet another option for DMPA owing to its two hydroxyl groups and one carboxylic acid group. Recently palm oil-based DHA was made and its effect as an internal emulsifier was studied [84]. A novel itaconic acid-based internal emulsifier was also prepared by thiol-ene photo-click reaction of itaconic acid (IA) and 1-thioglycerol (TG). The higher content of this emulsifier led to formation of more stable dispersion with smaller particle size. In addition, it improved the modulus [85]. Nabid et. al made a sunflower oil-based emulsifier wherein at first polyol was made by epoxidation and ring-opening by methanol. Then saponification of this polyol was carried out to incorporate it in anionic PU dispersions [86].

Tartaric acid (TA) is an option to DMPA which is derived as a byproduct from the wine grape process. Unmodified castor oil-based PUD with TA as an emulsifier showed high thermal stability in the final stage of degradation than that DMPA based PUD. The T_g obtained was almost 10 °C lower than that of the DMPA based PUD. This was due to the elimination of the amines forming salts that stabilized the PUDs [87]. In a novel approach by Palanisamy et al., the phosphols were synthesized from epoxidized cottonseed oil

Fig. 19 Effects of emulsifiers in anionic PUD on transparency [81]



through the ring-opening hydrolysis of epoxy groups in presence of ortho-phosphoric acid. These were acting as ionic soft segments in PUD. The process followed is the sol–gel process to get a uniform hybrid network by covalent bonding at low temperatures. A prepolymer of phosphols and isocyanate was synthesized and then DMEA was added for neutralization of phosphoryl groups. Aminopropyl triethoxy silane (APTES) was then added to react with unmodified NCO groups. The ortho-phosphoric acid at a low concentration acted as a catalyst for ring-opening. However, at higher acid concentration, phosphoric acid acted as a reactant. The higher the counter ion available after neutralization, the smaller the size of PUD particle. This is due to an increase in the mutual coalescence of the dispersed particles and the decrease of the interionic electrostatic repulsive force. Another factor is the hydrophilicity of the segments. When the number of counter ions decreased it became difficult for water to penetrate. Hence, the hydrophilicity of the PUD decreased, leading to formation of larger particles [88]. The corrosion protection is represented in Fig. 20.

Wang et al. improved the fracture toughness and flame retardancy of soybean oil-based waterborne PU coatings by phosphorus-nitrogen chain extender. They used [bis(2-hydroxyethyl)amino]-methyl-phosphonic acid dimethyl ester (BH) and butanediol (BDO) as a chain extender. At an 80% molar ratio of BH and 20% of BDO, the fracture toughness (MJ/m^3) was highest i.e., 64.8 ± 5.5 . This value was significantly higher than values of castor oil-based WPU reported by Zhang and co-colleagues (toughness: $26.9 \text{ MJ}/\text{m}^3$) [74]. It was due to higher hard segment content with more BH and the physical cross-linking interaction via hydrogen bonds between phosphonic acid ester-bond and the urethane bond. Also, the TGA results indicate that the incorporation of BH had increased char residue production. This was potentially acting as a barrier to improve the flame retardancy [89, 90].

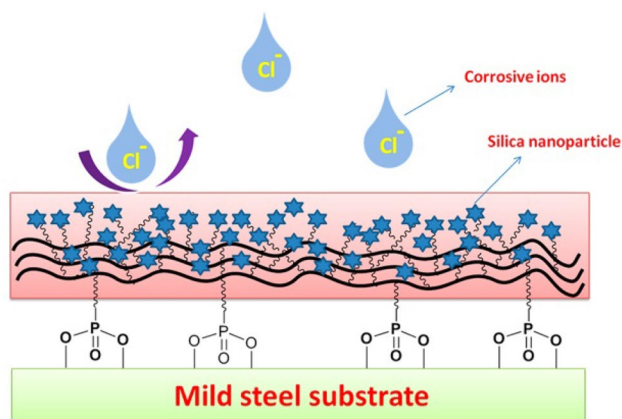


Fig. 20 Schematic representation of corrosion protection in phosphol PUDs [88]

In another approach to making a vegetable oil-based emulsifier, epoxidized soybean oil and glutaric acid were reacted without any kind of catalyst addition. The epoxide rings were opened by glutaric acid. Authors made PUD with the fixed ratio of NCO: OH, where in the OH mole was 50:50 contribution from emulsifier and polyol. It was again evident that two factors affect the particle size of the PUDs. One is the high OH number which, leads to high crosslinking density, leading to large particle size. Another factor is the emulsifier content, the higher the emulsifier content the higher is the surface charge density of the particles. Hence, it leads to higher electrostatic repulsion, leading to small particle size. Particle size also affects the transparency of the PU; the higher the particle size more the transparency of the PUD. The obtained dispersion had excellent stability and the solid content was high (45%) [91].

Advances in PU Adhesives

PU adhesives are mostly produced by reacting petroleum-based polyols with diisocyanates. These adhesives show excellent adhesion, flexibility, high cohesive strength, low-temperature performance and amenable curing speeds. Majorly footwear, packaging, automotive components and the furniture industry uses PU adhesives. Vegetable oil-based PU adhesives is not a recent topic of discussion but at present more and more studies are being carried out in search of green adhesives. It is also found that castor oil-based PU adhesive showed better lap shear strength than the commercial wood adhesives. The bonding mechanism of adhesives includes forces that hold the substrate together. The forces such as hydrogen bonding, attractive weak Vander Walls forces hold them together, but most of the adhesives are sensitive to hydrolysis and stress scission. The long dangling chain of the vegetable oil polyol plays a significant role in increasing hydrophobic properties. These prevent the penetration of water molecules into adhesives that can hydrolyze the ester bonds, hence increased hydrolysis resistance is observed [19, 92–94].

PU adhesives based on castor oil have a highly crosslinked polymeric structure and act as very good adhesives for various substrates. PU adhesives based on polyester polyols of castor oil with maleic, fumaric or oxalic acid were found to give better bonding properties for wood-to-wood specimens. The increase in hydroxyl value of polyol was found to have a direct linear relation with the lap strength of the PU adhesive, due to the formation of more compact network structure within the adhesive. The joint strength was found to be increased from 23 to 45 MPa as hydroxyl value increased from 130 to 345 mgKOH/g. The gel time was found to decrease with an increase in the hydroxyl value. Viscosity is another important parameter as an ideal adhesive should

achieve good molecular contact with the surface by spreading or flow nature. Increase in viscosity was observed with an increasing NCO/OH ratio. The overall adhesive properties can be related to the free NCO group which can react with hydroxyl groups present on the cellulosic material of wood and show bonding but the upside-down result can be observed if excess NCO is used. The substrate bond fails due to increase in the strength of the adhesive bond itself than the substrate. The prepared PU adhesives have good resistance to cold and hot water but the bond tends to easily hydrolyze in the presence of acid and alkali which results in a deterioration of the adhesive strength [95]. The same results as above were obtained with hydroxylated and alcoholized jatropha oil polyol based PU [96]. Inter crosslinked polymer network (ICPN) based on castor oil (CO) PU and epoxy (DGEBA) was made by Jia et al. At first –NCO group-terminated CO-PU was synthesized by reacting CO with 4, 4'-diphenylmethane-diisocyanate (MDI) and then DGEBA was mixed in varying ratio. The tensile strength increased at first with increasing CO-PU content but then decreased when the CO-PU content was beyond 20%. The maximum lap shear strength of 5.7 MPa was observed at 20% CO-PU [97].

A recycled polyol was obtained from glycolysis of PET with triethylene glycol (TEG). The glycolized oligoester polyol was obtained by keeping the molar ratio of PET repeating unit to TEG, 1:2. The hydroxyl value was 370 mgKOH/g. The castor oil-based polyol was then synthesized by the reaction between the glycolized oligoester and castor oil at a weight ratio of 1:10. The hydroxyl value of the final polyol was 414 mgKOH/g. The APTES in the weight % of 0.5, 1 and 2 were added in WPU of castor oil to react with excess NCO to get PU/silica nanocomposite dispersions. This increase in APTES content had increased thermal degradation temperature by increasing Si–O bonding. The increase in T_g from 55.3 to 63.4 °C for APTES from 0 to 1.5 wt%, was observed but dropped to 63.0 °C for 2 wt% dosing. This is due to competition between the increased crosslinking and the increased free volume of the nanocomposites [98]. In a similar attempt, hydrophilic NS was used instead of APTES. It was observed that lower SiO₂ content resulted in a uniform distribution of nanoparticles. As the SiO₂ content increased the clusters were seen easily. The increase in OH number was observed to increase the particle size [99].

In another attempt, a soy polyol based WPU was used to increase the wet strength of soy protein-based adhesive. As a replacement for urea–formaldehyde adhesive, Soy protein-based adhesives are available in the markets, but these adhesives struggle for their poor water resistance as compared to dry strength. This limits their application as high-performance wood adhesives compared to phenol–formaldehyde adhesives. The reason behind this is the hydrophilicity of soy proteins which is due to amino acid

groups. The hydrophobicity of soy oil polyol was introduced into the adhesives to increase the wet strength. At first soy protein isolate (SPI) was separated from soy flour by dispersing and centrifuging it. A WPU of soy polyol was made with DMPA and TEA. Then WPU was added in increasing quantity in a slurry of 10 wt% of SPI. The water contact angle of pure SPI slurry was $33 \pm 2^\circ$ and it increased up to $52 \pm 2^\circ$ for soy polyol of 117 mgKOH/g hydroxyl value. The water-resistance was found the best at 50% incorporation of WPU in SPI. There was 66.7% increase in wet strength at 50% incorporation of WPU in SPI. It was due to an increase in interactions between SPI and WPU, as seen in Fig. 21. The interactions are due to covalent bonds as well as non-covalent linkages such as hydrophobic interaction and hydrogen bonds [100].

A UV triggered castor oil-based adhesive was prepared by Borrero-López et al. They prepared and used bis(4,5-dimethoxy-2-nitrobenzyl)pentane-1,5-diyldicarbamate as a photo trigger for the release of the diamine cadaverine. This resulted in formulations with suitably controlled curing by photoactivation. This material showed faster curing when UV light is applied as compared to curing in the absence of irradiation. The adhesion performance was superior, the lap shear strength value of up to 4600 kPa was achieved [101].

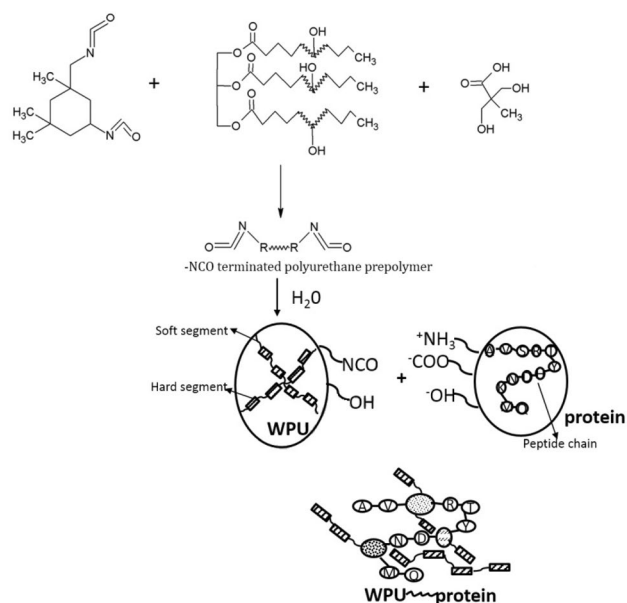


Fig. 21 Proposed chemical scheme of possible interactions between WPU and SPI: covalent linkage; hydrogen bond; hydrophobic interaction; physical entanglement [100]

Future Perspective and Concluding Remarks

Today PUs have become one of the most researched topics globally due to their versatility and industrial importance. It has been successfully used in various applications such as foams (flexible, semi-rigid and rigid), elastomers, adhesives, coatings, fibers, etc. In recent decades, researchers have focused on using renewable and sustainable resources for the development of PU. The idea is to replace petroleum-derived polyols with those derived from vegetable oils. The use of vegetable oils has received increasing attention due to attractive properties related to the specific structures of vegetable oils. Vegetable oils are abundant, easily available, inexpensive resources and have always been well studied in coatings and adhesives industries. Since these are organically grown, they are inevitably becoming established as renewable raw materials for environment friendly materials. Vegetable oils such as castor oil, flaxseed oil, soybean oil, rapeseed oil, and palm oil are becoming increasingly important as renewable raw materials. Vegetable oils are beginning to play a variety of roles in water-based coatings. Historically, dimethylol propionic acid served as an internal emulsifier, but is now being replaced by vegetable oils. The shortcomings associated with dimethylol propionic acid have been successfully eliminated and vegetable oils play a more advanced role as internal emulsifiers. There have also been efforts to increase the bio-based content of the final product. This is a great initiative to start your journey to 100% green materials.

The manuscript provides insight into recent advances in vegetable oil-based PU coatings and adhesives. The use of vegetable oils is undoubtedly a biological and environment friendly source. Simple chemical reactions result in value-added products that can be used in a variety of protective coatings. However commercialization of consistent vegetable oil-based polyols for PU remains a challenge due to changes in the composition of fatty acids in triglycerides depending on geographic location, soil type, climate type, etc. The issues mentioned are nothing to what we are facing due to crude oil-based raw materials. Vegetable oil-based PUs see a bright future due to both vigorous academic and industrial research being carried out to unlock their full potential.

Author Contribution The manuscript was written by Mr. Dhiraj Kaidake and revised by Dr. Anagha Sabnis.

Funding: No funding was availed from any source.

Declarations

Conflict of interest This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue. The authors are affiliated to the Institute of Chemical Technology, Mumbai, India.

References

- Karak N, Gogoi S (2014) Biobased biodegradable waterborne hyperbranched polyurethane as an ecofriendly sustainable material. *ACS Sustain Chem Eng* 2:2730–2738. <https://doi.org/10.1021/sc5006022>
- Zhang C et al (2017) A solvent-free and scalable method to prepare soybean-oil-based polyols by Thiol–Ene photo-click reaction and biobased polyurethanes therefrom. *ACS Sustain Chem Eng* 5:7365–7373. <https://doi.org/10.1021/acsschemeng.7b01672>
- Karak N, Thakur S (2013) Castor oil-based hyperbranched polyurethanes as advanced surface coating materials. *Prog Org Coat* 76:157–164. <https://doi.org/10.1016/j.porgcoat.2012.09.001>
- Adhikari B, Ghasemlou M, Daver F, Ivanova EP (2019) Polyurethanes from seed oil-based polyols: a review of synthesis, mechanical and thermal properties. *Ind. Crops Prod* 142:111841. <https://doi.org/10.1016/j.indcrop.2019.111841>
- Market Research Engine (2020) Polyurethane Market, 115
- Brand Essence Research Report (2020) Polyurethane Coatings Market 2020, 193
- Markets and Markets (2019) POLYURETHANE ADHESIVES MARKET
- Industryarc (2021) Polyurethane coating market overview. <https://www.industryarc.com/Research/Polyurethane-Coating-Market-Research-500192>
- Industryarc (2021) Polyurethane adhesives market overview. <https://www.industryarc.com/Research/Polyurethane-Adhesives-Market-Research-502850>
- Plastixportal Polyurethanes plastic material info. https://www.plastixportal.co.za/polyurethane_information.html
- Das A, Mahanwar P (2020) A brief discussion on advances in polyurethane applications. *Adv Ind Eng Polym Res* 3:93–101. <https://doi.org/10.1016/j.aiepr.2020.07.002>
- Sánchez MC, Tenorio-Alfonso A, Franco JM (2019) Synthesis and mechanical properties of bio-sourced polyurethane adhesives obtained from castor oil and MDI-modified cellulose acetate: influence of cellulose acetate modification. *Int J Adhes Adhes* 95:102404. <https://doi.org/10.1016/j.ijadhadh.2019.102404>
- Chattopadhyay DK, Raju KVS (2007) Structural engineering of polyurethane coatings for high performance applications. *Prog Polym Sci* 32:352–418. <https://doi.org/10.1016/j.progpolymsci.2006.05.003>
- Luo Z, Shi Y, Zhao D, He M (2011) Synthesis of epoxidated castor oil and its effect on the properties of waterborne polyurethane. *Procedia Eng* 18:37–42. <https://doi.org/10.1016/j.proeng.2011.11.006>
- Yuan T, Yang Z (2019) A renewable and multifunctional eco-friendly coating from novel tung oil-based cationic waterborne polyurethane dispersions. *J Clean Prod* 241:118341. <https://doi.org/10.1016/j.jclepro.2019.118341>
- He M et al (2016) Synthesis and characterization of UV-curable castor oil-based polyfunctional polyurethane acrylate via photo-click chemistry and isocyanate polyurethane reaction. *Prog Org Coat* 93:11–16. <https://doi.org/10.1016/j.porgcoat.2015.12.015>
- Larock RC, Lu Y (2011) Synthesis and properties of grafted latices from a soybean oil-based waterborne polyurethane and acrylics. *J Appl Polym Sci* 119:3305–3314. <https://doi.org/10.1002/app.29029>
- Zhang S, Zhinguo Su, Wang P, Miao S (2014) Vegetable-oil-based polymers as future polymeric biomaterials. *Acta Biomater* 10(4):1692–1704. <https://doi.org/10.1016/j.actbio.2013.08.040>
- Curtis JM, Kong X, Liu G (2011) Characterization of canola oil based polyurethane wood adhesives. *Int J Adhes Adhes* 31:559–564. <https://doi.org/10.1016/j.ijadhadh.2011.05.004>

20. Valdés O et al (2020) Development of eco-friendly polyurethane foams based on *Lesquerella fendleri* (A. Grey) oil-based polyol. *Eur Polym J*. <https://doi.org/10.1016/j.eurpolymj.2020.109606>
21. Kessler MR, Zhang C, Chen R (2014) Anionic waterborne polyurethane dispersion from a bio-based ionic segment. *RSC Adv* 4:35476–35483. <https://doi.org/10.1039/c4ra07519f>
22. Zhang C et al (2018) Bio-based cationic waterborne polyurethanes dispersions prepared from different vegetable oils. *Ind Crops Prod* 122:448–455. <https://doi.org/10.1016/j.indcrop.2018.06.006>
23. Kurańska M et al (2018) Effect of bio-polyols with different chemical structures on foaming of polyurethane systems and foam properties. *Ind Crops Prod* 120:262–270. <https://doi.org/10.1016/j.indcrop.2018.04.046>
24. Saalah S et al (2018) Colloidal stability and rheology of *Jatropha* oil-based waterborne polyurethane (JPU) dispersion. *Prog Org Coat* 125:348–357. <https://doi.org/10.1016/j.porgcoat.2018.09.018>
25. Yemul OS, Gaikwad MS, Gite VV, Mahulikar PP, Hundiware DG (2015) Eco-friendly polyurethane coatings from cottonseed and karanja oil. *Prog Org Coat* 86:164–172. <https://doi.org/10.1016/j.porgcoat.2015.05.014>
26. Mouloungui Z, Nohra B, Candy L, Blanco J-F, Guerin C, Raoul Y (2013) From petrochemical polyurethanes to biobased polyhydroxyurethanes. *Macromolecules* 46(10):3771–3792. <https://doi.org/10.1021/ma400197c>
27. Kaikade DS, Sabnis AS (2022) Polyurethane foams from vegetable oil-based polyols: a review. *Polym Bull*. <https://doi.org/10.1007/s00289-022-04155-9>
28. Larock RC, Pfister DP, Xia Y (2011) Recent advances in vegetable oil-based polyurethanes. *Chemsuschem* 4:703–717. <https://doi.org/10.1002/cssc.201000378>
29. Paraskar PM, Prabhudesai MS, Kulkarni RD (2020) Synthesis and characterizations of air-cured polyurethane coatings from vegetable oils and itaconic acid. *React Funct Polym*. <https://doi.org/10.1016/j.reactfunctpolym.2020.104734>
30. Petrović ZS (2008) Polyurethanes from vegetable oils. *Polym Rev* 48:109–155. <https://doi.org/10.1080/15583720701834224>
31. Fridrihsone A, Stirna U, Lazdina B, Misane M, Vilsone D (2013) Characterization of polyurethane networks structure and properties based on rapeseed oil derived polyol. *Eur Polym J* 49:1204–1214. <https://doi.org/10.1016/j.eurpolymj.2013.03.012>
32. Wilkes GL, Pechar TW, Zhou B, Luo N (2007) Characterization of soy-based polyurethane networks prepared with different diisocyanates and their blends with petroleum-based polyols. *J Appl Polym Sci* 106:2350–2362. <https://doi.org/10.1002/app.26569>
33. Ahmad S, Akram D, Sharmin E (2008) Synthesis, characterization and corrosion protective properties of boron-modified polyurethane from natural polyol. *Prog Org Coat* 63:25–32. <https://doi.org/10.1016/j.porgcoat.2008.04.003>
34. Ahmad S, Kashif M (2014) Polyorthotoluidine dispersed castor oil polyurethane anticorrosive nanocomposite coatings. *RSC Adv* 4:20984–20999. <https://doi.org/10.1039/c4ra00587b>
35. Ahmad S, Rahman OU, Ghosal A (2015) High-performance soya polyurethane networked silica hybrid nanocomposite coatings. *Ind Eng Chem Res* 54(51):12770–12787. <https://doi.org/10.1021/acs.iecr.5b02098>
36. Kulkarni RD, Prabhudesai MS, Paraskar PM, Deshpande PS (2020) Utilization of oleic acid in synthesis of epoxidized soybean oil based green polyurethane coating and its comparative study with petrochemical based polyurethane. *J Polym Res*. <https://doi.org/10.1007/s10965-020-02170-w>
37. Teng Y, Huang J, Xiong Y, Xiaohua Z, Zhuohong Y (2022) A novel polyfunctional polyurethane acrylate prepolymer derived from bio-based polyols for UV-curable coatings applications. *Polym Test*. <https://doi.org/10.1016/j.polymertesting.2021.107439>
38. Zhuohong Y, Teng Y, Yanwu C, Zhuangzhuang C, Pengsong L (2021) One-pot and solvent-free synthesis of castor oil-based polyurethane acrylate oligomers for UV-curable coatings applications. *Prog Org Coat*. <https://doi.org/10.1016/j.porgcoat.2021.106398>
39. Smita M, Krishnan K, Debasmita M (2022) Synthesis of castor oil-based polyols applicable in acrylated polyurethane coating with higher mechanical properties. *Polym Int*. <https://doi.org/10.1002/pi.6462>
40. Akram D, Hakami O, Sharmin E, Ahmad S (2017) Castor and linseed oil polyurethane/TEOS hybrids as protective coatings: a synergistic approach utilising plant oil polyols, a sustainable resource. *Prog Org Coat* 108:1–14. <https://doi.org/10.1016/j.porgcoat.2017.03.012>
41. Irfan MH (1998) 10. hybrid polymers. *Chemistry and technology of thermosetting polymers in construction applications*. Kluwer Academic Publishers, Amsterdam, pp 240–257
42. Hong SC et al (2018) Functional soybean oil-based polyols as sustainable feedstocks for polyurethane coatings. *Ind Crops Prod* 113:249–258. <https://doi.org/10.1016/j.indcrop.2018.01.041>
43. Shaik A, Bhosale N, Mandal SK (2015) Synthesis and characterization of Castor oil based hybrid polymers and their polyurethane-urea/silica coatings. *RSC Adv* 5:103625–103635. <https://doi.org/10.1039/C5RA20356B>
44. Bianchi O, Ourique PA, Krindges I, Aguzzoli C, Figueroa CA, Amalvy J, Wanke CH (2017) Synthesis, properties, and applications of hybrid polyurethane–urea obtained from air-oxidized soybean oil. *Prog. Org. Coat*. 108:15–24. <https://doi.org/10.1016/j.porgcoat.2017.04.002>
45. Patil CK et al (2017) Synthesis of bio-based polyurethane coatings from vegetable oil and dicarboxylic acids. *Prog Org Coat* 106:87–95. <https://doi.org/10.1016/j.porgcoat.2016.11.024>
46. Paraskar PM, Doke R, Kulkarni RD, Rajput YN (2021) Synthesis and characterization of green polyurethane coatings derived from niger-seed-oil-based polyesteramide polyols. *Eur J Lipid Sci Technol*. <https://doi.org/10.1002/ejlt.202100171>
47. Li S et al (2017) Preparation and properties of castor oil-based dual cross-linked polymer networks with polyurethane and polyoxazolidinone structures. *ACS Sustain Chem Eng* 5:6883–6893. <https://doi.org/10.1021/acssuschemeng.7b01103>
48. Gite V, Chaudhari A, Kuwar A, Mahulikar P, Hundiware D, Kulkarni R (2014) Development of anticorrosive two pack polyurethane coatings based on modified fatty amide of *Azadirachta indica* Juss oil cured at room temperature—a sustainable resource. *RSC Adv* 4:17866. <https://doi.org/10.1039/c4ra01880j>
49. Yang Z et al (2019) One-pot synthesis of polyurethane-imides with tailored performance from castor and tung oil. *Prog Org Coat* 132:62–69. <https://doi.org/10.1016/j.porgcoat.2019.03.035>
50. Das S, Pandey P, Mohanty S, Nayak SK (2016) Effect of nanosilica on the physicochemical, morphological and curing characteristics of transesterified castor oil based polyurethane coatings. *Prog Org Coat* 97:233–243. <https://doi.org/10.1016/j.porgcoat.2016.04.012>
51. Kong X, Zhao L, Curtis JM (2016) Polyurethane nanocomposites incorporating biobased polyols and reinforced with a low fraction of cellulose nanocrystals. *Carbohydr Polym* 152:487–495. <https://doi.org/10.1016/j.carbpol.2016.07.032>
52. Das S, Pandey P, Mohanty S, Nayak SK (2017) Evaluation of biodegradability of green polyurethane/nanosilica composite synthesized from transesterified castor oil and palm oil based isocyanate. *Int Biodeterior Biodegrad* 117:278–288. <https://doi.org/10.1016/j.ibiod.2017.01.015>

53. Xie H et al (2012) Natural fibrous nanoclay reinforced soy polyol-based polyurethane. *Mater Lett* 78:85–87. <https://doi.org/10.1016/j.matlet.2012.03.067>
54. Kaushik A, Ahuja D, Salwani V (2011) Synthesis and characterization of organically modified clay/castor oil based chain extended polyurethane nanocomposites. *Compos Part A* 42:1534–1541. <https://doi.org/10.1016/j.compositesa.2011.07.009>
55. Mandal AB, Jaisankar SN, Meera KMS, Sankar RM, Paul J (2014) The influence of applied silica nanoparticles on a bio-renewable castor oil based polyurethane nanocomposite and its physicochemical properties. *Phys Chem Chem Phys* 16(20):9276–9288. <https://doi.org/10.1039/c4cp00516c>
56. Alam M, Alandis NM, Zafar F, Sharmin E, Al-Mohammadi YM (2018) Polyurethane-TiO₂ nanocomposite coatings from sunflower-oil-based amide diol as soft segment. *J Macromol Sci Part Pure Appl Chem*. <https://doi.org/10.1080/10601325.2018.1526638>
57. Liu Z, Zhang M, Tian H, Guo Y, Zheng L, Li YC (2019) Biobased polyurethane, epoxy resin, and polyolefin wax composite coating for controlled-release fertilizer. *ACS Appl Mater Interfaces* 11:5380–5392. <https://doi.org/10.1021/acsami.8b16030>
58. Zhang C et al (2019) Tunable thermo-physical performance of castor oil-based polyurethanes with tailored release of coated fertilizers. *J Clean Prod* 210:1207–1215. <https://doi.org/10.1016/j.jclepro.2018.11.047>
59. Ribeiro C, Polito WL, Guimarães G, Bortoletto-Santos R, Cruz D (2017) Role of polymeric coating on the phosphate availability as fertilizer: insight from phosphate release in soil castor polyurethane coatings. *J Agric Food Chem* 65:5890–5895. <https://doi.org/10.1021/acs.jafc.7b01686>
60. Shi S et al (2022) Castor oil-based transparent and omniphobic polyurethane coatings with high hardness, anti-smudge and anti-corrosive properties. *Prog Org Coat*. <https://doi.org/10.1016/j.porgcoat.2022.107120>
61. Zhang W, Wei D, Li M, Liang L, Yong Q (2022) Development of biobased polyol from epoxidized soybean oil for polyurethane anti-smudge coatings. *J Appl Polym Sci*. <https://doi.org/10.1002/app.53101>
62. Dholakiya BZ, Raychura AJ, Jauhari S, Prajapati VS (2018) Synthesis and performance evaluation of vegetable oil based wood finish polyurethane coating. *Bioresour Technol Rep* 3:88–94. <https://doi.org/10.1016/j.biteb.2018.06.007>
63. Dholakiya BZ, Jauhari S, Raychura AJ (2018) Development of wood protective polyurethane coatings from mahua oil-based polyetheramide polyol: a renewable approach. *Soft Mater* 16(3):209–219. <https://doi.org/10.1080/1539445X.2018.1474117>
64. Saalah S et al (2015) Waterborne polyurethane dispersions synthesized from jatropha oil. *Ind Crops Prod* 64:194–200. <https://doi.org/10.1016/j.indcrop.2014.10.046>
65. Larock RC, Kessler MR, Garrison TF (2014) Effects of unsaturation and different ring-opening methods on the properties of vegetable oil-based polyurethane coatings. *Polymer* 55:1004–1011. <https://doi.org/10.1016/j.polymer.2014.01.014>
66. Zhang C, Chen M, Jingyi Lu, Liu L, Liang H (2018) Castor oil-based cationic waterborne polyurethane dispersions: storage stability, thermo-physical properties and antibacterial properties. *Ind Crops Prod* 117:169–178. <https://doi.org/10.1016/j.indcrop.2018.02.084>
67. Kessler MR, Zhang C, Chen R (2015) Polyols and polyurethanes prepared from epoxidized soybean oil ring-opened by polyhydroxy fatty acids with varying OH numbers. *J Appl Polym Sci* 132:41213. <https://doi.org/10.1002/app.41213>
68. Kessler MR, Ding R, Zhang C (2014) Reduction of epoxidized vegetable oils: a novel method to prepare bio-based polyols for polyurethanes. *Macromol Rapid Commun* 35:1068–1074. <https://doi.org/10.1002/marc.201400039>
69. Saetung N, Sukhawipat N, Kalkornsurapranee E, Saetung A, Raksanak W (2020) A new hybrid waterborne polyurethane coating synthesized from natural rubber and rubber seed oil with grafted acrylate. *Prog Org Coat* 141:105554. <https://doi.org/10.1016/j.porgcoat.2020.105554>
70. Pang H, Liu W, Meng Y, Lv P, Liu Qi, Liao B (2019) Preparation and characterization of soybean oil-based waterborne polyurethane/acrylate hybrid emulsions for self-matting coatings. *New J Chem* 43:19193–19199. <https://doi.org/10.1039/c9nj04538d>
71. Mohamed HA, Badran BM, Morsi SMM, Rabie AM (2014) Synthesis and characterization of aqueous (polyurethane/aromatic polyamide sulfone) copolymer dispersions from castor oil. *Prog Org Coat* 77:965–974. <https://doi.org/10.1016/j.porgcoat.2014.01.026>
72. Zushun Xu et al (2019) Design and synthesis of novel aminosiloxane crosslinked linseed oil-based waterborne polyurethane composites and its physicochemical properties. *Prog Org Coat* 127:194–201. <https://doi.org/10.1016/j.porgcoat.2018.11.020>
73. Jianning Wu, Liu Z, Wan J, Hao N (2017) Morphology and mechanical properties of UV-curable castor oil-based waterborne polyurethane/organic montmorillonite nanocomposites. *Plast RUBBER Compos* 46:346–354. <https://doi.org/10.1080/14658011.2017.1356974>
74. Luo Y et al (2019) Synthesis and properties of castor oil-based waterborne polyurethane/ sodium alginate composites with tunable properties. *Carbohydr Polym* 208:391–397. <https://doi.org/10.1016/j.carbpol.2018.12.090>
75. Zhang C et al (2020) Waterborne polyurethanes from castor oil-based polyols for next generation of environmentally-friendly hair-styling agents. *Prog Org Coat* 142:105588. <https://doi.org/10.1016/j.porgcoat.2020.105588>
76. Tang J, Yu G, Dong L, Lei C, Long M, Shen R (2022) Anticorrosive waterborne polyurethane coatings derived from castor oil and renewable diols. *Chem Eng J*. <https://doi.org/10.1016/j.cej.2021.134470>
77. He X et al (2021) Preparation and properties of green UV-curable itaconic acid cross-linked modified waterborne polyurethane coating. *J Appl Polym Sci*. <https://doi.org/10.1002/app.52042>
78. Ma J, Gao D, Lyu B, Zhang H (2022) Improving the property of castor oil-based waterborne polyurethane by polyhydroxy sapium sebiferum oil as crosslinking agent. *Prog Org Coat*. <https://doi.org/10.1016/j.porgcoat.2022.106893>
79. Gurunathan T, Chung JS (2016) Physicochemical properties of amino-silane-terminated vegetable oil-based waterborne polyurethane nanocomposites. *ACS Sustain Chem Eng* 4(9):4645–4653. <https://doi.org/10.1021/acssuschemeng.6b00768>
80. Heqing Fu, Liao L, Li X, Wang Y, Li Y (2016) Effects of surface structure and morphology of nanoclays on the properties of Jatropha Curcas oil-based waterborne polyurethane/clay nanocomposites. *Ind Eng Chem Res* 55(45):11689–11699. <https://doi.org/10.1021/acs.iecr.6b02527>
81. Zhang C et al (2018) Aqueous anionic polyurethane dispersions from castor oil. *Ind Crops Prod* 122:182–189. <https://doi.org/10.1016/j.indcrop.2018.05.079>
82. Palanisamy A, Gaddam SK (2015) Anionic waterborne polyurethane dispersions from maleated cotton seed oil polyol carrying ionisable groups. *Colloid Polym Sci*. <https://doi.org/10.1007/s00396-015-3787-1>
83. Palanisamy A, Gaddam SK (2017) Anionic waterborne polyurethane-imide dispersions from cottonseedoil based ionic polyol. *Ind Crops Prod* 96:132–139. <https://doi.org/10.1016/j.indcrop.2016.11.054>

84. KosheelaDevi PP et al (2016) Performance of palm oil-based dihydroxystearic acid as ionizable molecule in waterborne polyurethane dispersions. *J Appl Polym Sci* 133:43614. <https://doi.org/10.1002/app.43614>
85. Hyun DK, Chang YW, Moon SK (2022) Synthesis and characterization of a novel itaconic acid-based internal emulsifier for anionic waterborne polyurethane. *J Polym Sci* 61(2):123–131. <https://doi.org/10.1002/pol.20220406>
86. Nabid MR, Shendi HK, Omrani I, Ahmadi A, Farhadian A, Babanejad N (2017) Synthesis and characterization of a novel internal emulsifier derived from sunflower oil for the preparation of waterborne polyurethane and their application in coatings. *Prog Org Coat* 105:303–309. <https://doi.org/10.1016/j.porgcoat.2016.11.033>
87. Mucci VL, Aranguren MI, Hormaiztegui MEV (2018) Synthesis and characterization of a waterborne polyurethane made from castor oil and tartaric acid. *Eur Polym J* 102:151–160. <https://doi.org/10.1016/j.eurpolymj.2018.03.020>
88. Palanisamy A, Kutcherlapati SNR, Gaddam SK (2017) Self-cross-linkable anionic waterborne polyurethane–silanol dispersions from cottonseed-oil-based phosphorylated polyol as ionic soft segment. *ACS Sustain Chem Eng* 5:6447–6455. <https://doi.org/10.1021/acssuschemeng.7b00327>
89. Wang CS, Zhang J, Wang H, He M, Ding L, Zhao WW (2021) Simultaneously improving the fracture toughness and flame retardancy of soybean oil-based waterborne polyurethane coatings by phosphorus-nitrogen chain extender. *Ind Crops Prod*. <https://doi.org/10.1016/j.indcrop.2021.113328>
90. Wang C, Zhang J, Jieru H, Han W, Meng H, Liang D (2021) Flame retardant modified bio-based waterborne polyurethane dispersions derived from castor oil and soy polyol. *Eur J Lipid Sci Technol* 123(4):2000248
91. Zhang C et al (2019) Thermosetting polyurethanes prepared with the aid of a fully bio-based emulsifier with high bio-content, high solid content, and superior mechanical properties. *Green Chem* 21:526–537. <https://doi.org/10.1039/c8gc03560a>
92. Sinha VK, Patel JV, Desai SD (2003) Polyurethane adhesive system from biomaterial-based polyol for bonding wood. *Int J Adhes Adhes* 23:393–399. [https://doi.org/10.1016/S0143-7496\(03\)00070-8](https://doi.org/10.1016/S0143-7496(03)00070-8)
93. Lee CS, Ang KP, Cheng SF, Chuah CH (2014) Synthesis of palm oil-based polyester polyol for polyurethane adhesive production. *J Appl Polym Sci* 131:39967. <https://doi.org/10.1002/app.39967>
94. Rakshit AK, Kansara SS, Somani KP, Patel NK (2003) Castor oil based polyurethane adhesives for wood-to-wood bonding. *Int J Adhes Adhes* 23:269–275. [https://doi.org/10.1016/S0143-7496\(03\)00044-7](https://doi.org/10.1016/S0143-7496(03)00044-7)
95. Moghadam PN, Yarmohamadi M, Hasanzadeh R, Nuri S (2016) Preparation of polyurethane wood adhesives by polyols formulated with polyester polyols based on castor oil. *Int J Adhes Adhes* 68:273–282. <https://doi.org/10.1016/j.ijadhadh.2016.04.004>
96. Aung MM, Yaakob Z, Kamarudin S, Abdullah LC (2014) Synthesis and characterization of Jatropha (*Jatropha curcas* L.) oil-based polyurethane wood adhesive. *Ind Crops Prod* 60:177–185. <https://doi.org/10.1016/j.indcrop.2014.05.038>
97. Jia J, Qin Y, Mei Q, Huang Z (2014) Castor oil-based polyurethane/epoxy intercross-linked polymer network adhesives for metal substrates. *J Macromol Sci Part B Phys* 53:1621–1628. <https://doi.org/10.1080/00222348.2014.898999>
98. Cakić SM, Valčić MD, Ristić IS, Radusin T, Cvetinović MJ, Budinski-Simendić J (2019) Waterborne polyurethane-silica nanocomposite adhesives based on castor oil-recycled polyols: Effects of (3-aminopropyl)triethoxysilane (APTES) content on properties. *Int J Adhes Adhes* 90:22–31. <https://doi.org/10.1016/j.ijadhadh.2019.01.005>
99. Cakić SM, Ristić IS, Cincović MM, Stojiljković DT, Simendić JB (2016) Preparation and characterization of waterborne polyurethane/silica hybrid dispersions from castor oil polyols obtained by glycolysis poly (ethylene terephthalate) waste. *Int J Adhes Adhes* 70:329–341. <https://doi.org/10.1016/j.ijadhadh.2016.07.010>
100. Sun XS, Liu H, Li C (2017) Soy-oil-based waterborne polyurethane improved wet strength of soy protein adhesives on wood. *Int J Adhes Adhes* 73:66–74. <https://doi.org/10.1016/j.ijadhadh.2016.09.006>
101. Borrero-López AM et al (2021) Toward UV-triggered curing of solvent-free polyurethane adhesives based on castor oil. *ACS Sustain Chem Eng* 9:11032–11040. <https://doi.org/10.1021/acssuschemeng.1c02461>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.