Properties and Characterization Techniques for Waterborne Polyurethanes

M. Ramesh, L. Rajeshkumar, D. Balaji, and M. Priyadharshini

Abstract

Polyurethanes are a class of polymeric materials possessing a broad range of properties and characteristics both chemical and physical when compared with monolithic materials. Due to a wide availability of monolithic materials commercially and due to the fact that the properties of those materials could be altered suitably, combination of polyurethanes to obtain customizable properties cater to the growing needs of contemporary technologies including elastomers, foams, coatings, glass, paper, wood and adhesives. Waterborne Polyurethanes (WPUs) are currently in the research limelight among various researchers due to its novelty, unique properties and wide scope for applicability in fields like caulking materials, paint additives, various fibers, emulsion polymerization media, dyes and primers for metals, pigment pastes and defoamers. WPUs are considered to be green elements which are characterized by non-flammability, non-toxicity and less environment degradability and for this reason these materials are taken up for research during recent times. Surface oxygen groups of WPUs are amended during the recent researchers for converting them into polymer nano-composites. Due to the unique phase characteristics, nano-structured organic and inorganic hybrid composites possess better and enhanced functional characteristics. Such unique phase characteristics arise due to exfoliation and interlayer collation which increases the interfacial bond between organic and inorganic phased thus improving the composite properties. Manufacturing of such hybrid materials requires special attention toward their miscibility since agglomeration and accretion are considered to be major problems that results due to poor interaction between polymer and dispersoid along with least homogeneity.

Keywords

Polyurethanes • Waterborne • Properties • Characterization • Nano-fillers • Nano-composites

1 Introduction

Polyurethanes (PU) are fabricated by stacking the rigid and flexible polymer layers alternatively and are considered to be much better in terms of their performance. Fabrication of Pus comprises of two steps: Formation of a thick viscous liquid called as prepolymer is the first step, which has its molecular weight in medium range, as a result of reaction between polyol and isocyanate. Secondly, the molecular weight of the prepolymer is shifted to higher values by making it to react with diamine or diol chain extender. Various final polymeric configurations can be obtained by producing the PUs by changing the reactants nature to such as catalysts and additives, di-isocyanates and polyols. Usually PUs are characterized by few note-worthy properties such as toughness, flexibility, abrasion and scratch resistance and resistance toward chemicals. PUs mostly comprises of a notable quantity of free isocyanates and a major quantity of volatile organic compounds (VOC) in most of the cases (Hepburn, 1992). But the presence of toxic organic compounds may pollute the environment. Hence, during late 1960s, aqueous PU dispersions were discovered and the WPU contains the PU particulates suspended in an aqueous medium, thus forming a binary colloidal solution. But PUs are discordant toward water and they have to be modified to behave as

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waterborne compounds. During further developments, WPUs were manufactured from polymers containing many hydrophilic groups so as to have better solubility in water. This could be done by addition of hydrophilic monomers that contain ionic functions into the polymers. Such materials include carboxylate or sulfonate groups and quaternary ammonium. Resulting materials are termed as PU ionomers and internal emulsifiers respectively. WPUs are most widely applied in many areas due to the following advantages: Minimizing the release of solvent into atmosphere due to the organization's administrative regulations, high cost of the currently used solvents and the WPUs quality is most suited for various applications. Generally, WPUs are ecofriendly, non-polluting of air and water and non-toxic and non-flammable. Only product from the reaction involving WPUs is the evaporation of water, which is no way hazardous to the environment. WPUs find their majority of application in the areas including waterproof textiles, coatings, films for packaging, adhesives, biomaterials and membranes, ink binder, synthetic leathers, paper sizing and glass fibers (Arnolds, 1990).

Composite materials find more applications in the field of engineering and technology due to its superior characteristics like low price, less in weight, ease of manufacturability and corrosion resistant nature. Specifically, organic polymers have very high applicability in many high-end products which reoriented the research on organic polymers to newer directions and heights. Nevertheless, these materials are poor conductors of heat and so their applicability in electronic products and other heat involved devices are relatively low. Thus, organic polymers with better heat transfer and heat dissipation characteristics has to be developed (Dieterich et al., 1970; Rosthauser & Nachtkamp, 1987). Few researches stated that the analysis of thermal conductivity of organic polymers contains two different aspects: First aspect is the synthesis of organic polymers with ordered structures to enhance the phonon mobility, materials with high degree of crystallinity, materials with higher order polarization structure, enhanced pathway strategy to improve heat transfer or materials with conjugated radicle. Few such materials are polypyrrole (PPY), polyacetylene (PA) and polyaniline (PANI). Second, incorporation of fillers into the matrix for enhancing the heat transfer by the way of composing a heat transfer path with conductive matrix and fillers (Garcia-Pacios et al., 2013). Results of the experiments indicate that the heat transfer network is affected by the usage of less amount of fillers incorporated in polymers. This renders lower connectivity between the particles within the path of heat transfer, hinders the phonon transport and increases the heat resistance on the interfacial surface of the two elements and reduces the conduction rate between those particles. Heat network is formed between two particles in the path of heat transfer when the number of particles present in the network goes beyond the threshold of percolation. One such organic polymer incorporated with filler is PU whose characteristics ranges between a rigid thermoplastic to an elastomer which possess far better tensile strength, solvent resistance, physical properties and abrasion and tear resistance (Poussard et al., 2016).

Utilization of PU in higher end applications can be easily carried out by customizing its properties since PUs have a property of existing with adaptable chemical structures unlike the non-tailorable monomers. By the way, development of ecofriendly WPUs is also increasing these days due to the current day demands of minimizing the emissions from VOCs. WPUs are most widely used in coating industries and technologies where VOCs evolution during drying process is of major concern when conventional materials are used. Unlike traditional solvent-based polymers, WPUs offer numerous advantages like high molecular weight, good adaptability and low viscosity which make them suitable for electromagnetic shielding and coating on electronics devices that needs enhanced thermal conductivity (Zhou et al., 2015a).

Thermal properties of WPUs can be easily tailored by incorporating conductive fillers of nano-size into them which percolate them even at minimum loads. Graphene, which is the single laminate of the graphite sheet can act as an important nano-filler with carbon as base for not only enhancing the thermal conductivity but also the strength of the nano-composite. Graphene-based nano-materials and nano-platelets can be developed by researchers, as these materials are easy to process and are easily soluble, for applications in polymer-based nano-composites that were enhanced mechanically and thermally. Such carbon-based materials like graphene, single and multiwalled carbon nanotubes (CNTs) and graphite can be hybridized with WPUs for the enhancement of its thermal conductivity. Current chapter focuses on WPU filled with hybrid additives for enhancing the thermal conductivity along with chemical and physical amendments (Bai et al., 2007).

2 Bio-Based Water Polyurethanes

Generally, bio-based WPUs were manufactured by addition of natural filler into the polymer matrix. Few researchers used castor oil (CO) and tartaric acid (TA) as additives and cellulose nano-crystals (CNCs) as fillers to form a bio-based WPUs. Since CNC is a bio-based reinforcement, these materials were coated over the metal substrate to obtain numerous tailored properties. CNCs were emulsified with WPUs in various concentrations and the mixed suspensions were obtained as aqueous suspensions in various concentrations of 5% and 10% by weight on dry state. These suspensions were adjusted for their viscosity so that they could be used for coating of aluminum substrate by dip-coating. Such coatings were subjected to contact angle tests and knife and tape tests. Additionally, nano-scratch, nano-indentation and wear tests were carried out on the coated aluminum and the tests revealed the feasibility of utilizing nano-size filled WPUs as coatings to metal substrates (Meng et al., 2009).

2.1 Synthesis of WPUs

WPUs were manufactured in a two-step process: First, CO is mixed with Isophorone diisocyanate (IPDI) in a 250 ml flask at a temperature of 78 ºC for a period of two and half an hour. The flask is attached with a mechanical stirrer, a nitrogen gas inlet and a condenser. Second, TA is mixed with 30% by weight of dimethyl formamide (DMF) while 20 ml of acetone is added to the mixture for controlling the viscosity of the emulsion. After this tetra ethanolamine (TEA) was added in equimolar ratio to TA into the final mixture and the temperature was brought down to 60 ºC. In order to obtain an aqueous mixture, the above constituents were stirred aggressively at about 800 rpm and distilled water is added to it. If any unsettled organic solvents were present in the stirred mixture, they were removed from the system with the help of a vacuum evaporator at a temperature of 30 ºC. Figure 1 shows the final chemical structure of CO-based WPUs for various types of emulsions. These WPUs were nomenclated as WPU-TA. Another configuration of WPUs was prepared by using polycaprolactone (PCL) which partly replaces CO in the mixture and serves as an alternative for 16% of –OH groups in CO. During this synthesis PCL was added during the initial step in the process while the other steps remain the same (Liu et al., 2017; Ramesh & Rajesh Kumar, 2018). These WPUs were nomenclated as WPU-TA-PCL. Few cationic and anionic series of WPUs were prepared based on castor oil with feed ratios as listed in Table 1.

WPU-TA samples were subjected to macroscopic examinations and they revealed that these samples were harder film coatings. Nano-indentation tests also supported the above results rendering quantitative data. On the other hand, WPU-TA-PCL samples were found to be more elastic than former sample owing to the addition of PCL into the mixture. This enhanced the possibility of using them as self-standing films with better mechanical characteristics. Incorporation of CNC into WPUs rendered better properties such as lower coefficient of friction, elastic recovery, high hardness, wear resistance and lower plastic deformation. WPU-TA-PCL samples with 5% CNC has better properties comparatively with better wear resistance, hardness and adhesion (Zhang et al., 2020).

Analysis of the effects of moisture imbibition of the PU films and its mechanical characteristics, effects of CO functional groups, particle size of WPUs due to chain extension were carried out by various researchers. WPUs exhibited better stability during storage for about 24 months. Resultant PUs exhibited low hydrophilicity, low moisture intake, better mechanical properties and high transmittance. Test results on WPUs indicated a Young's modulus of about 50 MPa, moisture intake of about less than 4%, and an elongation ranging between 15 and 300%. These WPUs were also tested by applying on animal skins and they displayed better hair-styling performance with practically no skin irritation. Hence, these castor oil-based PU can be utilized as potential substitutes for hair-styling commodities (Bloor et al., 2006).

WPUs were also synthesized by using trimethyol ethane (TME) which is a bio-based epoxy resin along with some chemicals likeneopentyl glycol, diethanolamine and N-benzylethanolamine. When these WPU polyols were subjected to testing their glass transition temperature and storage modulus increased with the presence of aromatic ring and larger hydroxyl value in the crosslinked polymer (Sim et al., 2005). Presence of tertiary amines affected the thermal stability of the crosslinked polymers while the WPU amino polyols without tertiary amines executed better thermal stability due to the absence of C-N bonds. WPUs combined with amino polyols, on the other hand, can render a better efficiency on development of coating film which also minimizes the VOC toxic emissions (Riffat & Ma, 2003).

2.2 WPU Synthesis from Cellulose Nano-Fibers

Interests were shown by some researchers in processing of WPUs using cellulose nano-fibers (CNF) because of its environmental friendliness and easily tailorable properties. Since CNFs are hydrophilic in nature, aqueous-based reinforcements can also be used for synthesis. Usage of CNFs poses greater advantages like better specific properties, naturally available and less in cost. Though CNFs need few compatibility alterations, their advantages mask this fact. CNFs were generally obtained from the carboxylation and mechanical disintegration of hardwood kraft pulp that was bleached by standard procedures. When the degrees of carboxylation along with number of passes and processing time was varied, various configurations of WPU incorporated with CNFs could be obtained. Analysis was carried out to evaluate the influence of degree of carboxylation over the mechanical properties of the WPU-CNF nano-composites. Unreinforced WPUs exhibited poor thermal, mechanical and thermo-mechanical characteristics than the CNF reinforced WPUs in spite of damage in cellulose structure and its crystallinity index caused by the carboxylation process (Saqr et al., 2008). WPUs reinforced with carboxylated CNF fibers exhibited 86% of breaking stress, 167% of modulus and

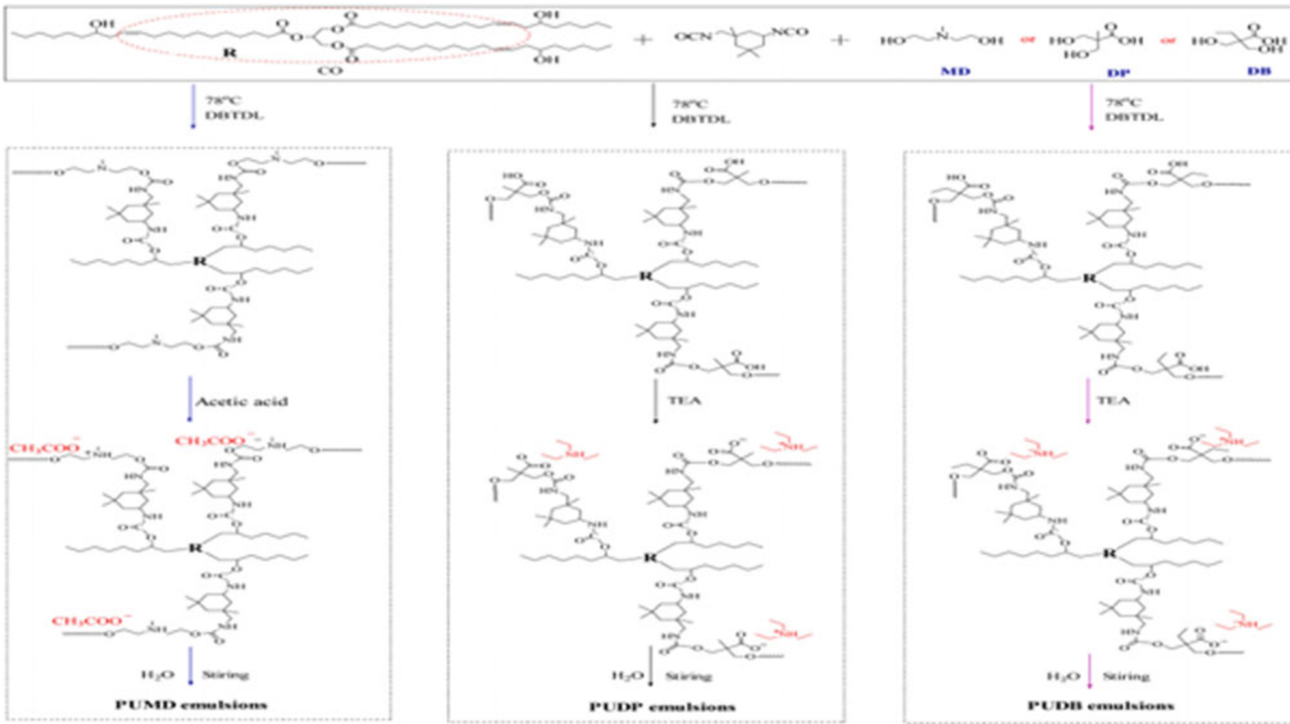

Fig. 1 Representation of castor oil-based WPUs (Zhang et al., 2020)

Table 1 Reaction conditions of WBPUs (Zhou et al., 2015b)

S. No.	Sample	Time and steps	Equivalent ratios	NCO/OH ratio	ACID/TEA ratio
1	WBPU-TA	2.5 h and 2 h 2 steps	CO/TA = 0.8	1.6	1.0
2	WBPU-TA-PCL	2.5 h and 2 h 2 steps	(CO + PCL)/TA = 0.8	1.6	1.0

377% of yield stress when compared with its counterparts. Interaction between the matrix and the reinforcement at the interface was also found to be improved as a result of presence of carboxyl groups on the CNF surfaces. It could be seen from the above test results that carboxylation process on CNF fibers have a positive effect on the WPU-CNF composites. Nevertheless, when the degree of carboxylation crosses certain limit, the crystal structure of CNF undergoes damage which in turn decreases the composite properties (Bozlar et al., 2010; Han & Fina, 2011).

3 Synthetic Water Polyurethanes

Many researchers prepared synthetic-based WPUs from various artificial sources such as silane-based inorganic compounds. Siloxane-functionalized polyether carbonate (Si-PEC) containing a maximum of 9.8% by weight of siloxane was synthesized along with WPUs and compounds of various molecular weights were prepared. Above prepared emulsion had a particle size ranging between 100 and 684 nm and this range is due to the variation of siloxane content. Carbonate unit of polyol enhanced the oxidation and mechanical resistance while the siloxane content rendered better thermal stability and cross-link density to WPUs. Si-PEC-WPU compounds displayed a good mechanical performance with an elongation of 684%, enhanced hydrophobic nature and a tensile strength of 17 MPa owing to the presence of siloxane and carbonate units. These compounds could be used as better substitutes for petroleum derived polyols as far as synthetic WPU application is concerned (Maldovan, 2013).

Experiments were conducted by many researchers in view of enhancing the hydrophobicity of cationic WPUs by manufacturing them with octadecyl side chains containing compounds such as 1-monostearoyl-rac-glycerol using cathodic electrode position technique (CED). Figure 2 shows the schematic of synthesis of CED coatings. Characterization of such synthesized compounds portrayed that there is an increase in the phase separation rate between hard and soft segments of WPUs due to the introduction of octadecyl chains into them. Water absorption and water contact angle analysis revealed that when the above emulsion was used as coatings then the water resistance of the substrates increase due to the formation of hydrogen bonds on the surface and low surface energy. CED coatings also possessed better flexibility, hardness, impact resistance and adhesion in the tests conducted by international standardization test of paints and varnishes. These coatings displayed an optical transmittance of 90% during optical transmittance tests and the thermal stability of the coatings was also improved (He et al., 2020).

4 Self-Healable Waterborne Polyurethanes

WPUs were generally prepared by a process called acetone process and in case of damage of the WPU coatings an inorganic resin or curing agent is infused which induces a crosslinking reaction resulting in curing process. Various characterization techniques could be used to analyze the incorporation of curing agent into the system quantitatively (Sanada et al., 2009). Few researchers tried to prepare a self-curing or self-healable WPUs from either organic or inorganic sources. WPUs were synthesized by developing a dynamic covalent bond within them through aromatic schiff base (ASB) under visible light. These ASB-WPUs have shown a better self-healing ability with an efficiency of 84% when exposed to LED table lamp for a period of 24 h at a temperature of around 25 ºC. These polymers, when maintained at room temperature, exhibited enhanced mechanical properties such as 14.35 MPs of tensile stress and 65 MJ/m^3 of toughness. These enhanced properties were possible primarily due to the imine metathesis present in the ASB bonds which were elicited by visible light (Xie et al., 2005). Meanwhile, interactions of H-bonds in the urethane were also responsible for such a better self-healing of the ASB-WPU composites. It was also a supporting fact that these ASB-WPU composites could be repaired and rehabilitated for obtaining better mechanical properties after damage under visible light. Next-generation smart materials could be easily prepared from the above-stated manufacturing process and it could possibly result in room temperature self-healing WPU composites which can be reprocessed under clean and safe visible light to restore their mechanical properties to the maximum possible extent (Im & Kim, 2012; Lee et al., 2009). Figure 3a shows the schematic of processing of polymers under visible light and the resulting ASB-WPU composites. Figure 3b shows the chemical structure of self-healing mechanisms happening under visible light.

Self-matting WPUs were prepared by some researchers by incorporating hydrophilic elements into hard and soft segments of WPUs. This could be easily done by addition of PCKL polyols that comprises of carboxylate groups into the WPUs for enhancement of their hydrophilicity and matting characteristics (Choi et al., 2011). Characterization techniques like FTIR and SEM were used for confirmation of chemical structure and WPU morphology respectively. Upon analysis of details pertaining to the manufacturing of WPUs, it was determined that hydrophilic units added to the WPUs influence the particle size as well as the surface gloss of WPUs. Surface gloss was found to be directly proportional to the increase in sulfonates or carboxylates contents while the particle size was inversely proportional to it. It was found from the experiments that when the dispersion particle size was about 3 microns, the size of coated surface was less than 1 mm. Thermo gravimetric analysis was carried out to

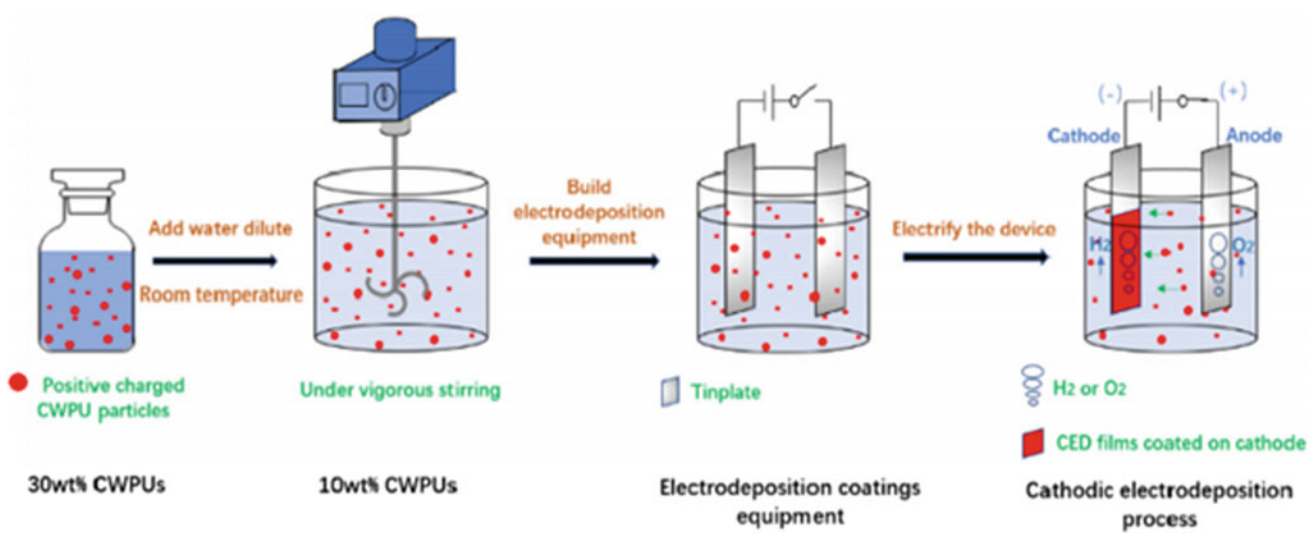

Fig. 2 Preparation of CED coatings and the cathodic electrode position process (He et al., 2020)

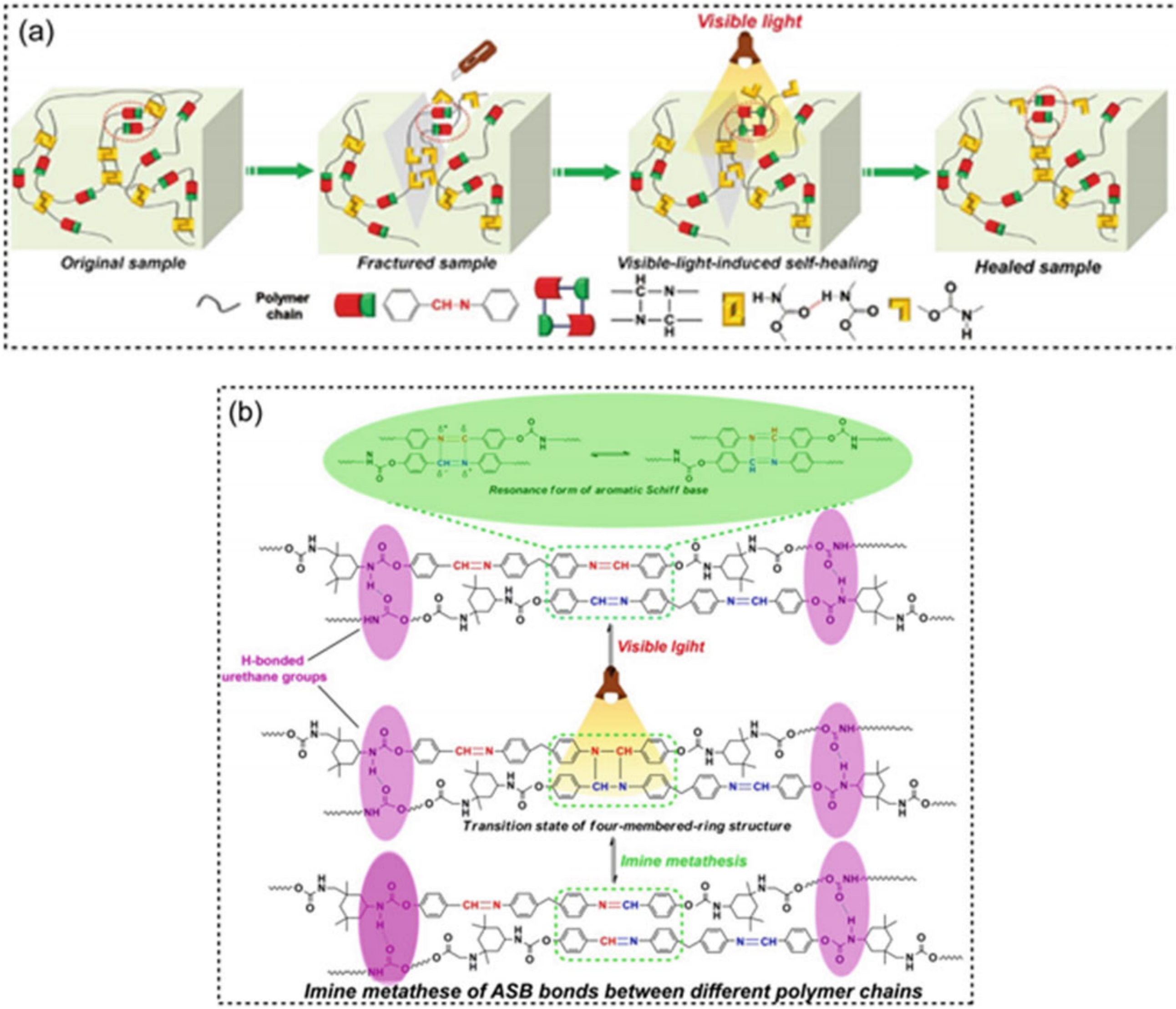

Fig. 3 **a** Schematic depicting the healing process of ASB-WPU polymers; **b** the proposed self-healing mechanisms (Fan et al., 2020)

assess the thermal stability of the WPU coatings from which the initial decomposition temperature of the coatings was observed to be greater than 285 ºC with the coatings being thermally stable. Such coatings can readily be used in leather finishing applications because of its aforementioned attributes (Kim et al., 2003).

Diels–Alder (DA) chemistry was used to prepare WPU dispersions with ultraviolet (UV) curable resin. Crosslinked WPUs obtained by this method were expected to possess better recycling and healing characteristics. Hence the WPUs prepared by acetone process were then prepared by DA chemistry where the chain extender in acetone process is substituted by DA adduct with acrylic chain in this process enabling the UV curing and cross-linking (Jeong & Lee, 2003). It was found from the photo differential scanning calorimetry (PDSC) that DA adduct supports UV cross-linkages in the coating. Existence of DA and retro DA reaction at 60 ºC and 120 ºC respectively in cross-linked polymers was noticed from characterization methods like DSC, FTIR and rheological experimentations. Presence of these reactions enhanced the permeability of materials toward CO_2 and enhanced the ability to reprocess and heal by also sustaining its mechanical properties. Yet it should be taken into consideration that a balance has to be maintained at all times between acrylic double bond component and DA adduct so that the cross-link density is kept low while the ability to recycle enhances (Jeong et al., 2003; Lee et al., 2019; Ramesh et al., 2020; Wang et al., 2009). These facts, when further researched, may pave way to develop sustainable WPU coatings. Figure 4 shows the self-healing of a scratch induced at the surface of WPUs synthesized by DA chemistry.

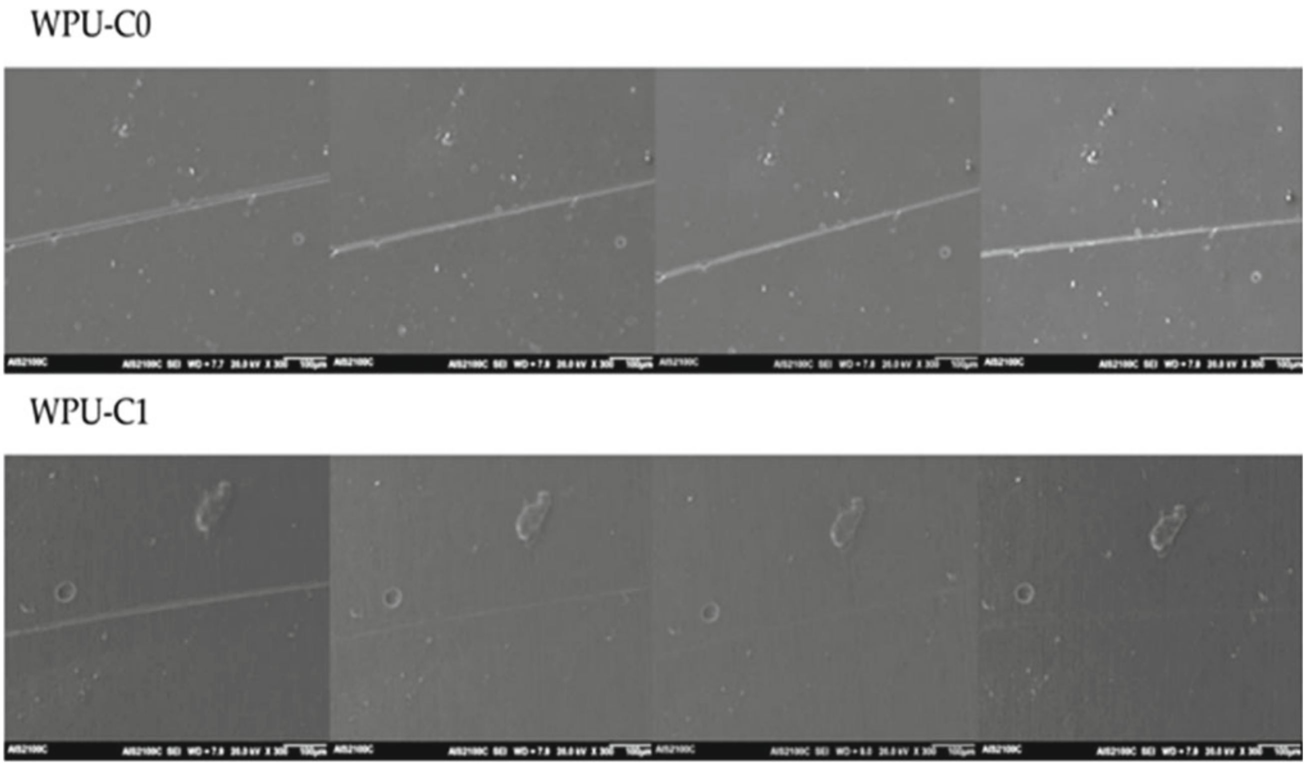

Fig. 4 SEM micrograph of self-healable WPUs with DA adduct (Lee et al., 2019)

5 Water Polyurethanes Adhesives

The challenge lies in developing the novel adhesives which are soft in nature is hard brought in the property of adhesion to the materials with least surface energy. By holding this as a key, WPU dispersions based on (PEO) poly (ethylene oxide) homopolymer and (PEO-b-PPO-b-PEO) poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) and (PPO-b-PEO-b-PPO) poly (propylene oxide-b-ethylene oxide-b-propylene oxide) triblock coexisting polymers were produced (Chung, 2004). Adhesives prepared by dispersions unveiled better bond on least surface energy (PP—polypropylene) probe over the more surface energy probe made of steel. Furthermore, with the intention of enhancing the performance of adhesive made of WPUUs for (PSA-Pressure Sensitive Adhesive) applications, the designed optimized to bilayer system. The bilayer is made up of solid layer and as well liquid layer of two different types of WPUUs to attain the viscoelastic nature to generate a gradient with the property of viscoelasticity. This tactic directed to adhesives that unveiled fibrillation during the measurement of probe tack with the assistance of a steel probe, it is of PSA variant. At last, adhesive tapes prototype were developed by the system of bilayer (Lerf et al., 1998). The peel test was conducted over these adhesive tapes which unveil the performance in par with the other conventional adhesive tape, create the interest for its considerable application (Stankovich et al., 2006).

In general, to summary, the novel developed adhesives revealing the considerable performance compared over the steel and high surface energy. This outcome is partly accredited to higher surface energy, which lay path to better thermodynamic efficiency of adhesion, and triblock coexisting polymer-based WPUUs which diminishes the elastic modulus to accomplish the Dahl Quist criteria. Subsequently, these WPUU dispersions might be employed as a soft adhesive for attachment to least energy surfaces. Mixing these two WPUUs (in 2 dissimilar proportions) has not improved the performance adhesives, in comparison over the performance of adhesive with neat WPUUs. Quite reverse, the bilayer systems made up of the same 2 WPUUs employed in the combinations, liquid layer and solid layer in combination led to a plateau in the probe tack curves like steel, which result in fibrillation (Lomeda et al., 2008; Xu et al., 2009). Therefore, the built bilayer system is an efficacious tactic for the enhancement of the performance of adhesive made up of WPUUs to attain the performance like PSA, mean that can be employed as base of PSAs, led to formulate PSAs by amending the surface agents so as to tailor the various properties. The upper liquid layer provides tack, while the solid-based bottom layer donates to cohesion

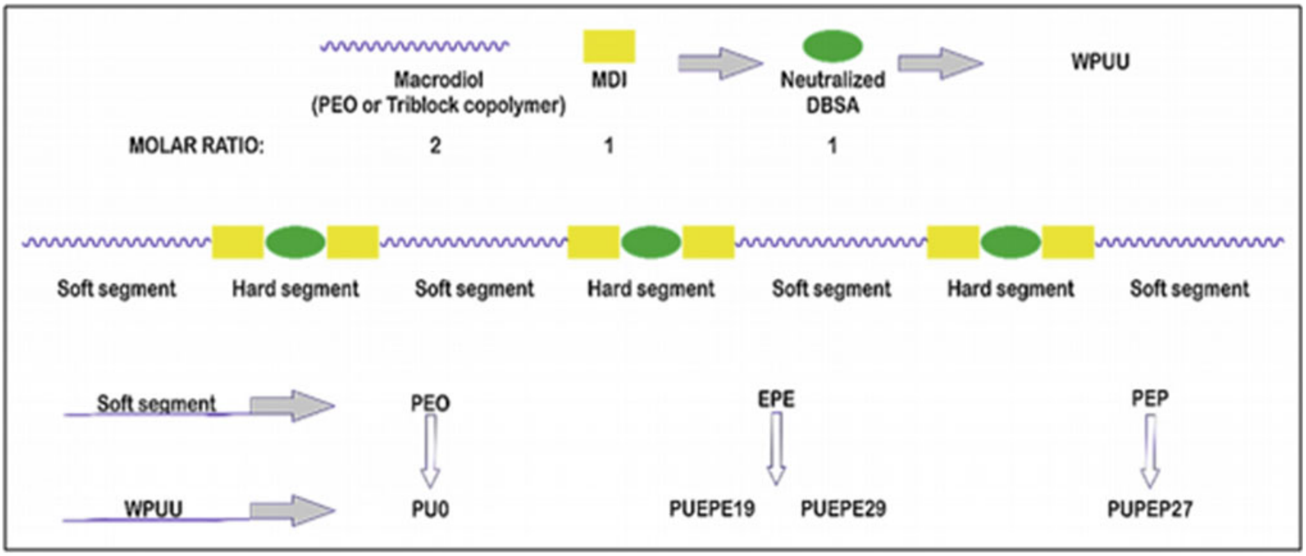

Fig. 5 Synthesis of the waterborne poly(urethane-urea)s (Díez-García et al., 2020)

and which aids fibrillation. Constructing on the performance of adhesive which developed by bilayer systems by selecting the best-performing bilayer of adhesives. The bilayer-based adhesive applied over the PP supporting the peel force is found to be in the range of domestic conventional tape. The peel force unveiled by the aluminum surface was found to be superior over the domestic tape. Nevertheless, the bilayer tape thickness is greater than that of the adhesive's thickness in conventional tape, and supplementary optimization is essential to attain satisfactory performance of thin layer thickness (Díez-García et al., 2020). Figure 5 illustrates the process of synthesis of WPUs based on triblock copolymers.

6 Water Polyurethanes Coatings

Metallic elements and particles were also used as additives and fillers in WPUs for coating them over the substrates. Some researchers tried to prepare a sturdy antistatic WPUs incorporated with ZrO_2 nano-particles by means of sol–gel technique (Bekyarova et al., 2009). In order to carry over this process, the coating surface resistivity and the performance of the resin has to be clearly analyzed. WPUs reinforced with 6% by weight of ZrO_2 nano-particles exhibited a surface resistivity of $9 \times 10^9\ \Omega\ sq^{-1}$ while it discharges the electrostatic charges effectively. Its strength of adhesion was found to be 31% higher than the unreinforced resin. Surface roughness of the above composite was measured to be 27 nm which impedes the penetration of dust into the surface of the composite and this was possible due to the homogenous distribution of the ZrO_2 nano-particles into WPUs (Bourlinos et al., 2003). Such sturdy WPU-ZrO_2 composite coatings can give way for the development of eco-friendly antistatic surfaces. The enhanced property of these coatings was primarily due to: (i) ZrO_2 nano-particles strongly adhere to the surface of WPU resin after undergoing cross-linking reaction, (ii) Surface of the coating is filled with uneven chemical structures, (iii) Homogenous distribution of the reinforcement is ensured by suitable adaptation of the resin. WPU- ZrO_2 antistatic coatings can be used in industrial antistatic surfaces for the aversion of dust over the surface and also for the purpose of electrical insulation (Hormaiztegui et al., 2018; Hormaiztegui et al., 2020; Madbouly et al., 2013; Pramoda et al., 2010).

Experiments were also carried out for the preparation of WPU coatings with fluorinated silicon (FSWPU) by using additives like 3-(2-Aminoethylamino) propyl trimethoxysilane (AEAPTES), PCL diol and 2,2,3,3-Tetrafluoro-1,4-butanediol. Particle size of FSWPUs were analyzed by dynamic light scattering, molecular weight by gel permeation chromatography (GPC), thermal properties by TGA and other characteristics of by FTIR and energy dispersive X-ray spectroscopy (EDS) (Larraza et al., 2020; Ma et al., 2020; Ramesh & Kumar 2020; Wijs, 1929; Wu et al., 2020). Its dynamic mechanical behavior, elongation, shear strength and tensile strength pre and post hydrolysis were investigated by a tensile testing machine. FSWPU emulsion coatings were applied over tiles for the measurement of surface tension, hydrophobicity and hydrophilicity through contact angle measuring apparatus (Aizpurua et al., 2020; Chang et al., 2020). Tape test was also carried out upon the tiles coated with FSWPUs for evaluation the coating adhesion over the substrate. From all the above test results it could be seen that AEAPTES groups enhanced the tensile strength, thermal stability and hydrophobicity while it minimized the surface energy and increased the coating adhesion with tiles

(Hsu et al., 2020; Sukhawipat et al., 2020; Yousefi et al., 2020). Hence, it could be concluded that FSWPUs can be used for better surface coating to improve the coating characteristics in various aspects.

7 Waterborne Polyurethane Nano-Composites

Solvent borne PUs have better hydrolytic strength, improved thermal stability and enhanced mechanical properties when compared with WPUs in humid conditions which is a note-worthy difference. Many researches underwent by performing experiments to enhance the properties of WPUs by all the way and it was determined that nano-particles could be incorporated into these materials to bridge the above-said lacuna. Blending of WPUs and silica nano-particles rendered a novel nano-particle dispersed WPUs (Serkis et al., 2016). This material blend comprises of two colloidal type commercial silica such as Ludox TMA and Ludox AS which were differentiated by their counter ions, shape and size. Results showcased the improvement in properties of WPUs when an appropriate content of silica was added to it and it was observed that when 5 wt.% of silica was added water resistance of the WPUs improved, when 32 wt.% was added functional properties improved and when 50 wt.% was added thermal stability was achieved. It was also noticed that TMA grade of silica performed better than AS grade owing to its strong cross-linking physical effect. Few attempts were also made to synthesize the WPUs using different proportions of cellulose nano-composites (CNC) to obtain WPU-CNC blends (Santamaria-Echart et al., 2016). Results showcased that soft segments crystallization was high when low proportions of CNC was used while the degree of crystallization reduced with the increase in content of CNC because of a strong PU chain and CNC interaction. Additionally few other characteristics such as hydrophilicity, thermal stability and mechanical properties were enhanced due to the incorporation of more amount of CNC to the WPUs. Few other researches attempted to fabricate WPUs with nano-silica composites by using preformed polymer (S1) and polytetrahydrofuran glycol (S2) dispersed silica individually (Cheng et al., 2012). From the results, it was observed that S1 rendered uniform dispersion of silica within them than S2 and alongside S1 rendered enhanced physical characteristics, thermal stability and water resistance to the WPUs than S2.

Few experiments focused in preparing aqueous PUs with functionally graded polyhedral oligomeric silsesquioxane (POSS) and between 0.3 and 4.6 wt.% of diols following prepolymer mixing technique (Honarkar et al., 2016a). An anionic emulsifier in the form of N,N-bis (2-hydroxyethyl-2-amino ethane sulfonic acid sodium salt was also used along with the above constituents. PU-POSS nano-composites were prepared based on the reaction between the precursor powders and the functional groups. Results of the experiments revealed that thermal stability, particle size of resulting PUs, tensile strength, viscosity, glass transition temperature (Tg) and modulus increased with the quantity of POSS. As a result of adding nano-particles into the PUs, their structural homogeneity and compatibility enhanced which could be noticed from the morphological analysis of PU-POSS composites (Honarkar et al., 2014, 2016b). In another experiment, WPU with transparent UV curable coating was prepared using silica nano-particles and they were characterized with good scratch resistance (Zhang et al., 2012). Results revealed that alkaline and acid silica had less dispersion within PU matrix while the nano-silica dispersed homogenously within it. It was also concluded that dispersion of silica nano-particles within PU matrix governed the transparency of the resulting thin films.

8 Castor Oil-Based WPU Nano-Composite Coatings

Traditional polymer matrix systems are getting replaced by nano-composite polymer materials as the nano-composites are characterized by improved properties and is of larger research importance these days. Nano-composites experimentally possess better properties than its organic counterparts due to the strong force of attraction at the interface of nano-sized grain boundaries at the material domain. Mechanical and thermal characteristics of the polymeric matrices could be enhanced by hybrid design and chemical treatment of the materials such as incorporation of organoclay or addition of heterocyclic group into the base matrix for thermal stability or using fillers to reduce the porosity of polymer network (Andjelkovic et al., 2005; Barikani et al., 2007; Cakić et al., 2013; Coutinho et al., 2001; Hourston et al., 1997; Li et al., 2014; Lu & Larock, 2010; Yang et al., 2002). Few experimenters prepared nano-composite prepolymer by substituting the CO by 15 wt.% into bio-polyol dispersing it in turn within Closite 30B (C30B) and diisocyanate where the catalyzed diol had undergone reaction with NCO prepolymer to result in a nano-composite PU (Alaa et al., 2015). Table 2 enlists various materials, processing techniques and applications of WPUs according to previous researchers.

Synergetic effect between the inorganic and organic constituents of the aforementioned materials enhance the characteristics significantly and induce a high level of coupling at the interface. Initially few works were carried out to prepare PU-based composite materials using functionally graded organoclay, polyol and organically modified silicate lamina by some researchers (Rahman et al., 2008). But

Table 2 Method of WPU synthesis and its applications

S. No.	Materials used for WPU synthesis	Processing method	Applications	References
1	Castor oil-based PUs with TDI and Closite 30B as nano-material	Prepolymer and blending by precursor melting	Advanced surface coating	Serkis et al., 2016)
2	Thermally cured castor oil-based Pus with hexamethylene diisocyanate and 3-mercaptopropyl trimethoxysilane as nano-material	Thiolene process and in situ sol–gel process	Mechanically modified PUs	Santamaria-Echart et al., 2016)
3	Castor oil/ pentaerythrito l triacrylate-based UV curable WPU with IPDI and 3-amino propyl trimethoxy silane and 3-glycidoxy propyl trimethoxy silaneas nanomaterial	Prepolymer method	Coating and related applications	Cheng et al., 2012)
4	Castor oil-based polyols and Hexamethoxyl methyl melamine for WPU with IPDI and Closite 30B as nano-material	Prepolymer method and ultrasonication process	Waterborne PU adhesive applications	Honarkar et al., 2016a)
5	Castor oil-based 2-package WPU with IPDI and 3-amino propyl trimethoxy silaneas nanomaterial	Two-step process	Wood and composite material coatings	Barikani et al., 2007)
6	UV curable WPU acrylate with IPDI and 3-amino propyl trimethoxy silaneas nanomaterial	Prepolymerizationtechnique	UV resistance coating and related applications	Rahman et al., 2008)
7	PU-prepolymer-based on castor oil with IPDI and 3-amino propyl trimethoxy silaneas nanomaterial	Siloxane-functionally graded CO and in situ sol–gel process	Substitutes for petrochemical polyols	Yang et al., 2006)
8	Polyurethane adhesives using castor oil derived polyols with IPDI and alkoxysilane castor oil as nanomaterial	Acetone process and transesterification reaction	Wood and steel panel coatings	Yu et al., 2004)
9	Aqueous castor oil-based PU/ polyamide sulfone copolymer dispersions with TDI and Closite 30 B as nano-material	Acetone process	Anticorrosive coatings	Jeon et al., 2007)
10	Epoxidatied CO on WPU with 1,4 TDI 80 and 3-mercaptopropyl trimethoxysilane as nanomaterial	Prepolymer method	Water resistance membrane in WPU dispersions	Deng et al., 2007)
11	Thermoset polyurethanes with TDI, HDI and IPDI	Mixing method	Coatings and mechanical applications	Kwon & Kim, 2005)

recently many materials such as multiwalled carbon nanotubes (MWCNT), silica, clay derivatives like laponite, bentonite, wollastonites, hectorite and montmorillonite, TiO_2 and ZnO were utilized for the manufacture of WPU nano-composites (Deng et al., 2007; Jeon et al., 2007; Kim et al., 2006; Kuan et al., 2005; Kwon & Kim, 2005; Lee & Lin, 2006; Liu et al., 2012; Meera et al., 2014; Mishra et al., 2010; Yang et al., 2006; Yeh et al., 2008; Yu et al., 2004). Clays are currently adopted as traditional thixotropic agents, among the other fillers, in WPU emulsions and coatings, but are recently analyzed as coating elements for some other applications and property improvements (Fu et al., 2015; Meera et al., 2014). Normally the properties of PU dispersions were controlled by many parameters like bonding between filler and host material, mean diameter of fillers and shape of the filler particle. In order to obtain the dispersion of nano-particles in high rates into the WPUs, the techniques used are: exfoliation method, nano-filler dispersion by interposing them within the layers of WPUs and mixing them with polymer solution (Chattopadhyay & Raju, 2007). Some researchers tried to manufacture bio-based WPU dispersions with CO/polyethylene glycol (PEG) and isophorone diisocyanate (IPDI) combined with a prepolymer of NCO/OH and HS in 1.4 and 50 wt.% respectively, in proportion with the solid constituent (Gao et al., 2012). These PU dispersions were converted into PU nano-composite film by intercalating the prepolymer layer with eucalyptus globulus CNC (ECN). When this material is subjected to mechanical characterization, results indicated that at low wt.% of ECN, the mechanical characteristics of the nano-composite films were higher. This improvement was correlated with the microphase segregation of HS from SS in the dispersion, homogenous dispersion of ECN within PU dispersions and the major contributor for the enhancement was reported to be the strong hydrogen bond between ECN and polymer matrix.

CO-based alkoxysilane and PU-based siloxane hybrid coating were prepared by the synthesis following the thiolene path by few researchers (Fu et al., 2014). It was observed from the results that PU-based Si coatings exhibited better mechanical and thermal characteristics when compared with the CO-based alkoxysilane. When the wt.% of Si varies from 0 to 5%, the contact angle of Si-PU systems increases which denotes the increase of hydrophobicity of the hybrid film and decrease of the free surface energy level. Few experimental trails focused on bio-based elastomeric PUs incorporated with hard segment content (HS) for assessing their properties and microstructure (Corcuera et al., 2010). Bulk polymerization method was used to synthesize the CO-based elatsomeric PUs in the form of SS and HDI hard domain without the application of any catalyst. From the results it was determined that due to the action of HS in the stress concentrated points of PUs at micro-level, the mechanical properties of the films did not show any significant variation with the increase in content of hard segment. A hybrid WPU based on CO and silica crosslinked material was developed by some experimenters (Fu et al., 2015) and was analyzed for various properties with respect to the content of silica. It was found that film transparency decreased with the increase in content of silica while other characteristics such as thermal stability, hydrophobicity and roughness of the films increased appreciably. Studies were also made focusing the analysis of effect of siloxane content on surface roughness and silica enrichment on the coating transmittance. It was noticed from the optical transmittance test results that the transmittance of the coatings decreased in ultraviolet region at a spectrum of 300–400 nm with the increase in silica content and phase separation rate which could be possibly due to optical loss during transmission from organic phase to the inorganic one. It was stated that when the hydrophobic coating material should possess better thermal stability, then core–shell structure fits better. Few other studies on the optical transmittance examination of organic PU-based coatings, same results were obtained owing to the scattering of the rays at PU and silica nano-particle interface (Meera et al., 2014).

Structural backbone network of CO was modified by incorporating novel hydrolyzable $-Si-OCH_3$ group into it and a smart hybrid coating was prepared by few researchers which potential and effective for many applications (Shaik et al., 2014) from which urea-PU/silica hybrid coatings were further processed. Results of experimental analysis revealed that these hybrid coatings exhibited enhanced thermal and mechanical characteristics when compared with the unmodified CO counterparts. Many experimental studies were performed to enhance various hybrid coating characteristics like surface properties, elasticity, thermal, toughness, mechanical, chemical resistance and rigidity using clay and other inorganic filler materials (Corcuera et al., 2010; Gao et al., 2012; Gurunathan et al., 2015; Shaik et al., 2014). Final application level characteristics for these hybrid coating systems were influenced by the cross-linking density in the three-dimensional network, filler used and the polymeric chain network. Many research group attempted to prepare CO-based WPU dispersions using C30 reinforcements and the effect of reinforcing C30 nano-filler into PU dispersion nano-composite was experimentally evaluated (Gurunathan et al., 2015). Results showcased that when the C30 nano-filler of 2 wt.% was incorporated into PU matrix, mechanical and thermal properties of the hybrid fil increased appreciably which was solely due to the matrix and filler interaction at the interface of C30 nano-filler and PUs. In few experiments 3 wt.% of C30B nano-filler rendered better tensile and other mechanical and coating characteristics for CO-based WPU systems when compared with their traditional counterparts (Panda et al., 2016). This could be due to the strong structural nano-filler network structure, enhanced matrix cross-linking with the nano-filler and better interfacial adhesion between filler and matrix.

Strength of the interfacial bonding was observed from the assessment of hydrogen bonding established between the PU matrix and the nano-filler. Due to the increase in NCO/OH ratio in PU nano-composites, many results concluded that the utilization of inorganioc content was high and so was the enhancement in mechanical characteristics of CO/PU-based nano-composites (Gurunathan et al., 2016; Yeganeh & Mehdizadeh, 2004). Trimethoxysilane groups undergo hydrolysis reaction and render functionally active silanols groups which renders improved mechanical properties for WPUs when potentially cross-linked with them. It was also studied by few authors that for enhancing mechanical characteristics and thermal stability of PU hybrid coatings, a small weight proportion of organoclay would suffice due to the intense formation of C=C double bonds within the inorganic and organic resin network. Few experiments were carried out to determine the adhesion, drying time, hardness, flexibility, chemical and impact resistance of mild steel substrate panels coated with bio-based WPU dispersion organic coatings (Gurunathan et al., 2015; Meera et al., 2014; Panda et al., , 2016; Patel et al., 2011) and it was found that the increase in inorganic constituents proportion increased the thermal stability of the WPU hybrid coatings. As stated above, few researchers tried to reinforce 3–4 wt.% of organoclay with WPUs and found that the values of strength and modulus improved when compared with pure PUs. It was also noticed that as the organoclay content increases mechanical, dynamic mechanical, modulus of elasticity and yield properties increased whereas the breaking stress and strain decreased considerably (Gurunathan et al., 2015; Yeganeh & Mehdizadeh, 2004). Many other researchers also studied the properties like operating temperature and heat resistance for the CO-based WPUs reinforced with organoclay and found that even those properties improved appreciably when compared with the unreinforced pure WPUs. It could be concluded from the above discussions that CO-based WPU dispersions when reinforced with nano-composites or nano-fillers may exhibit sound mechanical, thermal and other properties and could be potentially applied in various fields of coating and other applications.

9 Conclusion

This chapter was intended to provide an outline about the process of fabrication of WPUs and the materials associated with it. WPUs are promising class of materials with attributes like bio-based, ecofriendly, renewable and hydrophilic materials. Apart from its wide real-time applications, these materials have become the latest concern of academicians and industrialists. Due to its better performance, WPUs can be employed in manufacturing water-based inks. Particularly, the content of VOCs can be tailored for producing printing inks. This created a lot of interest among researchers for manufacturing novel WPUs. Addition of organic fluorides or natural elements may also increase the effectiveness of WPUs. Reduced mechanical property or poorly hydrophobic is the glitches concerned with the hydrophilic portions of WPUs, specifically by the ionic groups. This could be eradicated by hybridization of WPUs with composite emulsions, latex blending, latex interpenetrating network, copolymerization with emulsion and hybridizing with inorganic clay. From the above discussions, it could be concluded that, development and use of bio-based WPUs with fillers may contribute much for sustainable future and also paves way for the development of novel materials with enhanced performance. Current research progress on the processing and synthesis of WPUs is expected to reach newer heights for infusing novelty in it so that it can be used in various applications like water-based inks.

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