

DEVELOPMENT IN SYNTHESIS AND COATING APPLICATIONS OF POLYURETHANE

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ABSTRACT

Polyurethanes as one of the leading elastomers are explored in academics as well as in industry. These are segmented macromolecules having alternate sequence of soft and hard segments. Structure-property correlation between these segments has been extensively reported in the literature. PUs are used widely in coatings, varnishes, glues, foams, adhesives, sealants, automobile parts, synthetic leather etc. Its application in biomedical devices is also growing rapidly. It is therefore need to highlights the recent developments in this fast growing field. The present article is summarized the conventional and ecofriendly synthetic routes for the preparation of PUs. Conventionally, PUs was synthesized by isocyanates route, later shortcoming of this method explore new synthesis method in which either used biobased polyol or non isocyanates route for preparation of ecofriendly PUs. The applications of different types of PUs coating in various fields are also highlighted in this review.

Keywords: Polyurethane, polyols, isocyanates, catalyst, chain extenders.

1. INTRODUCTION

PUs are one of the leading commercial elastomers widely used in industry in the form of coatings, varnishes, foams, adhesives, sealants, packings, synthetic leather membranes, automobiles parts and biomedical apparatus[1]. PUs rank sixth in annual worldwide production of polymers and 26 million tones of PUs production is expected to reach in 2021[2].

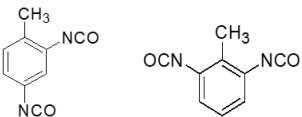
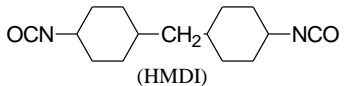
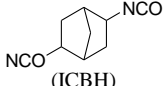
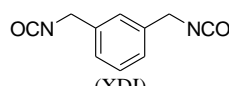
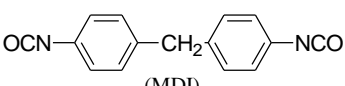
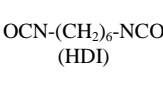
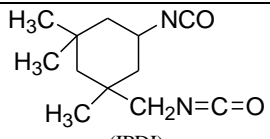
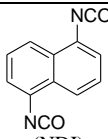
PUs are segmented linear macromolecules having alternate sequence of soft and hard segments. The soft segments consist of polyether / polyester diols, whereas hard segments consist of diisocyanate and diols/diamines which act as chain extenders [3]. The soft segments exhibit the elastomeric property while hard segments show crosslinking and high strength. Variation of ratio of segments affect the structure and properties of PUs such as curing time, hardness, UV stability, weather ability, chemical resistance and gloss etc.

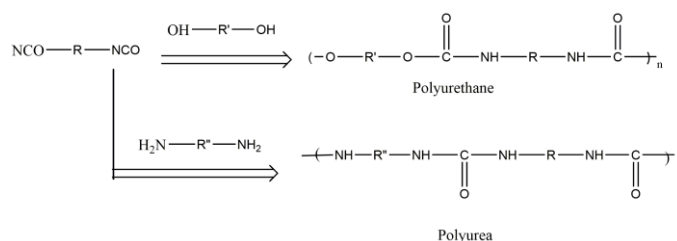
PUs monomers are usually based on petrochemical resources. These resources are limited; PUs conventional synthesis majorly rely on isocyanates which is highly sensitive to moisture, toxic, and carcinogenic nature. Hence, researchers seek easily available renewable natural resources that would be cost-effective and eco-friendly in nature [4]. Synthesis of isocyanates is also difficult due to reaction of phosgene or carbon monoxide with diamines. Therefore there is a need to investigate non-isocyanate routes for PU synthesis. This review is summarized the conventional methods as well as novel approaches of PU synthesis. The coatings applications of PUs in various fields are also reviewed.

2. Conventional approaches of PUs Synthesis

Conventionally, PUs have been synthesized by the reaction of multifunctional isocyanates with polymeric diols or amines to form urethane or urea linkage (Scheme 1). Carbonyl carbon readily react with water, alcohols or amine to form urethane or urea linkage [5, 6].

Table 1. Structures of some commercially used diisocyanates.

 <p>(TDI)</p>	 <p>(HMDI)</p>	 <p>(ICBH)</p>
 <p>(XDI)</p>	 <p>(MDI)</p>	 <p>(HDI)</p>
 <p>(IPDI)</p>	 <p>(NDI)</p>	



Scheme 1. Reaction sequence for Urethane and Urea linkage formation

The polyfunctional isocyanates could be aromatic/aliphatic/cycloaliphatic/polycyclic (Table 1). Aromatic diisocyanates give more rigid PUs than aliphatic but they show low oxidative and ultraviolet stability. The polyol component of the PUs may also be polyfunctional polyether or polyols such as PEG, PPG, polycaprolactone, polycarbonate polyol, castor oil etc. Long chain polyols with low functionality give soft, elastomeric PUs while short chain polyols with high functionality give more rigid crosslinked products [5]. Low molecular weight diols such as EG, 1,4-butanediol, 1, 6-hexanediol, etc. form the group of difunctional chain extenders for prepolymers of urethane-isocyanate. Liquid crystal linear PUs are synthesized from low-molecular weight diols or amines, called rigid mesogens. Some of these are 4, 4'-bis (2-hydroxyethoxy) biphenyl, 4, 4'-diaminobiphenyl, bis-(p-hydroxymethyl-phenyl) terephthalate[6].

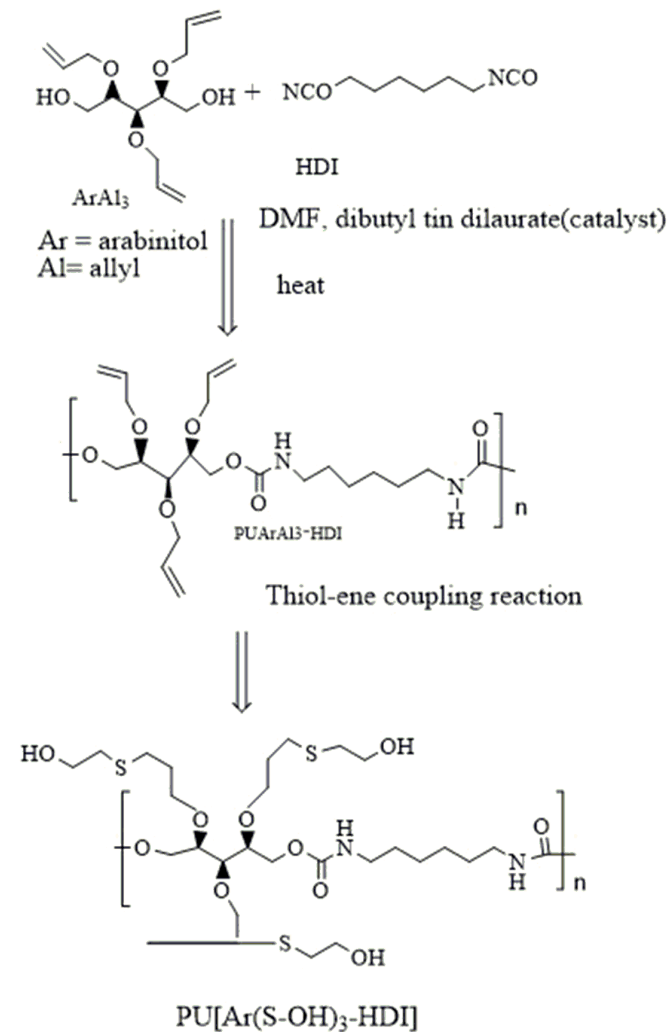
The catalysts are used widely in the preparation of PUs are tertiary amines such as trimethylamine, 1, 4-diaza bicyclo [2.2.2] octan, DBTDL, stannous octoate etc [7,8]. Organometallic compounds have good catalytic efficiency because they can easily formed complex with isocyanate and hydroxyl groups.

3. Novel approaches of PU synthesis

In these methods PUs are synthesized by agro based materials either isocyanate and non-isocyanate route.

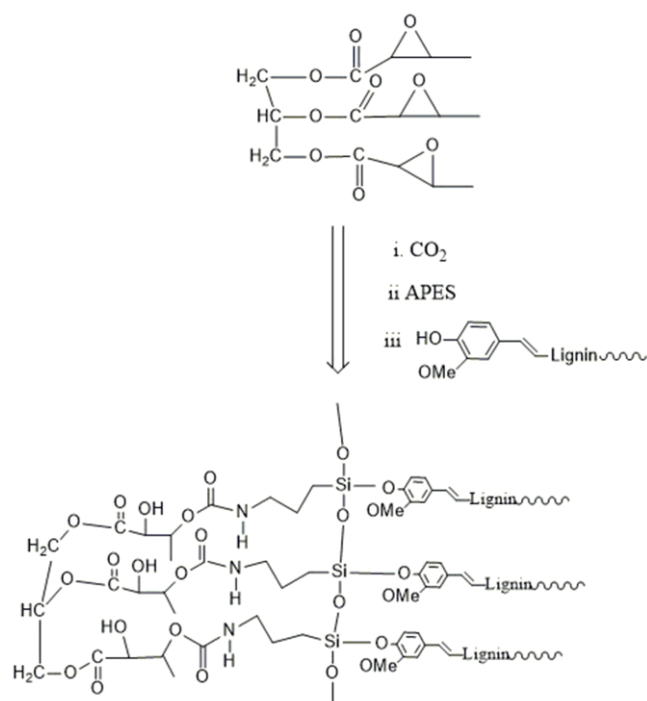
3.1 Isocyanate route from bio based polyols

Several natural products have been reported for the substitution of polyols in the PUs synthesis such as sugar, vegetables oils, biomass etc. Sugar based polyol increased hydrophilic nature of PUs. This was first synthesized by Kurita *et. al* by using xylitol and amino sugars without protecting hydroxyl groups with HMDI and MDI. PUs formed by MDI showed crosslinking because diisocyanates comonomers are highly reactive. This crosslinking problem is avoided by using urethane comonomers. The protected hydroxyl PUs show high resistance to hydrolytic degradation [9].



A L-arabinitol based PUs with varied degree of functionalization has been synthesized by using “click” reaction. PUs with multiple branched allyl groups was prepared by polyaddition reaction of allyl L-arabinitol ($ArAl_3$), HDI and then followed by thiol-ene reaction by 2-mercapto ethanol [10] Scheme 2.

Diols have also been obtained from natural occurring oleate and undecenoate derivatives. Then these diols are treated with MDI and tin (II) 2-ethylhexanoate as a catalyst to give TPU which exhibited good thermal and mechanical properties [11]. PUs was also synthesized by soyabean oil. The epoxidised soyabean oil was reacted with CO_2 to produce cyclic carbonates which were reacted with APES to produce a 3-dimensional structure. Addition of lignin yield a highly crosslinked PUs [12] Scheme 3.



A fatty acid based diisocyanates has been reported for preparation of TPU. This material exhibited good thermal stability and no remarkable loss of weight below $235\text{ }^\circ\text{C}$ [13]. Environmental friendly coatings of PUs are prepared from vegetable oils such as cotton seed and karanja oil. These materials exhibited various properties such as adhesive nature, impact defiance, malleability and gloss properties [14].

The synthesis of cross-linked PUs from lipidic polyols and MDI by using thiol-ene method has also been investigated using aluminium mold. The $[NCO] / [OH]$ ratio varies between from 1/1 to 1.1/1. The mixture was cured at $60\text{ }^\circ\text{C}$ for 1day and post-cured at $110\text{ }^\circ\text{C}$ for 1day [15]. A set of polyoxazoline-polyols were synthesized by thiol-ene addition of 2-mercaptoethanol under mild conditions. Further, these polyols were reacted with MDI to obtain a series of amorphous and semi crystalline PUs. Thus, PUs possesses the hard-rigid to soft-elastic materials characteristics [16]. A n adhesive material based on Jatropha oil has been synthesized with various advantages since it contains oil gums and transformed into sustainable material[17].

Linear organic-inorganic PUs with POSS has been synthesized with the help of 1, 4-butanediol as the chain extender with variable concentration of POSS. This type of PUs exhibited good shape memory effects, in contrast to conventional PUs [18]. Biobased PUs were also synthesized from organosilicon grafting cardanol based autocatalytic polyols [19]. A chitin-curcumin based PUs elastomers have prepared by step growth polymerization technique using HTPB, HDI, chitin and curcumin. Chitin increased the crystallinity of elastomers [20]. Ecofriendly PUs are also prepared from canola oil, caster oil and soyabean oil [21-23]. These all biobased polyols are summarized in Table 2.

Table 2. Bio-based Polyol.

S.No	Precursor source	Diisocyanate / other	Type of PUs	Role	References
1	Disaccharides and amino sugar	Aryl and alkyl diisocyanate	Linear hydrophilic PU	Resist to hydrolytic degradation	9
2	Xylitol	HMDI or MDI	Linear hydrophilic PU	High resistance to hydrolytic degradation.	9
3	2,3,4-tri-O-allyl Arabinitol	HDI	Thermoplastic PU	Biomedical and nanotechnological applications	10
4	Diols of oleate and undecenoate derivatives	MDI	Thermoplastic PU	-	11
5	Soyabean oil and lignin	CO ₂ and APES	Highly cross linked PU network	Thermoplastic film, coatings, adhesives, sealants, paintings, and elastomers	12
6	Castor oil	fatty acid based diisocyanate	Thermoplastic PU.	-	13
7	Vegetable oils (cotton seed and karanja oil).	MDI	-	Adhesiveness increased	14
8	Polyoxazoline	MDI	Cross-linked PU	Amorphous and semi-crystalline PU	15
9	Cardanol (derived from cashew nut shell)	PAPI	PU foam	High compression strength and thermal stability.	19
10	Chitin /Curcumin	MDI	PU elastomer	Crystallinity, elastomer increased	20
11	Kraft lignin and castor oil	MDI	PU sheet	Improve mechanical properties	21
12	Alkoxysilane castor oil	IPDI	PU/siloxane hybrid	Better mechanical properties and thermal properties	22
13	Castor oil	TDI	Hyperbranched PU	Advanced surface coating	23
14	Castor oil/pentaerythritol triacrylate	IPDI	UV curable WPU acrylate	Water resistance and mechanical properties	24
15	Soyabean oil	HDI, IDPI,MDI, TDI	PU coatings	Improve mechanical properties and adhesion	25
16	Glycerol, phthalic anhydride and oleic acid	TDI	PU coatings	Solvent resistance and corrosion resistant	26
17	Rapeseed fatty acid methyl esters	IPDI	Waterborne PU wood coatings	Improve chemical resistance and hydrophobicity	27
18	Canola oil	MDI	PUs	Hydrolytic stability and the alkali resistance	28
19	Phosphated cardanol-based polyol	MDI	Multifunction PU coatings	Anti-corrosion and antimicrobial	29
20	Vegetable based polyol	IDPI	PU	Thermomechanical performance	30
21	Soyabean oil	MDI	Rigid foam PU	Compression strength, thermal insulation, and thermal stability.	31
22	Caster oil	MDI	Thermoplastic PU	Mechanical and thermal stability	32

3.2 Non Isocyanate Route (NIR)

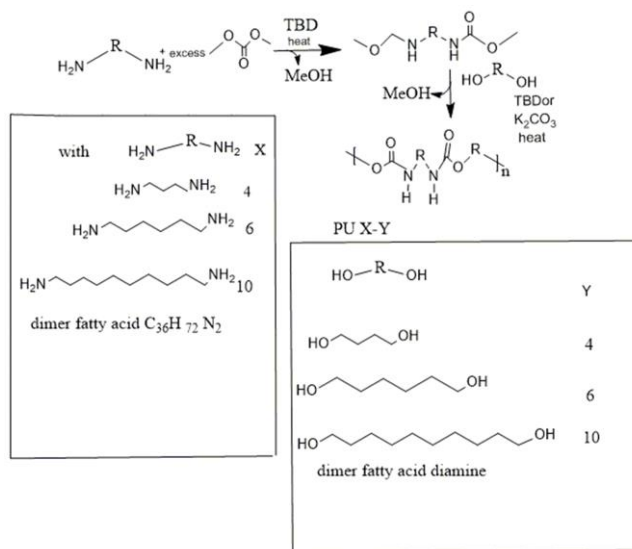
As mentioned earlier isocyanates are highly sensitive to moisture, carcinogenic and and corrosive material. Therefore attempts have been carried out to synthesis PUs by using non-isocyanate route. There are three ways investigated in literature for the preparation of PUs without using isocyanate precursors.

(i)The ring opening polymerization is reported for aziridine with carbon dioxide. This route has the major problem of high toxicity of aziridine [33].

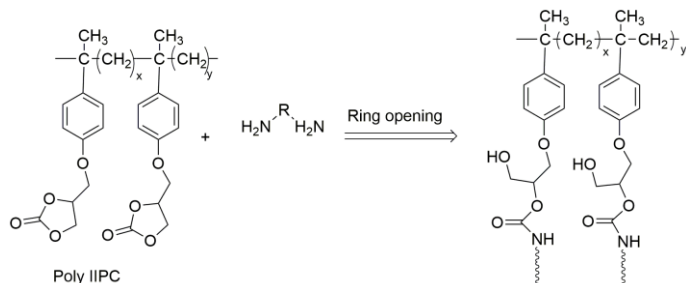
(ii) Self polycondensation of fatty monomers bearing hydroxyl and acyl azide functionalities on heating, with and without catalyst. Isocyanate formation takes place in situ via curtius rearrangement. Hence the toxicity problem of isocyanates is not solved [34-36].

(iii) Trans-urethanization reaction between bicyclic carbonates and diols, in presence of a catalyst such as titanium or TBD. This is considered most favorable method [37].

A two-step synthesis of NIPU was carried out by using DMC (a green solvent) and bio-sources diamines and diols, in presence of TBD or K₂CO₃ as a catalyst. Then diamines were reacted to give dimethyl dicarbamate. After that, polymerization reactions take place through trans urethanization with diols or diamines [38] Scheme 4.

**Scheme 4.** Synthesis of viable NIPU from DMC, diamines and diols[38].

The ring-opening reactions of polycyclic carbonates with diamines for the production of PUs have also been reported as green method [39-41]. This reaction involved a cyclic carbonate with aliphatic amines with β -hydroxyls as side-chain and resultant PUs exhibited hydrophilic nature [42]. TPU was synthesized by using IPPC dissolved in NMP, and adding to poly propylene ether diamine through NIR [43] Scheme 5. Polyhydroxyurethane was considered as a suitable substitution for PUs based on isocyanates [44]. One shot mechanism and epoxidation of cyclic carbonate was also reported [45,46]. These all are summarized in Table 3.



Scheme 5. Ring-opening reaction of poly IPPC with diamines [43].

Table 3. Non isocyanate route (NIR).

S.No	Approaches	Precursor	Role	References
1	Ring opening	Aziridine and carbon dioxide	Heat sensitive	33
2	Self polycondensation	Fatty monomers bearing hydroxyl and acyl azide	Thermoplastic behaviour	34-36, 39,40
3	Trans urethanization	Bicyclic carbonates and diols and catalyst such as titanium catalysts or TBD	-	37, 38
4	Epoxidation and formation of cyclic carbonate	Polyaddition of diamine with carbonated Sunflower oil	High tensile strength, Hardness, Thermal stability, Gloss, and Chemical resistance	45
5	One shot mechanism	Chitosan and Ricinoleic acid	High adsorption capacity	46

4. Coating Applications

In this article coating applications of PUs are focussed. These coatings are corrosion resistant, waterborne PUs dispersion, flame retardant, magnetic etc. and are discussed in the following section:

4.1 Corrosion resistant coatings

The inhibition of rusting of aluminum alloy is a great challenge in the industries. Chromated coatings are used for the corrosion inhibition of aluminum alloy. These coatings are carcinogenic in nature and deposited in water bodies. Therefore, an alternative option is required for the inhibition of rusting of aluminum alloy [47]. The materials are selected for coating possesses a high degree of hydrophobicity to improve rusting prevention. To improve corrosion resistance, corrosion inhibitors such as free molecules were incorporated into the coatings. PU-POSS coating was prepared and addition of POSS decreased the rusting properties of aluminium alloy [47].

POSS coating behavior depends upon the ratio of POSS to hydrogenated hydroxy terminated polybutadiene. As the amount of POSS was increased the coating became rigid and also, increased the hydrophilicity[48]. During its preparation polyester polyols were prepared with the help of sorbitol 1, 2, 3, 6-tetrahydro phthalic anhydride, adipic acid and EG. Then polyol is treated with isocyanate to form PUs coating. The impact resistances of these coatings are improved by adding ZnO NPs [49].

Table 4. Coating Application of PU Coatings.

S.No	Coating type	Precursor/Role/others	References
1	Corrosion resistant	Incorporation of POSS increases corrosion resistance, sorbitol, Zn NPs	48,49
2	WPUDs	Linseed oil, chitosan, sunflower oil.	58,59,60
3	WPUDs	Polycarbonates of 1,6-hexanediol	61
4	Flame-retardant WPUDs	Ammonium polyphosphate, PVA, soybean oil, castor and orange peel	70,71,72,79
5	Flame retardant PU Foams	Sucrose based polyether polyol and MDI along with castor oil, soybean oil	78
6	Fluorinated PUDs	Polyester polyol, dodecafluoroheptyl acrylate and diethanolamine.	81,82
7	UV curable coating	Nano ZnO obtained from APS.	84
8	UV curable coating (Shape memory effect)	PTMG, DMBA, IPDI and Nanosilica	92
9	Hybrid Coating	MWCNT use with PU to increase its corrosion resistance	98
10	Additive based coating	NPs increase Tg	102
11	Additive based coating	Silica NPs increase tensile strength, hardness	103

4.2 Waterborne PU dispersions (WPUDs)

WPUDs are used commercially due to restriction of release of volatile organic solvents and many harmful air pollutants in environment [50, 51]. Although solvent borne coatings showed good performance but are considered undesirable because these are flammable, toxic, costly, unsafe for workers and negative effects on environment [52, 53] hence, WPUDs used as alternative option in industry [54]. Beside ecofriendly nature, these coatings exhibited good mechanical and adhesion properties [55]. PUDs are generally utilized as flexible and hard coatings in textiles and wood & metallic surfaces, respectively [56]. PUs coatings exhibited good adhesive property on stainless steel surfaces and this property decline slightly by increasing the amount of polycarbonate of 1, 6 hexanediol [57]. Waterborne PU-silica hybrid materials with different weight ratios of APTMS and linseed oil monoglyceride were synthesized. Inclusion of APTMS in PUs matrix enhanced its mechanical properties remarkably [58].

Chitosan based WPUDs were prepared by the reaction among PEG, DMPA and IPDI and formed the isocyanate end capped prepolymer. This prepolymer further mixed with TEA and in the last step chain extension was carried out with the help of chitosan[59]. A dihydroxy acid obtained from sunflower oil has been act as chain extender and polycarbonate used during the preparation of WPUDs [60, 61] (Table 4).

4.3 Flame-retardant WPU dispersions

Flame retardant PUs foams could be synthesized by additive and reactive materials [62]. In the literature halogenated and non-halogenated additive/reactive flame retardants were discussed [63-67]. Flame retardancy property could be achieved by adding suspended form of flame retardants in the matrix of the foam. Tris (2-chloroisopropyl) phosphate and tris (1, 3-dichloroisopropyl) phosphate are two famous liquid flame retardants [68].

Various flame-retardant waterborne PUs with phosphorous-amine BPPO were prepared by the post-chain extension procedure. This was prepared by the reaction of PPG, DMPA and TEA. The post-chain extension process was initiated with BPPO and resultant formation of flame-retardant WPU emulsion. The phosphorus-containing chain extender enhanced the tensile strength but decline the elongation at break property [69].

A flame retardant was also synthesized using APP and OF resin. APP released polyphosphoric acid which promotes carbon residue coating over the surface of polymer matrix which helps in blockage of oxygen to stop the spread of flammable gases [70]. PVA modified melamine formaldehyde resin encapsulated APP, studied for flame retardant property on polypropylene [71].

Silica gel also encapsulated with APP and utilized as flame retardant TPU [72] Table 4. In this method, PU was first react with silicon and formed siloxane linkage. Polysiloxanes showed high thermal stability up to 300 °C. Hu *et al.* [73] studied the flame retardant property of Graphene oxide based PUs composites, are prepared by in-situ emulsion and self-assembly [74]. Halogen free flame retardant in the backbone of WPU, also reported which possess excellent flame retardant capacity. A variety of post-chain extension process synthesized WPU and investigated their thermal degradation mechanism [75, 76].

MBH ligand and its metal complexes were incorporated in PUs coating and evaluated for their flame retardancy property. Similarly, the inclusion of azomethine (-CH=N-) linkage in the PUs enhanced the thermal stability. The incorporation of aromatic ring improved flame retardant property due to stabilizing effect against thermal degradation. Superior flame retardant properties are also obtained by using of nitrogenous compounds [77].

A high flame retardant property of PU foam was achieved by using a variable ratios of diethyl allyl phosphonate, thioglycerol and other bio-based polyols [78,79] Table 3. Flame retardant efficiency is remarkably increased by the accumulation of phosphorus and nitrogen due to their synergistic effects [80].

4.4 Fluorinated PU dispersions (FPUDs)

FPUDs were synthesized by using HDI, polyester polyol, DMPA and TFE. On increasing TFE content, surface roughness increases since fluorinating agent moved on the surfaces and increase hydrophobic behavior. Nano indentation of coating showed that, the presence of fluorine on the coating possesses less stiffness and elastic modulus [81]. WPU medium length fluorinated diols 3-bis-(N, N-dihydroxyethyl) dodecafluoroheptyl acrylate were synthesized by using the Michael addition reaction [82].

4.5 UV Curable coatings

UV, oxygen and water are responsible for the degradation of organic coatings [83]. PU acrylates (PUA) are extensively used for UV coatings because they have impact strength, flexibility, corrosion resistance, hardness and transparency. These coatings showed benefits such as instant drying, formulation range, less energy utilization, low space and capital requirements of curing equipment. A various PUA / ZnO nanocomposite films with variable ZnO contents were synthesized by UV-curing system. ZnO improved the mechanical, optical and water transport properties of films [84] Table 4.

UV absorbers protect organic coatings from UV radiation. An inorganic UV absorber ZnO functions as UV stabilizer in organic coatings [84-88]. Nano ZnO even at low concentrations enhanced corrosion, scratch and abrasion resistances of coatings made from alkyl, epoxy and PUs [89,90]. The surface modification of nano ZnO by APS improved its efficacy and which depends also on ratios of ZnO-APS [91].

4.6 Hybrid Coatings

This type of coating usually made up of inorganic and organic components. The advantage of these coatings depends upon the interaction between the components [92]. The inclusion of inorganic insoluble pigments increases the intrinsic properties of the blend materials, affecting the mobility in the matrix of hybrid material by slow down the diffusion of aggressive species [93-96]. The physical blockade between the metallic substrate and the corrosive environment reduced the mobility of the ionic species. A stable blockade exhibited remarkable rusting inhibition properties [97]. The high corrosion resistance achieved by hybrid of MWCNT with PUs and applied to coat carbon steel ground grid. Its corrosion resistance was measured higher than as compare to neat steel [97].

4.7 Additive based Coatings

Additive such as pigments were added in PUs coatings to improve mechanical and anti-rusting properties [98,99]. NPs gain more attention for this purpose [100]. There is a direct relation between the T_g of coating and the interaction of resin with the NPs. NPs could increase the T_g of the coating when the resin is chemically bonded to it. NPs, might be migrated to the surface of coating or remain in the bulk, which depends upon the surface nature of NPs [101]. The tensile strength, modulus, hardness and abrasion resistance of the PU coatings has been enhanced by the addition of silica NPs [102]. Similarly, Ag NPs

significantly improved the mechanical properties of the PU coating [103]. To enhance the anticorrosion properties, Cr_2O_3 NPs are generally used in the organic coatings [104]. The nanoclay such as montmorillonite is stable at high temperature; better compacting strength and good flame retardant properties were used to prepare many polymers [105-107]. However, nanoclay is hydrophilic in nature which promotes to insufficient interfacial adhesion between the nanoclay filler and polymer matrix [108,109]. NCC possesses higher mechanical properties than Kevlar. Due to its high tensile strength, they are utilized to enhance PUs coating performance [110-113].

To enhance the rusting resistance of PUs coating surface modified NPs are added [114]. Surface modification of the nano silica with an amino silane improved significantly the mechanical properties of the PU coatings [115]. The Cr_2O_3 NPs were modified with 3-aminopropyl trimethoxy silane so that proper dispersion made and showed increment compatibility with the PUs coating. This coating was deposited on the steel substrates and increases toughness while decrease T_g and cross-linking density [116]. These all coating applications and their precursors are mentioned in Table 4.

CONCLUSION

Globally PU is one of the most research materials because it is easily available. It exhibit versatile coating material due to its mechanical properties such as tensile strength, modulus etc. It has been used for making paints, liquid coatings, elastomers, rigid insulated material, elastic fibers, foams which are soft and flexible and apply in biomedical field etc. Several polyols, diisocyanates, chain extenders, catalysts and additives are used for the production of PUs. For specific applications large variety of monomers are utilized to obtain PUs. Initially, most of the polyols were based on petroleum sources are used to prepare PUs but these are expensive and non ecofriendly which has increased the need for a more desirable and environment benign substitute. In this review we have focused on bio-synthesis and non isocyanate route of PUs production. This review also revealed different types of coating applications based on specific purpose such as flame retardant, UV curable, water borne etc. For further increase in performance, use of nanomaterials has been suggested. Thus, polyurethane could be considered as ecofriendly and cost effective as compared to other conventional polymers.

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ABBREVIATION

TDI	Toluene diisocyanate
XDI	Xylene diisocyanate
HMDI	4, 4'-Hexamethylenediisocyanate
MDI	4, 4'-methylene (diphenyl diisocyanate)
IPDI	Isophoronediiisocyanate
NDI	1, 5-naphthylenediisocyanate
ICBH	2, 5-bis (Isocyanatomethyl)bicyclo [2.2.1] heptane
HDI	1, 6- hexamethylenediisocyanate
PEG	Polyethylene glycol
PPG	Polypropylene glycol
DBTDL	Dibutyl tindilaurate
APES	3-aminopropyltrimethoxy silane
TPU	Thermoplastic polyurethane
POSS	Polyhedral oligomeric silsesquioxane
PAPI	Polyaryl polyethylene diisocyanate
HTPB	Hydroxy terminated polybutadiene
NIR	Non Isocyanate Route
TBD	1, 5, 7-triazabicyclo [4.4.0] dec-5-ene
DMC	Dimethyl carbonate
IPPC	4-isopropenylphenoxy propylene carbonate
NMP	N-methyl-2-pyrrolidone
WPUDs	Waterborne polyurethane dispersions
APTMS	3-aminopropyltrimethoxysilane
TEA	Triethylamine
PTMG	Polytetramethylene ether glycol
DMBA	Dimethylol butanoic acid

APS	2-aminoethyl-3-amino propyltrimethoxysilane
BPPO	bis (4-aminophenoxy) phenyl phosphine oxide
APP	Ammonium polyphosphate
OF	4, 4'-oxydianilineformaldehyde
MBH	<i>o</i> methoxy benzaldehyde benzoyl hydrazone
FPUDs	Flourinated polyurethane dispersions
DMPA	Dimethyl propionic acid
TFE	Trifluoroethanol
PUA	Polyurethane acrylates
MWCNT	Multiwalled carbon nanotube
NPs	Nanoparticles
Tg	Glass transition temperature
NCC	Nanocrystalline cellulose
NPs	Nanoparticles
EG	Ethylene glycol
IIPC	Isopropenylphenoxy propylene carbonate

CONFLICT OF INTEREST STATEMENT

On behalf of all authors, the I states that there is no conflict of interest.

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