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REVIEW PAPER

Recent trends in environmentally friendly water-borne polyurethane coatings: A review

Aqdas Noreen, Khalid Mahmood Zia†, Mohammad Zuber, Shazia Tabasum, and Muhammad Jawwad Saif

Institute of Chemistry, Government College University, Faisalabad 38030, Pakistan

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Abstract–Environmentally friendly waterborne polyurethane (WPU) coatings are used extensively due to their low VOCs emission than solvent based PU coatings. Additionally, WPU coatings have low temperature flexibility, pH stability, water resistance, superior solvent resistance, outstanding weathering resistance and desirable chemical and mechanical properties. This review provides an overview on the recent developments of WPU coatings and their value added applications in the coatings and paint industry. UV-cured WPU coatings provide an important class of green and eco-friendly coatings with outstanding mechanical properties and rapid curing system. Hyper-branched polyurethanes (PUs) show interesting properties, such as high solubility, reactivity and good rheological behavior owing to multiple end groups, compact molecular structure and diminishing chain entanglement. Inherently, WPU coatings have reduced stiffness and mechanical strength that can be increased by the addition of nanoparticles, like Ag, Cu, TiO_2, SiO_2 and many more. Fire retardants, commonly phosphorous, are incorporated in the WPU structure to increase the flame retardancy of WPU coatings.

Keywords: WPU, Eco-friendly Coatings, UV-WPU, Hyperbranched, Flame Retardant

INTRODUCTION

A variety of polymeric systems are employed in coating many products of everyday life including airplanes, automobiles, oil tankers, container ships, industrial machines, household refrigerators etc. [1-3]. Organic coatings protect the materials against aggressive environments such as moisture, radiation, biological deterioration, mechanical and chemical destruction as well as providing color and gloss to the material [4,5]. However, most of the traditional solvent-borne organic coatings contain a large amount of volatile organic compounds (VOCs), which are detrimental to the atmosphere and human health [6]. Therefore, environmentally friendly coatings, such as waterborne coatings, high-solid content coatings, powder coatings and radiation curable coatings, have proven to be a proper substitute for the traditional solvent-based coatings [7-10]. Among them WPU coatings have been paid progressive attention in the coating industry due to their low temperature flexibility, zero or less VOCs, water resistance, pH stability, superior solvent resistance, excellent weathering resistance and desirable chemical and mechanical properties [11-19]. UV-cured WPU coating technology is used extensively due to their environment friendly behavior, high curing speed and low energy consumption [20]. The mechanical strength and stiffness of WPU films is classically inferior to most solvent borne PU films; hence, incorporation of nanoparticles in WPU enhances the stiffness and mechanical strength [21-28]. Hyperbranched WPUs have been widely used to formulate high performance coatings, while fire resistance WPUs are employed in flame retardant coatings.

1. History and Key Development of Waterborne Polyurethane

Polyurethanes can be found in liquid coatings and paints, tough elastomers, rigid insulation, soft flexible foam, elastic fiber or as an integral skin. The development of PU adhesive can be traced back more than 50 years to the pioneering efforts of one man's genius. Otto Bayer's (1902-1982) and his co-workers' work dates back to the beginning of World War II, when it was first developed as a replacement for rubber. Bayer is recognized as the "father" of the PUs industry for his invention of the basic diisocyanate polyaddition process. During World War II, PU coatings were used for the impregnation of paper and the manufacture of mustard gas resistant garments, high-gloss airplane finishes and chemical and corrosion-resistant coatings to protect metal, wood and masonry [29]. At the same time, the first metal-to-plastic urethane adhesives were developed. The WPU was also being developed, with PU latex claimed to be useful as an adhesive disclosed in 1961 by DuPont [30]. With the development of a low-cost polyether polyol, flexible foams opened the door to the upholstery and automotive applications we know today. Today, PUs can be found in virtually everything we touch—desks, chairs, cars, clothes, footwear, appliances, beds as well as the insulation in our walls and roof and moldings on our homes [31-36].

WATER-BORNE POLYURETHANE (WPU) COATINGS

Due to strict regulations all over the world about volatile organic compounds (VOCs), which affect health and atmosphere, environmentally friendly coatings are becoming popular and acceptable to meet the growing consumer demands but maintaining excellent performance and cost. Among these low VOCs technologies the non-solvent based system is the best choice. Particularly,

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†To whom correspondence should be addressed.
E-mail: ziakmpkpolym@yahoo.com

Table 1. Composition and characterization techniques of different WPU coatings and their potential applications [49-100]

Sr. No.	Composition	Characterization techniques	Potential applications	Ref.
1	WPU	ESEM, FTIR, Taber test and falling abrasive test	Wood coatings for interior applications	[49]
2	1K WPU	FTIR, AFM, SEM	PVC, PU Synthetic leather surface coatings	[50]
3	WPU elastomer	ATR-FTIR, UV-vis, optical microscope, FTIR	High reflectivity coating in lighting panels and reflective roof coatings	[51]
4	WPU dispersion with different polyols	TEM, DSC, TGA	High chemical resistance coatings for stainless steel	[52]
5	UVWPPU-acrylate	FTIR, UV-visible spectroscopy	Weathering resistance coatings for automotive finishes	[53]
6	UVWPU-acrylate	FTIR, DSC, TGA	Solvent resistance coatings	[54]
7	UVWPU modified by melamine	FTIR, TGA, DSC	Heat-resistance coatings for flooring and furniture	[55]
8	WPU-acrylic copolymers	FTIR, TGA, TEM, DLS, SEM	Humidity sensitive interior wall coatings	[56]
9	WPU dispersions/ (3-aminopropyl)triethoxysilane	FTIR, ATR, DMTA, TGA, FESEM, TEM, XRD	High transparence coatings	[57]
10	WPU functionalized with (3-aminopropyl)triethoxysilane	DMTA, ^{13}C NMR, DSC, Lap Shear Test, Peel Test, SAFT Test	Self-curable coatings with good adhesion	[58]
11	2K-WPU	FEG-SEM, magnetic inductive gauge, micro-scale scratch tester	Hard coatings on glass and polycarbonate	[59]
12	Polycarbonate hexanediol/ WPU dispersions	TEM, TGA, DSC, ATR-IR	Coating material	[60]
13	WPU-Silicone	FTIR, TEM, AFM, SEM, DSC, TGA, UV-vis spectrophotometer, mechanical tests	High performance coating for aluminum alloy	[61]
14	Nano-silver/2K WPU	SEM, FTIR, DSC, TGA	Antimicrobial coatings	[62]
15	WPU-urea/Ni-Zn ferrite composite	FTIR-ATR, SEM, ^{1}HNMR, EDS	Microwave absorbing coatings in aircrafts and ships	[63]
16	Graphene-reinforced WPU nanocomposite	FTIR, ^{29}Si NMR, GPC, TGA, DMA, ^{1}H-NMR, AFM, TEM, XPS	High performance coatings	[64]
17	Radiation curable PU dispersions	AFM, TMA, DSC	High performance pigmented coatings for wood furniture	[65]
18	Polycarbonates of 1,6-hexanediol/ WPU dispersions	Viscometry, TEM, ATR-IR, DSC, TGA, FTIR	Flexible coatings for textiles	[66]
19	WPU using an amphiphilic diol	FTIR, TGA, SEM	Breathable waterproof textile coatings	[67]
20	2K WPU	EIMS, FTIR, GPC	Two component topcoat	[68]
21	Cationomeric WPU Dispersions	FTIR, UV-Vis spectroscopy, DSC, TGA, SEM, DMTA, Salt spray test	Anti corrosive coatings	[69]
22	WPU/acrylic hybrid	DLS	Coating material	[70]
23	WPU/ZnO hybrid dispersions	TGA, DMTA, SEM, gel content and contact angle measurements, FTIR	Corrosion resistance coatings	[71]
24	2K WPU/water soluble acrylic resin and HDI Biuret	FTIR, TEM	Transparent and high gloss films with high crosslinking density	[72]
25	UVWPU/silica nanocomposites	SEM, DMTA, XRD, AFM	High performance coatings	[73]

Table 1. Continued

Sr. No.	Composition	Characterization techniques	Potential applications	Ref.
26	Polyester polyols for WPU & hybrid dispersions	TGA, DSC, SEM, FTIR	Hybrid coatings	[74]
27	Castor oil based 2K-WPU	GPC, FTIR, DMA, TGA	Wood coatings	[75]
28	WPU/phosphorous	FTIR, ^{1}HNMR, TEM	Flame retardant coatings	[76]
29	WPU/phosphorous	^{31}PNMR, IR, DSC	Flame retardant coatings	[77]
30	WPU/Na$^+$-MMT clay nanocomposite	^{1}HNMR; FTIR, XRD, TGA, DSC, UV-Vis transmission spectroscopy, TEM, GPA	Environmentally friendly coatings	[78]
31	WPU-colloidal silica hybrids	FTIR, ^{13}CNMR, SEM, TGA, DSC, XRD, UV-Vis spectroscopy	Tunable transparent films	[79]
32	Crosslinking of 2K WPU	FTIR	Film formation	[80]
33	Polycarbonate diols based WPU	FTIR, TGA, DSC, XRD, DMA, contact angle	Coatings with excellent hydrolysis resistance and weatherability	[81]
34	WPU/submicron-sized diamond particles	EIS, FTIR, SEM	Thermally conductive coating	[82]
35	Polyethylene glycol-containing PU hydrogel	FTIR, EIS, SEM	Neural electrode applications	[83]
36	Jatropha oil based WPU dispersion	ATR-FTIR, contact-angle, TGA	Binder for wood and decorative coatings	[84]
37	WPU/Glycolyzed PET waste/ castor oil-based polyol/ hexamethoxymethyl melamine	FTIR, TGA, ^{1}HNMR, GPC, DTA	Thermally stable coatings	[85]
38	Rape seed fatty acid methylesters/WPU	Zetasizer, gloss measurements	Wood coatings	[86]
39	Linseed-oil-based UVWPU	FTIR, ATR, GPC, DMA	High-performance coatings for furniture finishing and wood coating	[87]
40	Anionic terpene-based polyol PU dispersion	FTIR, ^{13}CNMR, AFM, TGA	Smooth and transparent film	[88]
41	Soybean oil based WPU-poly(styrene-butyl acrylate) core-shell hybrid	TGA, DSC, TEM,	Decorative and protective coatings	[89]
42	WPU dispersion from cardanol	FTIR, DSC, EIS	Self-crosslinking coatings having better performane	[90]
43	Hyperbranched WPU-urea/silica hybrid	FTIR, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, TGA, SEM, AFM, DMTA	High performance coatings	[91]
44	Hyperbranched UV cured PU acrylate/ ZnO hybrid	TGA, DMTA, XRD and SEM, ^{1}HNMR, ^{13}CNMR and FTIR	High performance hybrid coatings	[92]
45	WPU acrylate dispersions/hyperbranched aliphatic polyester	FTIR	Improved UV-curable coating material	[93]
46	WPU acrylate dispersions/hyperbranched aliphatic polyester	DMTA	Coating materials with improved properties	[94]
47	WPU/hyperbranched acrylate dispersions	FTIR	UV curable coatings	[95]
48	Hyperbranched PU-urea coatings	^{1}H NMR, FTIR, DMTA, TGA	Thermally stable coatings	[96]
49	WB hyperbranched aliphatic polyester	FTIR	Waterborne clear coats	[97]
50	2K-WPU	-	High performance coatings	[98]
51	UVWPU-acrylate nanocomposite containing alumina silica nanoparticles	TEM, ATR-FTIR	Wood coatings	[99]
52	WPU-dispersions	AFM	Water-borne coatings	[100]

water-based systems have become a popular non-solvent based option because water is a cheap, non-toxic and environmentally benign solvent, which may increase the rates and effectiveness of a wide variety of organic reactions [37-39]. Therefore, WPU material has gained an increasing attention in last few decades owing to having several advantages like good abrasion resistance, flexibility hardness, impact resistance, gloss, chemical resistance, reduced flammability, durability, high adhesive strength, easy cleaning, low viscosity and weather-ability in addition to zero or low emission of VOCs [40-48]. The viscosity of the WPU dispersion does not depend on molecular weight of the polymer; therefore, high solid content WPU dispersions can be prepared having a high molecular weight films with excellent quality merely by physical drying. In this short review, environmentally friendly WPU coatings are highlighted in addition to an outline of potential applications that have been investigated up till now, which are summarized in Table 1 [49-100].

WPU dispersions are considered as binary colloidal system in which PU particles are dispersed in aqueous media as a continuous phase [101]. Inherently, polyurethanes are not dispersible in water due to presence of hydrophobic isocyanates (also react with water), while WPUs are dispersible into aqueous media due to presence of ionic groups (i.e., PU ionomers) in linear thermoplastic PU backbone (Fig. 1(a)) [102,103]. PU ionomer is defined as a copolymer containing a PU backbone with the repeat units carrying pendant acid groups, which are completely or partially neutralized to form salts. These ionic groups act as an internal emulsifier [104, 105] may be (i) cationic-like quaternary ammonium groups, (ii) anionic-like carboxylated or sulfonated groups (iii) or nonionic, e.g., polyols with ethylene oxide end groups [106]. Schematic diagrams of micelles formed by (a) cationic and (b) anionic PU iono-

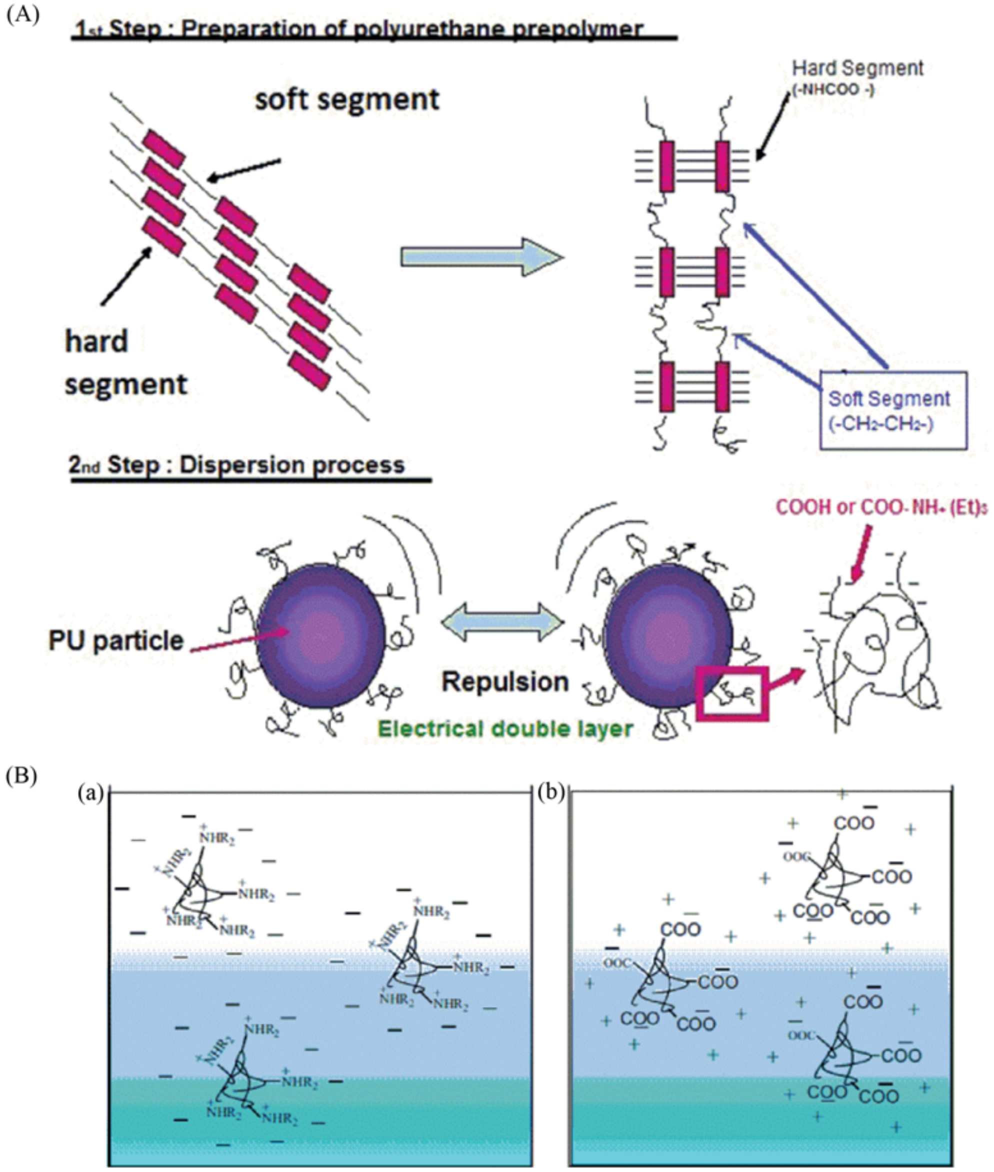

Fig. 1. (A) Schematic representation of WPU dispersion; (B) Schematic diagram of micelles formed by (a) cationic and (b) anionic PU ionomers in water [107].

mers in water are shown in Fig. 1(b) [107]. Types of ionomers, choice of isocyanate and types of polyols are major factors which influence the performance of the resulting WPU dispersions [108-112].

1. Synthetic Processes for WPU Dispersion

Several synthetic routes are developed to obtain WPU dispersion, including (i) acetone process, (ii) melt dispersion process, (iii) prepolymer mixing process, and (iv) ketamine process [113-115]. However, the first step is common to all of these processes, that is, the reaction of appropriate diols or polyols, generally macrodilos like polyethers or polyesters, with a molar excess of diisocynates or polyisocynates to yield a low molecular weight prepolymer. In the reaction mixture a diol with an ionic group or a nonionic group is usually an internal emulsifier which becomes part of the main chain of the prepolymer. Dispersion of the prepolymer in aqueous media and the molecular weight buildup is the key step in which the various synthetic pathways differ [116-119]. The most well-known process for synthesizing WPU dispersion is the prepolymer blending process and acetone process (Fig. 2(a) & (b)). The WPU dispersions properties are chiefly determined by hard and soft segment interactions and by ionic groups interactions. Recent studies [120-129] established that the segmented structure, ionic group content, molecular weight of the polyol, the kind of chain extender and the hard and soft segments ratio decides the WPU dispersions properties. A variety of polyols, depending on the required properties, are used in WPU dispersion synthesis to change its structure and consequently design their properties. The most common macrodiols used in PU synthesis are polyester, polyether, and polycarbonate and polycaprolactone diols.

2. One-component WPU Coatings

One-component WPU dispersions have now acquired a considerable market value. These dispersions, typically based on the aliphatic diisocyanates, are characterized by their high level of elasticity and toughness. One-component system WPU dispersions allow the construction of storage stable thermoplastic coatings. Highly crosslinked PU films are formed, under the influence of temperature, radiation or atmospheric oxygen. Hydrogen bonding in PU plays an essential role in determining the macroscopic properties of thermoplastic PU films. The hydrogen bonding produces

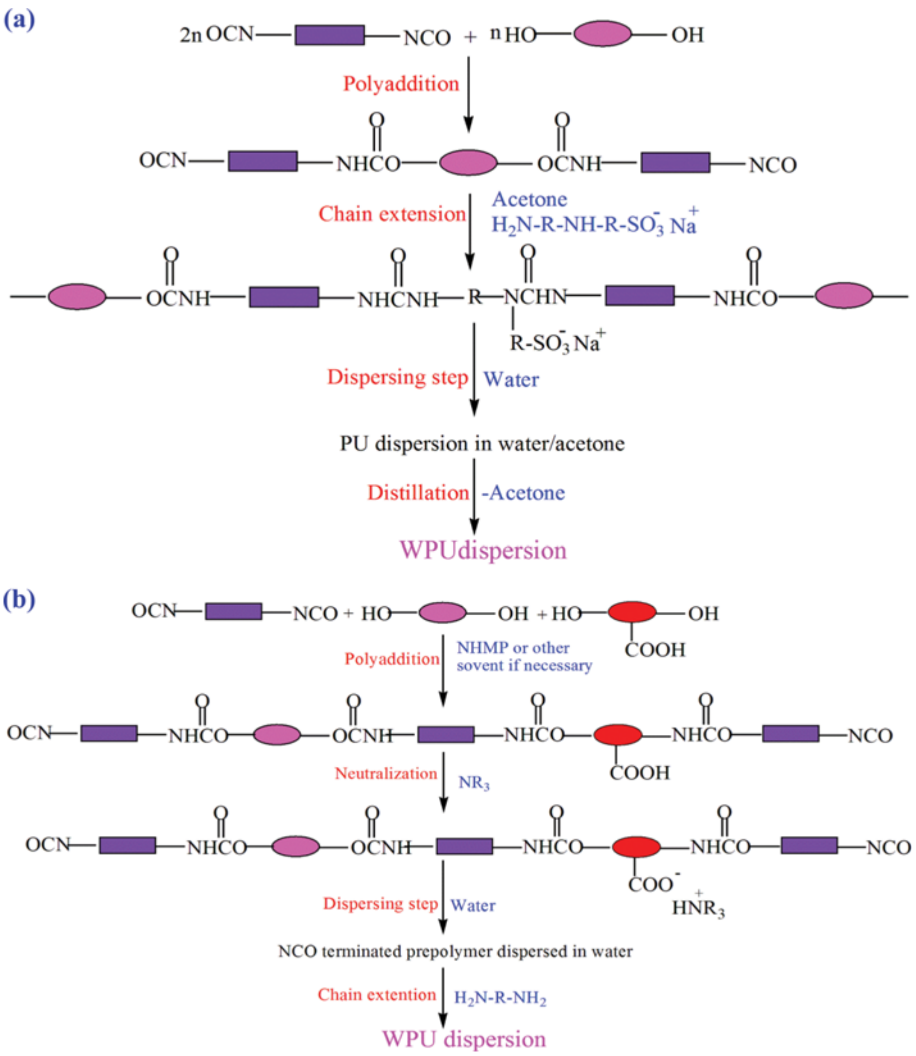

Fig. 2. (a) Schematic synthesis of WPU dispersion by acetone process; (b) schematic synthesis of WPU dispersion by pre-polymer mixing process [129].

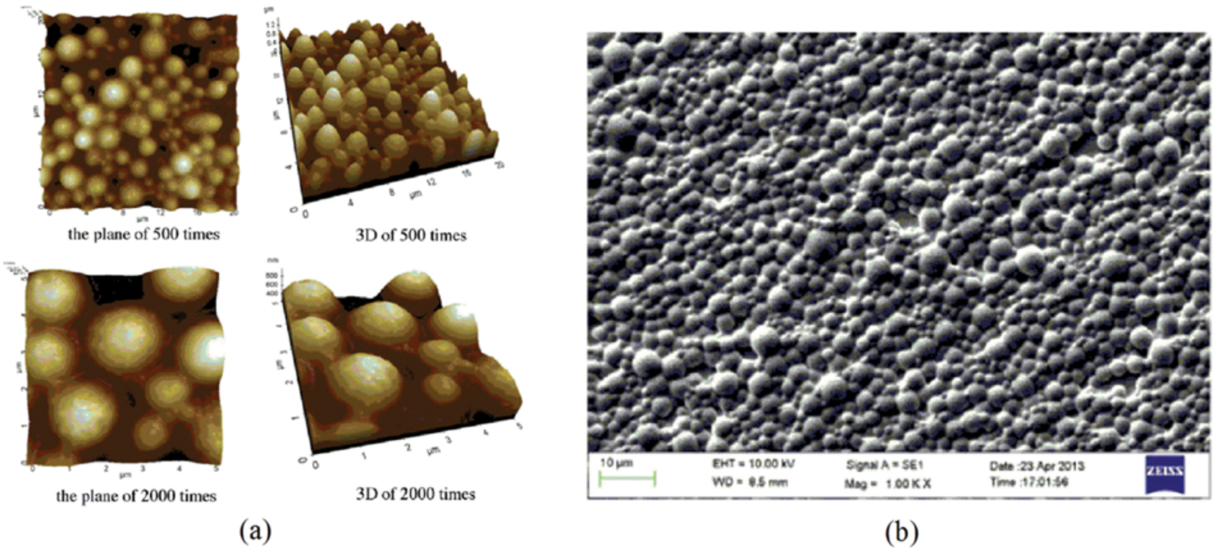

Fig. 3. The AFM (a) and SEM (b) images of low gloss WPU films [139].

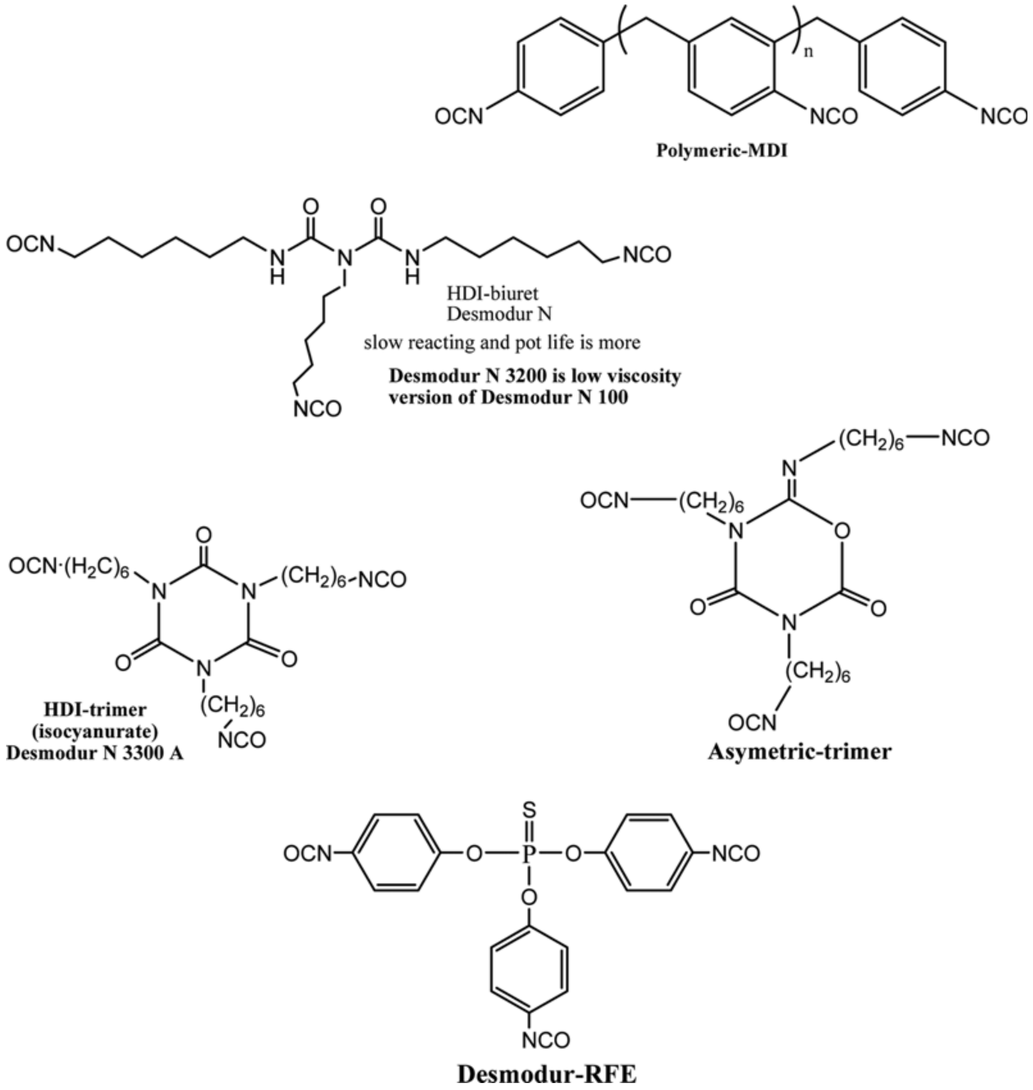

Fig. 4. Industrially important low viscous polyisocyanate cross-linker [146].

physical crosslinks, thereby, strengthening the PU matrix and increasing its stiffness and strength [130-132].

2-1. One-component WPU Coating for Leather Material: A Novel Coating Material

Coatings, having low degree of gloss for leather materials, are often prepared by addition of inorganic matting agent with definite particle size distribution (such as SiO_2 particles) [133,134]. But there is a progressive loss of matting agent with time, which leads to increase in the degree of gloss of leather surfaces, because of their incompatibility with the other organic constitutions of coatings. Therefore, matting agents are not firmly attached and can be rubbed out from the coating easily [135-139]. Currently, one-component WPU matting dispersions without inorganic matting agents have been paid more and more attention in the coating industry. One-component WPU coatings with low gloss are used to alter the gloss of leather. Atomic force microscopy (Fig. 3(a)) and scanning electron microscopy (Fig. 3(b)) images of the WPU film showed that the micro surface was coarse with a number of spherical granules that made the incident light to bend strongly, which is important in producing low gloss leather surface.

3. Two-component WPU Coatings

Two-component waterborne PU (2K-WPU) coatings, usually used in wood and furniture industry [140], are produced with the aim to increase working temperature range and final performance by the introduction of chemical crosslinker in the PU structure. One component of 2K-WPU is usually synthesized by polyols, diisocyanates and hydrophilic group by using the acetone process or a prepolymer mixing process. Hardener or crosslinker, another component of 2K-WPU, is commonly divided into aliphatic and aromatic isocyanates [141-145]. Some of the industrially significant low viscous polyisocyanate crosslinkers for the production of thermoset high solid PU coatings are shown in Fig. 4 [146].

UV-CURABLE WPU COATINGS

During the last decade, UV-cured waterborne coatings technology has been increasingly successful in the industrial coating market due to less environmental impact along with novel performance areas proper to protecting the material in aggressive conditions. The UV curable coatings are cured in a short time under UV irradiation that provides the coatings with exceptional performance [147-152]. The UV-curable WPU has the advantages of both UV technology and waterborne coatings [153-155]. Attractively, UV-curable WPU (UV-WPU) coatings have been most generally studied because of their non-toxicity, versatility, chemical resistance and excellent mechanical properties [156-160]. The UV-WPU coatings formulations typically contain three chief components: oligomer, photoinitiator and reactive diluent [161]. The oligomer is functionalized with reactive ending groups that contribute to the film production process and the visco-elastic properties of the final cured film are governed by the structure of the oligomer. The reactive diluents reduce the viscosity of the resin and copolymerize with oligomer to give the crosslinked film [162]. There are three main kinds of oligomers extensively used in free radical UV-cured coatings: epoxy acrylate, polyester acrylate and urethane acrylate oligomer [163-168]. Usually, acrylic or methacrylic monomers are used as reactive diluents (Fig. 5) for free radical based UV-curing systems [169].

Despite the several advantages, UV-WPU coatings have less resistance to solvents and thermal stability than those of traditional solvent-based PU coatings, and their tensile strength is reduced severely at an external temperature higher than 80 °C [170,171]. Melamine, a nitrogen-rich chemical, can be broadly used as additive to generate melamine resin, which is a synthetic heat-resistant polymer [172]. The TGA curves of the UV-WPU films, Fig. 6(left), showed that the melamine modified UV-WPU film has higher initial thermal decomposition temperature than film without melamine. The Tg of the unmodified film is lower than the modified film due to increase in rigidity of content of the PU chain as illustrated in the DSC curves (Fig. 6-right).

HYPERBRANCHED WPU COATINGS

Hyperbranched polymers are a relatively new class of macromolecules with three-dimensional molecular architectures, which have gained significant attention to formulate high performance coatings [173-177]. Hyperbranched polymers are quite altered from their customary linear counterparts due to their unusual molecular structures such as multiple end groups, compact molecular nature and diminishing chain entanglement [178,179]. Extremely branched

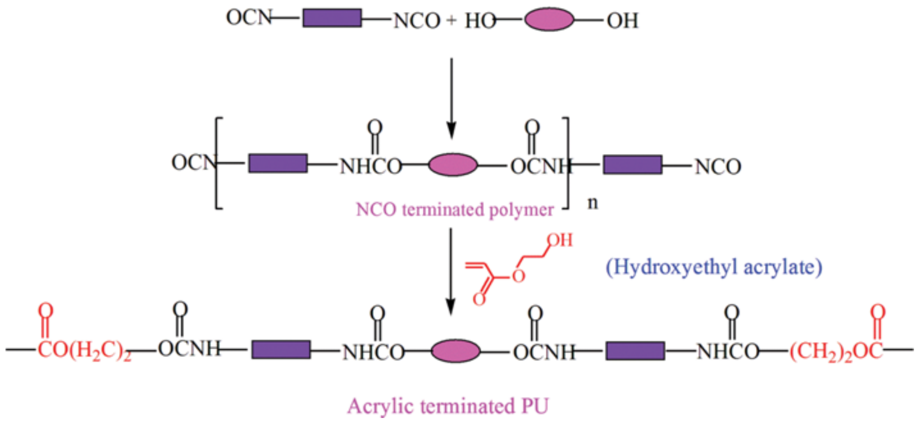

Fig. 5. Preparation of acrylic-terminated PU pre-polymer for UV cure coatings [169].

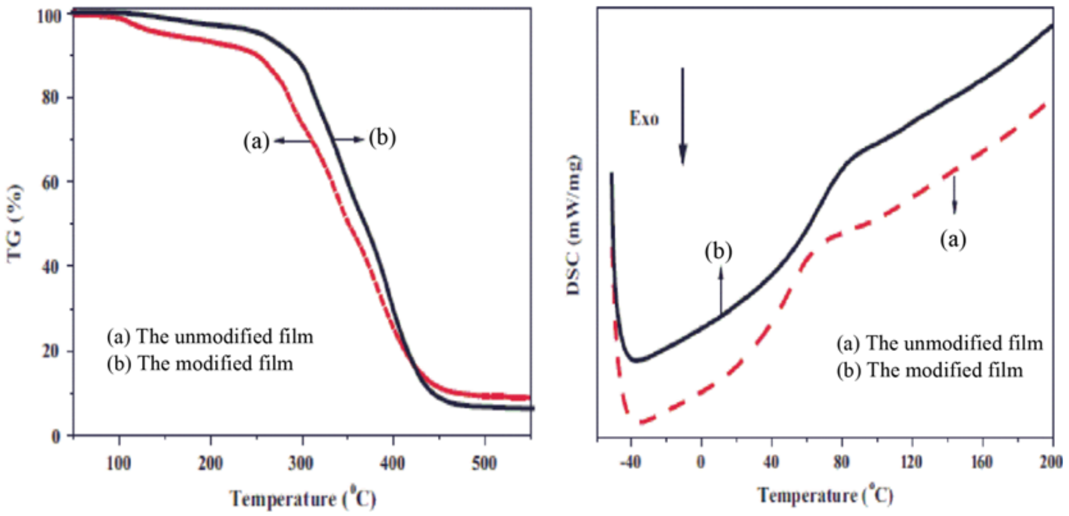

Fig. 6. The TGA curves of the UV-WPU films at the heating rate of 10 °C/min (left) and The DSC curves of the UV-WPU films at the heating rate of 20 °C/min (right) [172].

polymers show the most interesting properties, such as high solubility and reactivity and good rheological behavior; thus they have great potential applications. Various types of hyperbranched polymers, like polycarbonate [180], polyphenylene [181], polyesters [182], poly(ether ketone) [183,184], polyamides [185,186], poly(4-chloromethylstyrene) [187] polyurethanes [188] etc., are commonly developed by step-growth polycondensation route. Recently, hyperbranched polyurethane (HBPU) coatings have been employed ex-

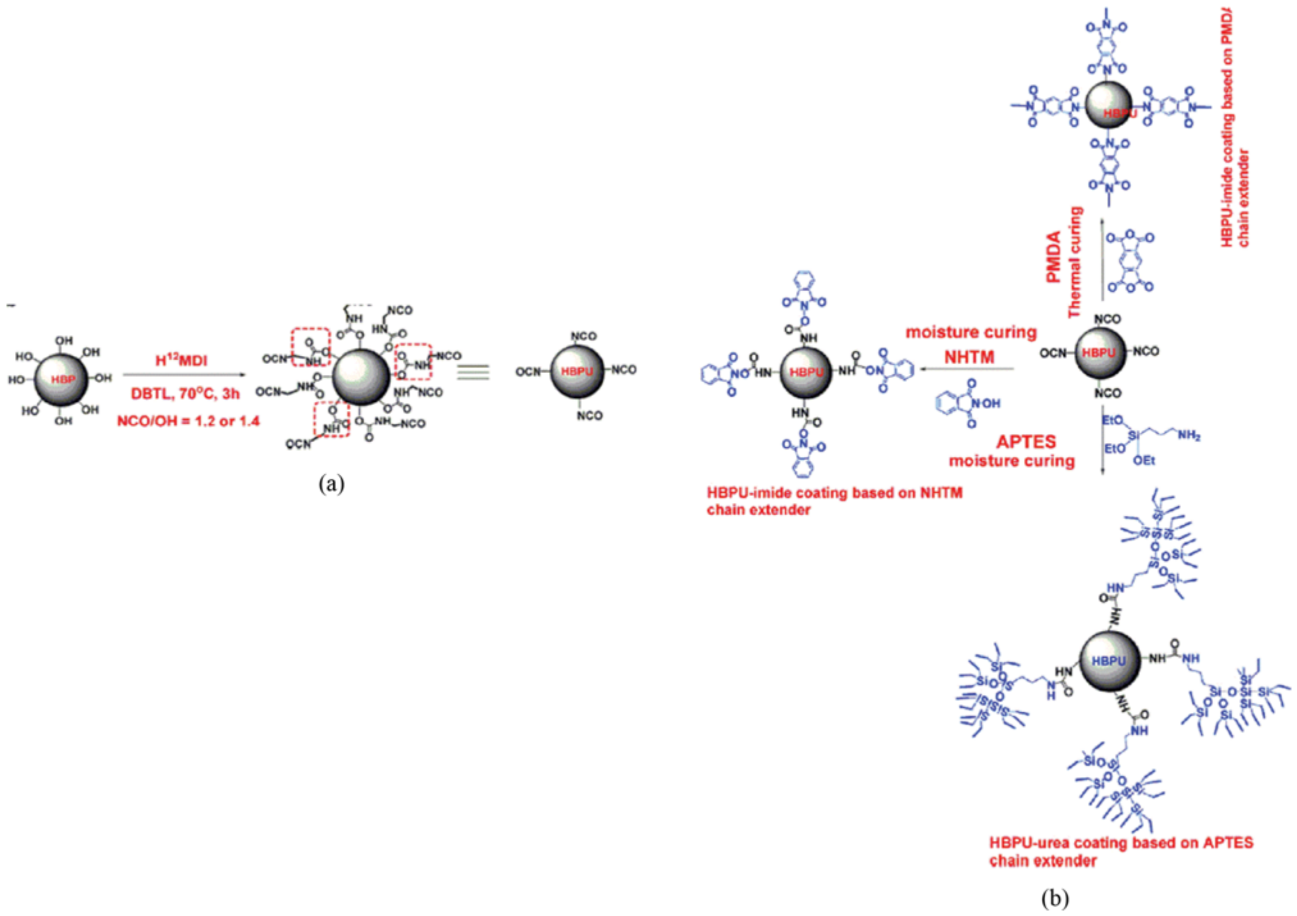

Fig. 7. The steps involved along with the reaction conditions used for the synthesis of (a) HBPU prepolymers and (b) the reaction scheme for the synthesis of different chain extender based HBPU coatings [192].

tensively. Thermal and physical properties of PUs are changed by varying the compositions and soft and hard segment ratios [189-191]. Synthesis of HBPU-urea or HBPU-imide coatings with the detailed reaction condition and chain extenders used is shown in Fig. 7 [192].

NANOCOMPOSITE WPU COATINGS

Waterborne polyurethane (WPU) coatings display an excellent toughness and elasticity, while the stiffness and mechanical strength of these films is obviously lower compared to most solvent based PU coatings. Addition of nano-sized inorganic fillers into WPU dispersions to form nano-structured coatings has become a successful strategy to augment the properties of WPU. Conventionally, fillers are added to coatings for improving pigmentation, hiding power, abrasion resistance, chalking resistance and offering anti-sagging and other flow properties, but they reduce coating clarity and gloss [193,194]. Consequently, now fillers are investigated more on nanoscale. The particle size of fillers significantly influences the characteristics of coatings like mechanical properties, rheology, corrosion protection, barrier properties, etc., particularly when fillers have an average particle diameter below 500 nm [195]. The WPU nano-composites containing nano-scale fillers, such as silica, ZnO, TiO_2, Fe_2O_3, SiO_2, clay, cellulose nano-crystals, have distinctive properties that are not studied with traditional microscale fillers. Additionally, thermal stability can be enhanced by incorporation of polyhedral oligomeric silsesquioxane (POSS) structures, the incorporation of Si-O-Si cross-linker, use of functionalized fullerenes in PUs and incorporation of carbon nanotubes (CNT) into PU [196-201].

1. Nanoparticle Containing Antimicrobial Coatings

Nanotechnology and biology both have extended the utilization of nano-particles (NP) as potential antimicrobial agents. Basically, metals used for nanoparticles, e.g., Si, Cu, Ti, Zn and other NP, in coatings are extremely toxic against micro-organisms, which diminishes their active growth. Broad spectrum antimicrobial activity is commonly exhibited by Ag NP, which is a renowned biocide [202-206]. In antibacterial hygienic coatings, nano-metal oxides like TiO_2, ZnO, Al_2O_3, SiO_2 are used, and these nano-metal oxides also find applications in marine coatings, which hinders the attachment of detrimental micro-organisms to the surface and making biofilms. Metal NP displays shape- and size-dependent interactions with a microbial surface. The antimicrobial activity increases by decreasing the size of metal NP due to their larger surface area per unit volume. The small size aids the NP to dislodge the cell membrane, simply penetrate into the bacterial cell and obstruct the normal cell functioning of the cell [207-210].

FLAME-RETARDANT WPU COATINGS

There is a development of flame retardant PU coatings by increasing the public awareness about their potential as fire hazards. Fire resistance of PU can be improved by incorporating either reactive or nonreactive additive type fire retardants. The additive type fire retardants (halogenated paraffins, chlorofluorocarbons (CFCs), inorganic oxides and hydroxides, inorganic carbonates, boron containing inorganic compounds, inorganic phosphorus containing compounds, triphenylphosphine oxide, red phosphorus, expandable graphite, melamine, etc.) are added into the PU by physical means, which may result in poor mechanical properties, low compatibility and leaching. Conversely, reactive type flame retardants are mainly organic compounds having a flame retarding moiety as well as active functional groups that can form covalent bonds with PUs [211]. Flame retardants are classified as organic materials such as halogenated and phosphorous compounds or inorganic material like metal hydroxide, metal oxide and metal borates. Although inorganic flame retardants are cost effective and have non-toxic byproducts, their efficacy is comparatively pitiable. Halogenated compounds are effective flame retardants, but an elevated temperture is required to begin the radical trapping activity and these compounds also possess hazards due to emission of toxic gases like hydrogen halides. Therefore, organic phosphorous-containing compounds are consideared to be non-toxic fire retardant additives by lowering the thermal decompostion and formation of char at elevated temperature. In addition, the flame-retardant ability of phosphorus-containing WPU is higher than that of halogenated compounds. Phosphorous acid is produced at high temperature, which helps in char formation and protects the polymer from flame and heat. According to another proposed mechanism, there is a reaction of phosphoric acid with carbodiimide which is formed during the thermolysis of PU [212-215].

THE ADVANTAGES OF THE RECENT STUDIES

The advantage of PU/polysiloxane hybrid coating/aluminum interface relies on the interaction between the inorganic component and a wide range of organic polymers that favor applicability over different metallic substrates or coatings [3]. Studies revealed that if an oil-based core molecule is well developed, it will surely be of advantageously reduced viscosity, which will facilitate the complete elimination of the use of solvents and reactive diluents in HYP coatings. Water-based coatings have been developed from vegetable oil generally prepared in water along with some co-solvent [7]. Furthermore, it is advantageous to use jatropha oil because it is non-edible and thus its usage will reduce the consumption of edible oils for chemical purposes [85]. Glycolyzed PET waste and castor oil-based polyols for WPU adhesives containing hexamethoxy methyl melamine [86] have also been presented. Although nanoparticles have been widely employed to prepare polymer composite materials with advanced properties due to the synergistic advantage of nano-scale dimensions, they tend to form agglomerates after incorporation into the polymeric matrix, leading to segregation of the inorganic particles or limited improvement of the properties of the composite materials [45]. Ultraviolet, water, and thermal aging studies of WPU elastomers-based high reflectivity coating [52] and the effects of the molecular weight and structure of polycarbonate diols on the properties of WPU [82] have been comprehensively discussed.

CONCLUSION

A solvent borne PU coating releases volatile organic compounds (VOCs) that affect health and atmosphere, hence waterborne polyurethane (WPU) coatings are now prepared. The WPU coatings have many advantages, such as low VOCs, flexibility, good mechanical and chemical properties. The WPU are dispersible in water due to presence of hydrophilic ionic or non ionic groups in their structure. Pre-polymer mixing process and acetone process are the most well-known methods for synthesizing WPU dispersions. Introduction of cross-linker in 2K WPU increased the thermal stability and final performances of coatings. The WPU coating cured by UV radiations is a promising technology to prepare environmentally safe, high curing rate and low energy consuming coatings. The UV-WPU film modified by melamine film has higher initial thermal decomposition temperature and Tg than film without melamine. The hyper-branched PUs have multiple end groups, compact molecular structure and diminishing chain entanglement; therefore, they are quite different from their customary linear counterparts in performance. Nano-particles like Ag, Cu, TiO_2, Al_2O_3, SiO_2, clay, CNT, POSS, are added to WPU to increase the stiffness and mechanical strength, which is lower in conventional WPU. Ag-containing WPU shows broad spectrum antimicrobial activity that increases by decreasing the size of metal NP due to their larger surface area per unit volume. Fire retardants, mostly phosphorous, are used to increase the flame retardancy of WPU coatings.

REFERENCES

1. C. Bangert, *Eur. Coat. J.*, **12**, 13 (2008).
2. M. Barletta, S. Pezzola, S. Vesco, V. Tagliaferri and F. Trovalusci, *Prog. Org. Coat.*, **77**, 636 (2014).
3. M.Visueta, T. Gaob, M. Soucekb and H. Castanedaa, *Prog. Org. Coat.*, **83**, 36 (2015).
4. M. Akbarian, M. E. Olya, M. Mahdavian and M. Ataeefard, *Prog. Org. Coat.*, **77**, 1233 (2014).
5. J. Zhang, W. Tua and Z. Daib, *Prog. Org. Coat.*, **75**, 579 (2012).
6. C. W. Chang and K. T. Lu, *Prog. Org. Coat.*, **75**, 435 (2012).
7. E. Sharmin, F. Zafar, D. Akram, M. Alam and S. Ahmad, *Ind. Crops Prod.*, **76**, 215 (2015).
8. M. Alam, D. Akram, E. Sharmin, F. Zafar and S. Ahmad, *Arabian J. Chem.*, **7**, 469 (2014).
9. K. D. Weiss, *Prog. Polym. Sci.*, **22**, 203 (1997).
10. P. J. A. Geurink, T. Scherer, R. Buter, A. Steenbergen and H. Henderiks, *Prog. Org. Coat.*, **55**, 119 (2006).
11. D. K. Chattopadhyay and K. V. S. N. Raju, *Prog. Polym. Sci.*, **32**, 352 (2007).
12. P. Russo, D. Acierno, G. Marletta and G. L. Destri, *Eur. Polym. J.*, **49**, 3155 (2013).
13. D. J. Mills, S. S. Jamali and K. Paprocka, *Surf. Coat. Technol.*, **209**, 137 (2012).
14. M. Rashvand, Z. Ranjnbar and S. Rastegar, *Prog. Org. Coat.*, **71**, 362 (2011).
15. A. Mobin, A. U. Malik, F. A. Muaili and M. A. Hajiri, *J. Coat. Technol. Res.*, **21**, 1292 (2012).
16. P. A. Sorensen, S. Kiil, K. D. Johansen and C. E. Weinell, *J. Coat. Technol. Res.*, **6**, 135 (2009).
17. Y. G. Garcıa, S. Gonzalez and R. M. Souto, *Corros. Sci.*, **49**, 3514 (2007).
18. H. Du, Y. Zhao, Q. Li, J. Wang, M. Kang, X. Wang and H. Xiang, *J. Appl. Polym. Sci.*, **110**, 1396 (2008).
19. B. S. Kim and B. K. Kim, *J. Appl. Polym. Sci.*, **97**, 1961 (2005).
20. V. D. Athawale and M. A. Kulkarni, *J. Coat. Technol. Res.*, **7**, 189 (2010).
21. C. H. Yang and W. T. Liao, *J. Colloid Interface Sci.*, **302**, 123 (2006).
22. B. S. Kim, S. H. Park and B. K. Kim, *Colloid Poly. Sci.*, **284**, 1067 (2006).
23. H. Yu and D. N. Wang, *J. Appl. Poly. Sci.*, **94**, 1347 (2004).
24. H. T. Jeon, M. K. Jang, B. K. Kim and K. H. Kim, *Colloid Surf.*, **302**, 559 (2007).
25. J. M. Yeh, C. T. Yao, C. F. Hsieh, H. C. Yang and C. P. Wu, *Euro. Poly. J.*, **44**, 2777 (2008).
26. H. T. Lee and L. H. Lin, *Macromol.*, **39**, 6133 (2006).
27. M. M. Rahman, H. D. Kim and W. K. Lee, *J. Appl. Poly. Sci.*, **110**, 3697 (2008).
28. X. Deng, F. Liu, Y. Luo, Y. Chen and D. Jia, *Prog. Org. Coat.*, **60**, 11 (2007).
29. H. T. Lee, J. J. Wang and H. J. Liu, *J. Polym. Sci. Part A: Polym. Chem.*, **44**, 5801 (2006).
30. E. I. du Pont, British Patent 987, 600; C.A. **63**, 3148 (1965).
31. S. Turri and M. Levi, *Macromol.*, **38**, 5569 (2005).
32. J. Won and H. Kim, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 3973 (2005).
33. H. C. Kuan, C. C. M. Ma, W. P. Chang, S. M. Yuen, H. H. Wu and T. M. Lee, *Composites Sci. Technol.*, **65**, 1703 (2005).
34. P. R. Chang, F. Ai, Y. Chen, A. Dufresne and J. Huang, *J. Polym. Sci. Part A: Polym. Chem.*, **111**, 619 (2009).
35. G. Chen, M. Wei, J. Chen, J. Huang, A. Dufresne and P. R. Chang, *Polym.*, **49**, 1860 (2008).
36. X. D. Cao, H. Dong and C. M. Li, *Biomacromol.*, **8**, 899 (2007).
37. M. Barrere and K. Landfester, *Macromol.*, **36**, 5119 (2003).
38. C. Xia, L. J. Lee, T. Widya and C. Macosko, *Polym.*, **46**, 775 (2005).
39. S. H. Baek and B. K. Kim, *Colloids Surf., A*, **220**, 191 (2003).
40. Y. H. Guo, J. J. Guo, H. Miao, L. J. Teng and Z. Huang, *Prog. Org. Coat.*, **77**, 988 (2014).
41. G. J. Wang, C. S. Kang and R. G. Jin, *Prog. Org. Coat.*, **50**, 55 (2004).
42. C. Li and C. Su, *Prog. Org. Coat.*, **49**, 252 (2004).
43. C. Decker, R. Vataj and A. Louati, *Prog. Org. Coat.*, **50**, 263 (2004).
44. W. Fan, W. Du, Z. Li, N. Dan and J. Huang, *Prog. Org. Coat.*, **86**, 125 (2015).
45. M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, Boca Raton, FL (1999).
46. H. D. Hwang and H. J. Kim, *J. Colloid Interface Sci.*, **362**, 274 (2011).
47. H. D. Hwang, C. H. Park, J. I. Moon, H. J. Kim and T. Masubuchi, *Prog. Org. Coat.*, **72**, 663 (2011).
48. D. K. Lee, Z. D. Yang, H. B. Tsai, R. S. Tsai and P. H. Chen, *Polym. Eng. Sci.*, **49**, 2264 (2009).
49. E. Scrinzi, S. Rossi, F. Deflorian and C. Zanella, *Prog. Org. Coat.*, **72**, 81 (2011).
50. J. Li, W. Zheng, W. Zeng, D. Zhang and X. Peng, *Appl. Surf. Sci.*, **307**, 255 (2014).
51. S. Bhargava, M. Kubota, R. D. Lewis, S. G. Advani, A. K. Prasad and J. M. Deitzel, *Prog. Org. Coat.*, **79**, 75 (2015).
52. V. G. Paciosa, M. Colerab, Y. Iwatab, J. M. M. Martinez, *Prog. Org. Coat.*, **76**, 1726 (2013).
53. C. Deckera, F. Massona and R. Schwalm, *Polym. Degrad. Stab.*, **83**, 309 (2004).

54. H. Xu, F. Qiu, Y. Wang, W. Wu, D. Yang and Q. Guo, *Prog. Org. Coat.*, **73**, 47 (2012).
55. Z. H. Fanga, H. Y. Duana, Z. H. Zhanga, J. Wanga, D. Q. Li, Y. X. Huanga, J. J. Shanga and Z. Y. Liua, *Appl. Surf. Sci.*, **257**, 4765 (2011).
56. S. F. Zhang, R. M. Wang, Y. F. He, P. F. Song and Z. M. Wu, *Prog. Org. Coat.*, **76**, 729 (2013).
57. H. Zhou, H. Wang, X. Tian, K. Zheng and Q. Cheng, *Prog. Org. Coat.*, **77**, 1073 (2014).
58. H. Sardon, L. Irusta, A. Gonzalez and M. J. F. Berridi, *Prog. Org. Coat.*, **76**, 1230 (2013).
59. M. Barletta, S. Pezzola, S. Vesco, V. Tagliaferri and F. Trovalusci, *Prog. Org. Coat.*, **77**, 636 (2014).
60. V. G. Pacios, V. Costa, M. Colera and J. M. M. Martinez, *Prog. Org. Coat.*, **71**, 136 (2011).
61. S. S. Pathak, A. Sharma and A. S. Khanna, *Prog. Org. Coat.*, **65**, 206 (2009).
62. M. Akbarian, M. E. Olya, M. Ataeefard and M. Mahdavian, *Prog. Org. Coat.*, **75**, 344 (2012).
63. E. Acikalin, O. Atici, A. Sayıntia, K. Cobana and H. Erkalfa, *Prog. Org. Coat.*, **76**, 972 (2013).
64. X. Wang, W. Xing, L. Song, H. Yang, Y. Hu and G. H. Yeoh, *Surf. Coat. Technol.*, **206**, 4778 (2012).
65. M. Tielemans, P. Roose, C. Ngo, R. Lazzaroni and P. Leclere, *Prog. Org. Coat.*, **75**, 560 (2012).
66. V. G. Pacios, J. A. J. Reche, V. Costa, M. Colera and J. M. M. Martinez, *Prog. Org. Coat.*, **76**, 1484 (2013).
67. Q. B. Meng, S. I. Lee, C. Nah and Y. S. Lee, *Prog. Org. Coat.*, **66**, 382 (2009).
68. J. Huybrechts, P. Bruylants, A. Vaes and A. D. Marre, *Prog. Org. Coat.*, **38**, 67 (2000).
69. T. Gurunathan, C. R. K. Rao, R. Narayan and K. V. S. N. Raju, *Prog. Org. Coat.*, **76**, 639 (2013).
70. A. C. Aznara, O. R. Pardini and J. I. Amalvy, *Prog. Org. Coat.*, **55**, 43 (2006).
71. A. K. Mishra, R. S. Mishra, R. Narayan and K. V. S. N. Raju, *Prog. Org. Coat.*, **67**, 405 (2010).
72. Z. Xinhua, T. U. Weiping and H. U. Jianqing, *Chinese J. Chem. Eng.*, **14**, 99 (2006).
73. S. W. Zhang, R. Liu, J. Q. Jiang, C. Yang, M. Chen and X. Y. Liu, *Prog. Org. Coat.*, **70**, 1 (2011).
74. V. D. Athawale and M. A. Kulkarni, *Prog. Org. Coat.*, **67**, 44 (2010).
75. C. W. Chang and K. T. Lu, *Prog. Org. Coat.*, **75**, 435 (2012).
76. H. Chen, Y. Luo, C. Chai, J. Wang, J. Li and M. Xia, *J. Appl. Polym. Sci.*, **110**, 3107 (2008).
77. F. Celebi, L. Aras, G. Gunduz and I. M. Akhemdov, *J. Coat. Technol.*, **75**, 65 (2003).
78. J. M. Yeh, C. T. Yao, C. F. Hsieh, L. H. Lin, P. Li Chen, J. C. Wuc, H. C. Yang and C. P. Wua, *Eur. Polym. J.*, **44**, 3046 (2008).
79. C. H. Yang, F. J. Liu, Y. P. Liu and W. T. Liao, *J. Colloid Interface Sci.*, **302**, 123 (2006).
80. D. B. Otts and M. W. Urban, *Polym.*, **46**, 2699 (2005).
81. N. Liu, Y. Zhao, M. Kang, J. Wang, X. Wang, Y. Feng, N. Yin and Q. Li, *Prog. Org. Coat.*, **82**, 46 (2015).
82. Y. G. Garcia, J. M. C. Mol, T. Muselle, I. D. Graeve, G. V. Assche, G. Scheltjens, B. V. Mele and H. Terryn, *Electrochim. Acta*, **56**, 9619 (2011).
83. L. Rao, H. Zhou, T. Li, C. Li and Y. Y. Duan, *Acta Biomaterialia*, **8**, 2233 (2012).
84. S. Saalah, L. C. Abdullah, M. M. Aung, M. Z. Sallehd, D. R. A. Biaka, M. Basrie and E. R. Jusoh, *Indust. Crops Pro.*, **64**, 194 (2015).
85. S. M. Caki, I. S. Risti, M. M. Cincovi, D. T. Stojiljkovi, C. J. Janosd, C. J. Miroslav and J. V. Stamenkovi, *Prog. Org. Coat.*, **78**, 357 (2015).
86. C. Philipp and S. Eschig, *Prog. Org. Coat.*, **74**, 705 (2012).
87. C. W. Chang and K. T. Lu, *Prog. Org. Coat.*, **76**, 1024 (2013).
88. G. Wu, Z. Kong, J. Chena, S. Huoa and G. Liu, *Prog. Org. Coat.*, **77**, 315 (2014).
89. Y. Lu, Y. Xia and R. C. Larock, *Prog. Org. Coat.*, **71**, 336 (2011).
90. C. J. Patel and V. Mannari, *Prog. Org. Coat.*, **77**, 997 (2014).
91. K. K. Jena, S. Sahoo, R. Narayan, T. M. Aminabhavi and K. V. S. N. Raju, *Polym. Int.*, **60**, 1504 (2011).
92. R. S. Mishra, A. K. Mishra and K. V. S. N. Raju, *Eur. Polym. J.*, **45**, 960 (2009).
93. A. Asif, C. Y. Huang and W. F. Shi, *Colloid. Polym. Sci.*, **283**, 200 (2004).
94. A. Asif, C. Y. Huang and W. F. Shi, *Colloid. Polym. Sci.*, **283**, 721 (2005).
95. A. Asif, L. Hu and W. F. Shi, *Colloid. Polym. Sci.*, **287**, 1041 (2009).
96. K. K. Jena, D. K. Chattopadhyay and K. V. S. N. Raju, *Eur. Polym. J.*, **43**, 1825 (2007).
97. C. L. Bao, L. S. Wang and A. Q. Zhang, *J. Taiwan Insti. Chem. Eng.*, **40**, 174 (2009).
98. M. Melchiors, M. Sonntag, C. Kobusch and E. Jurgens, *Prog. Org. Coat.*, **40**, 99 (2000).
99. C. Sow, B. Riedl and P. Blanchet, *J. Coat. Technol. Res.*, **8**, 211 (2011).
100. J. K. Oh, J. Anderson, B. Erdem, R. Drumright and G. Meyers, *Prog. Org. Coat.*, **72**, 253 (2011).
101. D. J. Hourston, G. Williams, R. Satguru, J. D. Padget and D. Pears, *J. Appl. Polym. Sci.*, **67**, 1437 (1998).
102. J. Y. Jang, Y. K. Jhon, I. W. Cheong and J. H. Kim, *Physicochem. Eng. Aspects.*, **196**, 135 (2002).
103. Z. W. Wicks, D. A. Wicks and J. W. Rosthauser, *Prog. Org. Coat.*, **44**, 161 (2002).
104. V. V. Gite, P. P. Mahulikar and D. G. Hundiwale, *Prog. Org. Coat.*, **68**, 307 (2010).
105. M. Barikani, H. Honarkar and M. Barikani, *Monatsh. Chem.*, **141**, 653 (2010).
106. B. Krol and P. Krol, *Colloid. Polym. Sci.*, **287**, 189 (2009).
107. R. Narayan, D. K. Chattopadhya, B. Sreedhar, K. V. S. N. Raju, N. N. Mallikarjuna and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **99**, 368 (2006).
108. D. Dieterich, *Prog. Org. Coat.*, **9**, 281 (1981).
109. B. K. Kim and J. C. Lee, *J. Polym. Sci. A*, **34**, 1095 (1996).
110. P. Krol, B. Krol, S. Pikus and M. Kozak, *Colloid. Polym. Sci.*, **285**, 169 (2006).
111. P. Krol, B. Krol, P. Holler and N. Telitsyna, *Colloid. Polym. Sci.*, **284**, 1107 (2006).
112. Y. Chen and Y. L. Chen, *J. Appl. Polym. Sci.*, **46**, 435 (1992).
113. A. Barni and M. Levi, *J. Appl. Polym. Sci.*, **88**, 716 (2003).
114. C. Fang, X. Zhou, Q. Yu, S. Liu, D. Guo, R. Yu and J. Hu, *Prog. Org. Coat.*, **77**, 61 (2014).

115. X. Zhou, Y. Li, C. Fang, S. Li, Y. Cheng and W. L. X. Meng *J. Mater. Sci. Technol.*, **31**, 708 (2015).
116. D. Dieterich and H. Reiff, *Adv. Urethane Sci. Technol.*, **4**, 112 (1976).
117. J. W. Rosthauser and R. Nachtkamp, *Adv. Urethane Sci. Technol.*, **10**, 121 (1987).
118. A. Eisenberg, *Macromol.*, **3**, 47 (1970).
119. F. Mumtaz, M. Zuber, K. M. Zia, T. Jamil and R. Hussain, *Korean J. Chem. Eng.*, **30**, 2259 (2013).
120. S. Zhang, W. Miao and Y. Zhou, *J. Polym. Sci.*, **92**, 161 (2004).
121. M. A. P. Liminana, F. A. Ais, A. M. T. Palau, A. C. O. Barcelo and J. M. M. Martinez, *Int. J. Adhes. Adhes.*, **25**, 507 (2005).
122. M. A. P. Liminana, F. A. Ais, A. M. T. Palau, A. C. O. Barcelo and J. M. M. Martinez, *Int. J. Adhes. Adhes.*, **21**, 755 (2007).
123. A. K. Nanda and D. A. Wicks, *Polym.*, **47**, 1805 (2006).
124. M. A. P. Liminana, F. A. Ais, A. M. T. Palau, A. C. O. Barcelo and J. M. M. Martinez, *J. Adhes. Sci. Technol.*, **20**, 519 (2006).
125. S. C. Wang and P. C. Chen, *React. Funct. Polym.*, **67**, 299 (2007).
126. S. Yamasaki, D. Nishiguchi, K. Kojio and M. Furukawa, *Polym.*, **48**, 4793 (2007).
127. S. Zhang, H. Jiang, Y. Xu and D. Zhang, *J. Appl. Polym. Sci.*, **103**, 1936 (2007).
128. D. K. Lee, H. B. Tsai, R. S. Tsai and P. H. Chen, *Polym. Eng. Sci.*, **47**, 695 (2007).
129. M. M. Rahman and H. D. Kim, *J. Adhes. Sci. Technol.*, **21**, 81 (2007).
130. L. H. Sperling, S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1725 (1966).
131. C. P. Christenson, M. A. Harthcock, M. D. Meadows, H. L. Spell, W. L. Howard and M. W. Creswick, *J. Polym. Sci. Polym. Phys.*, **24**, 1404 (1986).
132. A. K. Mishra, D. K. Chattopadhyay, B. Sreedhar and K. V. S. N. Raju, *Prog. Org. Coat.*, **55**, 231 (2006).
133. Q. G. Kong, H. Y. Qian, X. J. Song, T. Dong, K. Liu, X. Y. Zhang, J. Li and G. Z. Gao, *Powder Sci. Technol. China*, **18**, 50 (2012).
134. Y. C. Du, S. L. Shi, C. Y. Bu, H. X. Dai, Z. G. Guo and G. Y. Tang, *Part. Sci. Technol.*, **29**, 368 (2011).
135. T. E. Fletcher, *Prog. Org. Coat.*, **44**, 25 (2002).
136. L. Liang, Y. B. Zhu, F. Guo and J. H. Wang, *Chem. Mater. Const.*, **22**, 9 (2006).
137. S. P. Lu and P. J. Prucnal, US 5744522 A (1998).
138. A. T. Chen, P. E. Kestyn and H. Zhao, US 6331582 B1 (2001).
139. R. G. K. Gan, J. George and P. Anthony, CN 1735642A (2006).
140. X. Zhang and Z. Zhang, *China Leather*, **1**, 18 (2007).
141. U. M. Westhues, *Polyurethanes: Coatings, Adhesives and Sealants*, Vincentz Network GmbH & Co KG, Hannover, Germany (2007).
142. W. Cllong, A. Gobel, B. Kleuser, W. Lenhard and M. Sonntag, *Prog. Org. Coat.*, **45**, 205 (2002).
143. K. Haeberle, US Patent, 5,583,167 (1996).
144. S. K. Das, S. Kilic, R. E. Jennings, S. J. Thomas and J. M. Carney, US Patent, 5,633,307 (1997).
145. J. T. Martz, J. M. Carney, R. E. Jennings and K. D. Donnelly, US Patent, 5,744,542 (1998).
146. D. K. Chattopadhyay and K. V. S. N. Raju, *Prog. Polym. Sci.*, **32**, 352 (2002).
147. S. Jafarzadeh, M. Johansson, P. E. Sundell, M. Claudino, J. Pan and P. M. Claesson, *Polym. Adv. Technol.*, **7**, 668 (2013).
148. R. D. Toker, N. K. Apohan and M. V. Kahraman, *Prog. Org. Coat.*, **76**, 1243 (2013).
149. Y. Huang, L. Pang, H. Wang, R. Zhong, Z. Zeng and J. Yang, *Prog. Org. Coat.*, **76**, 654 (2013).
150. H. Xu, F. Qiu, Y. Wang, W. Wu, D. Yang and Q. Guo, *Prog. Org. Coat.*, **47**, 1 (2012).
152. Z. H. Fang, H. Y. Duan, Z. H. Zhang, J. Wang, D. Q. Li, Y. X. Huang and Z. Y. Liu, *Appl. Surf. Sci.*, **11**, 4765 (2011).
153. X. Wang, Y. Hu, L. Song, W. Xing, H. Lu, P. Lv and G. Jie, *J. Polym. Res.*, **4**, 721 (2011).
154. J. Xu, X. Rong, T. Chi, M. Wang, Y. Wang, D. Yang and F. Qiu, *J. Appl. Polym. Sci.*, **5**, 3142 (2013).
155. S. Zhang, A. Yu, X. Song and X. Liu, *Prog. Org. Coat.*, **76**, 1032 (2013).
156. T. C. Canak and I. E. Serhatli, *Prog. Org. Coat.*, **76**, 388 (2013).
157. Z. L. Yang, D. A. Wicks, C. E. Hoyle, H. T. Pu, J. J. Yuan, D. C. Wan and Y. S. Liu, *Polym.*, **50**, 1717 (2009).
158. C. Sow, B. Riedl and P. Blanchet, *Prog. Org. Coat.*, **67**, 188 (2010).
159. H. D. Hwang, J. I. Moon, J. H. Choi, H. J. Kim, S. D. Kim and J. C. Park, *J. Ind. Eng. Chem.*, **15**, 381 (2009).
159. M. M. Rahman and W. K. Lee, *J. Appl. Polym. Sci.*, **114**, 3767 (2009).
160. S. M. Cakic, J. V. Stamenkovic, D. M. Djordjevic and I. S. Ristic, *Polym. Degrad. Stab.*, **94**, 2015 (2009).
161. J. He, L. Zhou, M. D. Soucek, K. M. Wollyung and C. Wesdemiotis, *J. Appl. Polym. Sci.*, **105**, 2376 (2007).
162. X. Wang and M. D. Soucek, *Prog. Org. Coat.*, **76**, 1057 (2013).
163. I. V. Khudyakov, K. W. Swiderski and R. W. Greer, *J. Appl. Polym. Sci.*, **99**, 489 (2006).
164. H. V. Patel, J. P. Raval and P. S. Patel, *Arch. Appl. Sci. Res.*, **1**, 294 (2009).
165. B. H. Lee and H. J. Kim, *Polym. Degrad. Stab.*, **91**, 1025 (2006).
166. T. Y. Inan, E. Ekinci, E. Yildiz, A. Kuyuluand and A. Gungor, *Macromol. Chem. Phys.*, **202**, 532 (2001).
167. J. Y. Kwon, H. J. Yoo and H. D. Kim, *Fibers Polym.*, **2**, 141 (2001).
168. W. J. Blank, *Prog. Org. Coat.*, **20**, 235 (1992).
169. A. Srivastava, D. Agarwal, S. Mistry and J. Singh, *Pigment Resin Technol.*, **37**, 217 (2008).
170. X. Y. Ma and W. D. Zhang, *Polym. Degrad. Stab.*, **94**, 1103 (2009).
171. F. S. Chuang, H. Y. Tsi, J. D. Chow, W. C. Tsen, Y. C. Shu and S. C. Jang, *Polym. Degrad. Stab.*, **93**, 1753 (2008).
172. Y. Xu, L. G. Chen, H. Wang, X. P. Zhang, Q. L. Zeng, H. Y. Xu, L. Sun, Q. Zhao and L. Ding, *Anal. Chim. Acta*, **661**, 35 (2010).
173. C. R. Yates and W. Hayes, *Eur. Polym. J.*, **40**, 1257 (2004).
174. M. J. Cho, D. H. Choi, P. A. Sullivan, A. J. P. Akelaitis and L. R. Dalton, *Prog. Polym. Sci.*, **33**, 1013 (2008).
175. Q. Fu, L. L. Cheng, Y. Zhang and W. F. Shi, *Polym.*, **49**, 4981 (2008).
176. S. Vlad and S. Oprea, *E-Polym.*, **027** (2008).
177. Z. S. Petrovic, W. Zhang, A. Zlatanic, C. C. Lava and M. Ilavsky, *J. Polym. Environ.*, **10**, 5 (2002).
178. S. Fukao, J. P. McClure, A. Ito, T. Sato, I. Kimura and T. Tsuda, *Geophys. Res. Lett.*, **15**, 768 (1999).
179. B. Voit, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 2505 (2000).
180. D. H. Bolton and K. L. Wooley, *Macromol.*, **30**, 1890 (1997).
181. H. K. Young and W. W. Owen, *J. Am. Chem. Soc.*, **112**, 4592 (1990).

182. M. Trollsas, J. Hedrick, D. Mecerreyes, R. Jerome and P. H. Dubois, *J. Polym. Sci. Part A Polym. Chem.*, **36**, 3187 (1998).
183. A. Morikawa, *Macromol.*, **31**, 5999 (1998).
184. C. F. Shu and C. M. Leu, *Macromol.*, **32**, 100 (1999).
185. H. K. Young, *J. Am. Chem. Soc.*, **114**, 4947 (1992).
186. G. Yang, M. Jikei and M. Kakimoto, *Macromol.*, **32**, 2215 (1999).
187. M. W. Weimer, J. M. J. Frechet and I. Gitsov, *J. Polym. Sci. Part A Polym. Chem.*, **36**, 955 (1998).
188. Z. S. Petrovic, W. Zhang, A. Zlatanic, C. C. Lava and M. Ilavsky, *J. Polym. Environ.*, **10**, 5 (2002).
189. E. J. Woo, G. Farber, R. J. Farris, C. P. Lillya and J. C. W. Chien, *Polym. Eng. Sci.*, **25**, 834 (1985).
190. T. L. D. Wang and D. J. Lyman, *Polym. J. Sci. Part A Polym. Chem.*, **31**, 1983 (1993).
191. Y. Minoura, S. Yamashita, H. Okamoto, T. Matsuo, M. Izawa and S. Kohmoto, *J. Appl. Polym. Sci.*, **22**, 1817 (1978).
192. A. K. Mishra, R. Narayan, K. V. S. N. Raju, T. M. Aminabhavi, *Prog. Org. Coat.*, **74**, 134 (2012).
193. S. Paul, *Surface Coating Science and Technology*, 2nd Ed., Wiley, Chichester (1997).
194. D. R. Baer, P. E. Burrows and A. A. El-Azab, *Prog. Org. Coat.*, **47**, 342 (2003).
195. R. H. Fernando, *J. Coat. Technol.*, **1**, 32 (2004).
196. M. Rashvand, Z. Ranjbar and S. Rastegar, *Prog. Org. Coat.*, **71**, 362 (2011).
197. S. Saha, D. Kocaefe, C. Krause and T. Larouche, *Prog. Org. Coat.*, **70**, 170 (2011).
198. M. M. Rahman, H. D. Kim and W. K. Lee, *J. Appl. Polym. Sci.*, **110**, 3697 (2008).
199. A. K. Nanda, D. A. Wicks, S. A. Madbouly and J. U. Otaigbe, *Macromol.*, **39**, 7037 (2006).
200. A. B. Samui, J. G. Chavan and V. R. Hande, *Prog. Org. Coat.*, **57**, 301 (2006).
201. S. A. Madbouly and J. U. Otaigbe, *Prog. Polym. Sci.*, **34**, 1283 (2009).
202. M. Geraghty, J. F. Cronin, M. Devereux and M. Mc Cann, *Bio. Met.*, **13**, 1 (2000).
203. N. Cioffi, L. Torsi, N. Ditaranto, G. Tantillo, L. Ghibelli, L. Sabbatini, T. Bleve-Zacheo, M. D'Alessio, P. G. Zambonin and E. Traversa, *Chem. Mater.*, **17**, 5255 (2005).
204. N. Cioffi, L. Torsi, N. Ditaranto, L. Sabbatini, P. G. Zambonin, G. Tantillo, L. Ghibelli, M. D'Alessio, T. Bleve-Zacheo and E. Traversa, *Appl. Phys. Lett.*, **85**, 2417 (2004).
205. S. Pal, Y. K. Tak and J. M. Song, *Appl. Environ. Microbiol.*, **73**, 1712 (2007).
206. W. L. Low, C. Martin, D. J. Hill and M. A. Kenward, *Int. J. Antimicrob. Agents*, **37**, 162 (2011).
207. T. K. Sontakke, R. N. Jagtap, A. Singh and D. C. Kothari, *Prog. Org. Coat.*, **74**, 582 (2012).
208. J. H. Li, R. Y. Honga, M. Y. Li, H. Z. Li, Y. Zheng and J. Dinge, *Prog. Org. Coat.*, **64**, 504 (2009).
209. A. Rai, A. Prabhune and C. C. Perry, *J. Mater. Chem.*, **19**, 574 (2010).
210. M. Perez, G. Blustein, M. Garcia, B. del Amo and M. Stupak, *Prog. Org. Coat.*, **55**, 311 (2006).
211. D. K. Chattopadhyay and D. C. Webster, *Prog. Polym. Sci.*, **34**, 1068 (2009).
212. D. Akram, S. Ahmad, E. Sharmin and S. Ahmad, *Macromol. Chem. Phys.*, **211**, 412 (2010).
213. Y. L. Liu, G. H. Hsiue, Y. S. Chiu, R. J. Jeng and C. Ma, *J. Appl. Polym. Sci.*, **59**, 1619 (1996).
214. G. Camino, L. Costa and M. P. L. Cortemiglia, *Polym. Degrad. Stab.*, **33**, 141 (1991).
215. M. Ravey, I. Keidar, E. D. Weil and E. M. Pearce, *J. Appl. Polym. Sci.*, **68**, 217 (1998).