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UV-CURABLE WATERBORNE POLYURETHANE COATINGS: A STATE-OF-THE-ART AND RECENT ADVANCES REVIEW

Lucas Dall Agnol[1*], Fernanda Trindade Gonzalez Dias[2], Heitor Luiz Ornaghi Jr.[1], Marco Sangermano[3] and Otávio Bianchi[1,4]

[1] *Postgraduate Program in Materials Science and Engineering (PGMAT), University of Caxias do Sul (UCS), Caxias do Sul, RS, Brazil*

[2]*Postgraduate Program in Technology and Materials Engineering (PPG-TEM), Federal Institute of Rio Grande do Sul (IFRS), Feliz, RS, Brazil*

[3]*Department of Applied Science and Technology, Politecnico di Torino, C.so Duca Degli Abruzzi 24, Turin, 10129, Italy*

[4]*Department of Materials Engineering (DEMAT), Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil*

***Corresponding author.** *E-mail addresses:* ldagnol3@ucs.br (Lucas Dall Agnol)

ABSTRACT

Waterborne polyurethane coatings prepared by UV-induced photoreactions (UV-WPU) are becoming very attractive due to the increasingly stringent environmental demands. UV-WPUs were developed to replace solvent-based polyurethanes in the coatings of wood, paper, plastics, metal, and glass, mainly because of their good physicochemical, rheological, and optical properties. Several UV-WPU formulations have been tested over the years, making their research substantial. However, no valuable review of this literature, focusing on the significant influencing factors in UV-WPU's manufacture, is available to date. This work aims to answer specific questions about the state of these materials' art, such as: "which monomers have been used most in UV-WPU synthesis?", "what type of photo-initiator has promoted the most efficient curing of the material?", "what additives or particles have been tested for composite UV-WPUs?", "which applications have UV-WPUs been directed to?", "what adaptations and technologies have already been tested to overcome the challenges of the process?", among others. As a result of a systematized bibliographic search in four databases, considering the period from January 2000 to July 2020, a total of one hundred and thirty-eight distinct and relevant articles on UV-WPUs were found. From this study, we hope to give material engineers and industrials a scientific source on the current state-of-the-art of UV-WPU synthesis, offering these professionals new combinations of raw materials and intelligent solutions to mitigate the inconveniences of the process.

Keywords: waterborne polyurethane acrylate; UV-curable; photocurable waterborne; polyurethane/acrylate dispersion; systematic review.

1. INTRODUCTION

Polyurethanes (PU) are high-performance materials with a wide range of industrial applications [1], mainly due to their tunable physicochemical properties. They are block copolymers produced from the step polymerization reaction between a di/polyisocyanate and alcohol groups (diols), resulting in repeated urethane groups. More recently, non-isocyanate polyurethanes are also produced. They are synthesized from cyclic carbonate – primary amine [2]. Because the PU's block segments have differences in the solubility parameters, they are thermodynamically incompatible, contributing to phase separation and a structure composed of microdomains [3, 4]. Generally, the hard segments derived from the diisocyanates groups contain urethane or urea domains with strong hydrogen bonding and low-molar mass chain extenders. The hard segments of PU are responsible for providing mechanical resistance to the polymeric film, unlike the soft segments derived from polyols, which account for its impact properties [5, 6]. The chemical composition of PU in terms of the balance between rigid and flexible blocks will determine the polymer's final properties.

Regarding environmentally friendly PU-based materials, waterborne polyurethane (WPU) appears, with low levels of volatile organic compounds (VOCs) and the absence of isocyanate residues. WPUs are widely used as films and adhesives, especially in ecological coatings, as a substitute for traditional solvent-borne ones [7-9]. Polyurethane aqueous dispersions, the particles tend to present 10–300 nm sizes and high surface energy [8, 10]. The main difference between solvent-based PU and WPU is hydrophilic segments' presence in the polymer backbone, derived from a diol containing an acid group (such as carboxylic acid, sulfonate, or quaternary ammonium salt) that acts as an internal emulsifier [11]. Although the hydrophilic groups endow excellent colloidal stability, they cause adverse effects to surface properties, water resistance, and long-term performance of WPU-based materials [12, 13]. Several strategies can be employed to overcome these inconveniences, such as blending, cross-linking, copolymerizing, grafting of hydrophobic monomers, or incorporating nanofillers to WPU [14-19]. Among these approaches, the cross-linking proved to be most promising because it is based on incorporating acrylic double bonds to WPU, which allows UV curing through chain polymerization [12, 20]. The presence of crosslinks provides thermoset coatings with high chemical stability, enhanced tensile strength, excellent abrasion, acid-alkali, solvent resistance, and cure selectively limited to the irradiated area [21-23]. In contrast, this system has some limitations. First, water has to be driven out of the film by conventional dryers, microwave dryers, and/or IR lamps before UV curing. As a result, longer drying times and higher energy consumption can be required [24]. In addition, the density of photosensitive groups of the existing photo-curable resins can influence the film's performance. Depending on the content of these groups in the polymeric matrix, the hardness of the coating films can be poor, and the UV curing rate, slow, which limits its practical applications in some fields [25].

There are several methods for preparing UV-WPU coatings, such as physical blending, emulsion polymerization, and the interpenetrating polymer network (IPN)-based one [26-30]. The most conventional is to end-chain polyurethane with a single-hydroxyl acrylate or to introduce a double bond from hydroxyl-terminated polybutadiene or to incorporate vinyl groups into the polymer [31]. UV-WPU dispersions are usually prepared by acetone methods using a three-step procedure, as shown in Figure 1. In the first step, an excess of a difunctional diisocyanate is reacted with a polyol and end-capped with a hydroxyl (meth)acrylates synthesized in acetone. A part of the chain extender is replaced by a carboxylic acid functionalized diol to improve dispersibility in water. In the second step, the carboxylic acid is neutralized, and the acrylic end-capped polyurethane is dispersed in water. Finally, acetone is removed under vacuum to obtain a WPU dispersion that can give rise to a free-radical type UV curing step. Typically, the urethane dispersion has a pH 7–8 and a solids content of 30–40wt.%, remaining stable for several months [32]. Since the viscosity of polymeric dispersions is dependent on the concentration and particle size of the chains, it is possible to obtain systems with viscosities suitable for specific applications [33].

Before applying the UV-WPU dispersions on a substrate, the photopolymerizer is added to the solution, which is then exposed to a temperature for the evaporation of water. The ultraviolet light absorbed by the photoinitiator produces free radicals that promote the reaction between the prepolymer and the reactive monomers or diluents, generating the cured films. The dispersion stability and particle size, in addition to the product's final properties, will be influenced by the ionic group's content, rigid/flexible segments molar ratio, structure of the monomers, neutralization degree, acrylate double bond percentage, curing conditions, photoinitiator amount, and others. Moreover, the reaction parameters, such as temperature, stirring, component's feeding rate, and order of addition, significantly affect the aqueous dispersion properties [3, 34]. Monitoring the nanoparticle morphology produced in the synthesis is essential to control the interconnected network resulting from its aggregation, which will directly affect the quality of the PU film formed [10]. The film formation by the nanoparticles' aggregation is a complex phenomenon, due to the occurrence of simultaneous physicochemical processes, such as water evaporation, cross-linking reactions, phase separation, droplet coalescence, and others [35]. Thus, to obtain the best physical and mechanical properties of the UV cured product, one must consider the materials used and the conditions under which the film was formed. The reaction conditions will control the polymerization and the double bond conversion in the system.

So far, insufficient data has been reported in the literature on the relationship between polymeric structure, water-resistance, and coating performance for UV-curable WPU systems [25, 36]. Therefore, this review aimed to synthesize and discuss the information found in articles published in the Scopus, Web of Science, Science Direct, and Google Scholar databases from 2000 to 2020. As the preparation method of the aqueous PU dispersions is more consolidated in the literature [1, 5, 25, 34, 36-39], this study sought to focus specifically on the effect of formulation components on the final properties of UV-crosslinked films. The present work will assist the progress of research regarding the smarter choice of synthesis parameters and precursors, essential features for obtaining photocurable films with specific properties.

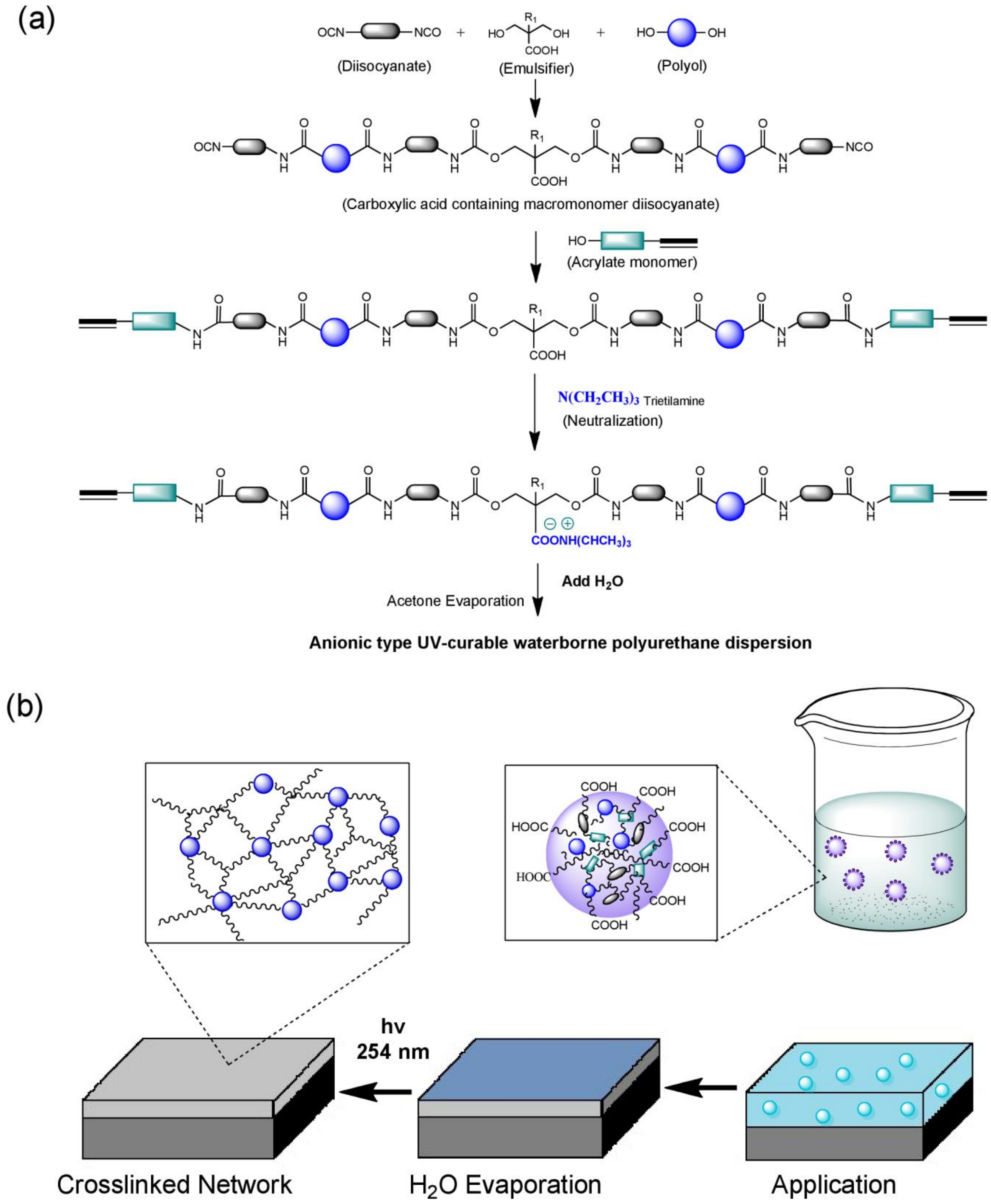

Figure 1. (a) Reaction scheme for UV-WPU synthesis and (b) schematic illustration of the film formation

2. REVIEW METHODOLOGY

The publications were searched using the Scopus (https://www.scopus.com), Web of Science (https://www.webofknowledge.com), Science Direct (https://www.sciencedirect.com), and Google Scholar (https://scholar.google.com.br) online databases. The keywords employed were:

(("waterborne polyurethane" OR "polyurethane acrylate dispersion" OR "polyurethane dispersions" OR "waterborne UV") AND ("UV curable" OR "UV cured" OR "photocurable" OR "ultraviolet curable" OR "UV crosslinking")). The search was limited to English language articles published from January 2000 to July 2020. The publications found were analyzed, and duplicate articles, revisions, or articles that did not produce UV-WPU, were excluded from the results. Articles of polyurethane acrylates that do not perform UV curing and articles that do not detail the UV-WPU composition were only used to support the review's discussion. Considering these criteria, a total of one hundred and thirty-eight (138) relevant publications were detected in the databases search, showed in Table 1 and mandatorily cited in this review. The parameters analyzed in the eligible articles were: UV-WPU composition, UV curing process, and final properties/application. The other references cited here were also used to support the review’s discussion.

3. RESULTS AND DISCUSSION

The literature research in Scopus, Web of Science, Science Direct, and Google Scholar databases identified six hundred and thirty (630) articles. From those, two hundred and fifty-one (251) were duplicate articles found in more than one of these four databases, and two hundred and forty-one (241) were discarded for not meeting the eligibility criteria, that is, either they were not written in English language or were not related UV-WPU formulations. A total of one hundred and thirty-eight (138) articles were then included in this study, which evaluated the last twenty years' reports. Table 1 summarizes the compositional characteristics, properties, and the leading applications reported for the UV-WPU systems described in these one hundred and thirty-eight (138) articles. The variety of possible monomer combinations for WPU synthesis was impressive. From the 138 results, twenty-seven (27) used polytetramethylene glycol (PTMG) as polyol [26, 40-66]. Polypropylene glycol (PPG) was the second most chosen polyol, being part of twenty two studies [12, 23, 32, 40, 52, 59, 65, 67-82], followed by poly(ethylene glycol) (PEG) (sixteen studies) [7, 21, 73, 83-96], poly(ε-caprolactone) (PCL) (thirteen studies) [6, 20, 31, 52, 59, 97-105], polyether diol (twelve studies) [22, 106-117], polycarbonate diol (PCD) (ten studies) [24, 33, 52, 103, 118-124], and hyperbranched aliphatic polyester (HBP) (nine studies) [11, 125-133], vegetable oil (castor, linseed or cardanol) (six studies) [134-139], as well as a mixture of two polyols [65, 140, 141]. Other polyols were also reported [9, 40, 73, 103, 142-152]. Regarding the isocyanate monomer, Table 1 shows that the most used for the UV-WPU synthesis is the isophorone diisocyanate (IPDI). Other diisocyanates also employed were toluene diisocyanate (TDI), aliphatic 4,4’-icyclohexylmethane diisocyanate (HMDI), hexamethylene diisocyanate (HDI), and methylene diphenyl 4,4-diisocyanate (MDI). Concerning the emulsifier, 2,2-bis(hydroxymethyl)butyric acid (DMBA), and 2,2-bis(hydroxymethyl) propionic acid (DMPA) were the most utilized. Triethylamine (TEA) was the most reported agent to neutralize the acid groups of the emulsifier. In a reaction between an isocyanate and alcohol, it is common to use catalysts to accelerate the reaction rate and avoid high temperatures. For the synthesis of WPUs, organotin compounds were adopted, especially the dibutyltin dilaurate (DBTDL). The 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), and pentaerythritol triacrylate (PETA) were the acrylic monomers most cited for the production of UV-WPU. Other acrylic monomers also used were pentaerythritol diacrylate (PEDA), 2,2-bis(prop-2-enoxymethyl)butan-1-ol (DiAE), 2-hydroxypropyl acrylate (HPA), hydroxypropyl methacrylate (HPMA), and trimethylolpropane monoethylene ether (TMPME). For the synthesis of UV-WPU, inhibitors such as hydroquinone (HQ) or 4-methoxyphenol (MEHQ) were generally added to prevent radical UV-initiated curing of the acrylate monomers during the reaction and storage of the emulsion. Acetone, methyl ethyl ketone (MEK), and N-methyl-2-pyrrolidone (NMP) were the most used solvents to lower the medium viscosity since their removal is facilitated and they do not react with isocyanate during the reaction. Chain extenders and inorganic nanoparticles have also been used to improve the properties of the materials. The choice for the photopolymerizer is restricted to water solubility and photoinitiator's compatibility with resins. Darocur 1173 and Irgacure 2959 are the most common photopolymerizers for the UV-WPU synthesis. Other options are Irgacure 184, Irgacure 500, 2,4,6-trimethylbenzoyldi-phenyl phosphine oxide (TPO), and benzophenone (BPO).

Regarding the characteristics of UV-WPU materials obtained after synthesis, it could be observed that their average particle sizes were 60–300 nm, except in specific cases [72, 90, 96, 118, 138]. After water evaporation, the films are photocured with a UV light incidence of 40–1000 W during photopolymerization times of 0.1–30 min, contents of up to 98% of double bond conversion degree are obtained. The produced films' average Pencil hardness is around HB–5H, with tensile strength and elongation reaching 3–25 MPa and 10–400% values, respectively. Also, the thermal degradation of UV-WPU materials can approach 200–310 °C, and their water absorption decreases to 4–20% values. The potential application of these materials is covering metal, fabric, and wood surfaces. As previously mentioned, the formulation of an efficient UV-WPU material depends on selecting an appropriate method, the nature of fillers, and the product's final application. Therefore, we discuss here the main findings regarding the composition and properties of UV-curable waterborne polyurethanes from the aforementioned search methodology, described in Table 1, mainly concerning the influence of the formulation and UV light intensity on the mechanical, chemical, and physical properties of WPUs.

3.1. Diisocyanates and polyols

3.1.1. Isocyanates

Isocyanates are highly reactive compounds and create chemically different products when combined with active hydrogen (–OH and –NH functional substances), forming urethane and urea groups. Isocyanates with aromatic, aliphatic, cycloaliphatic, or polycyclic in their structures prepare WPU coatings. By varying the type or content of diisocyanates, coatings with different properties can be produced [25]. For example, HMDI or MDI's selection will provide resins with enhanced mechanical properties due to the cyclic structure or benzene rings that these reagents have. On the other hand, by choosing HDI, flexible coatings will be obtained as a result of the long-chain alkane present in this diisocyanate or using IPDI to control the reaction process which can design the chemical structure of compounds due to the different reactivities of the two isocyanate groups present in IPDI at low temperature [25]. Aromatic diisocyanates give more rigid PUs than aliphatic ones, but their oxidative and ultraviolet stabilities are lower [39, 153]. Compared with other aromatic isocyanates, IPDI is a favored monomer to prepare UV-WPU, since it shows higher weather resistance, better controllable activity, and more rigidity also it is observed [71, 73]. Comparing the effects of using IPDI or TDI in the same formulation, the IPDI-based UV-WPU dispersion exhibited a more pronounced pseudoplastic behavior than the TDI-based one [92]. Chain entanglement and hydrogen bonding between urethane and urea linkages can be more readily formed in the IPDI-based prepolymer because of its chains' flexibility. However, the TDI-based chain-extended UV-WPU is superior in thermal stability than the IPDI-based counterpart. The incorporation of phenyl into the backbone relatively decreases the rotation of single bonds. Consequently, the molecular chains become more rigid, shifting the glass transition temperature (T_g) to higher temperatures. During coating curing, the conversion for the TDI-based UV-WPU drastically increased to a maximum of 75.4%, whereas the curing reaction for IPDI-based UV-WPU proceeded more steadily, as shown in Figure 2 (a). This is attributed to the difference in chain mobility. The reduction of the chain mobility caused by the stiffness in the hard segments of the TDI-based UV-WPU also anticipates the autoacceleration due to the gel effect. In contrast, there is a less gel effect during the IPDI-based UV-WPU curing because of its chain flexibility. However, this contrast in the different diisocyanates' curing behavior is attenuated for the UV-WPU from the 2000 g/mol molecular weight polyol [Figure 2 (b)]. This implies that increased soft portions attenuate the diisocyanate segment's effect on chain mobility [53]. A significant difference in the average size of particles formed from UV-WPU formulations prepared with HDI or TDI was observed [58]. While the average particle size of the formulation containing only HDI was 38 nm, the average particle size from the one that used only TDI was 158 nm. It is believed that aromatic rings show a better hardness in macroscopic properties, so the coating hardness increases with the increasing of TDI usage.

Environmentally-friendly coatings were also synthesized with different proportions of 4,4-methylene dicyclohexyl diisocyanate (H12MDI) and isocyanate functionalized aliphatic acrylic ester (IAAE). The IAEE promoted an increase in the cured coatings' tensile strength and pencil hardness, while the elongation decreased. This behavior can be associated to the high reactivity of IAAE, which has two isocyanates and two unsaturated functional groups, providing a high crosslink density [121].

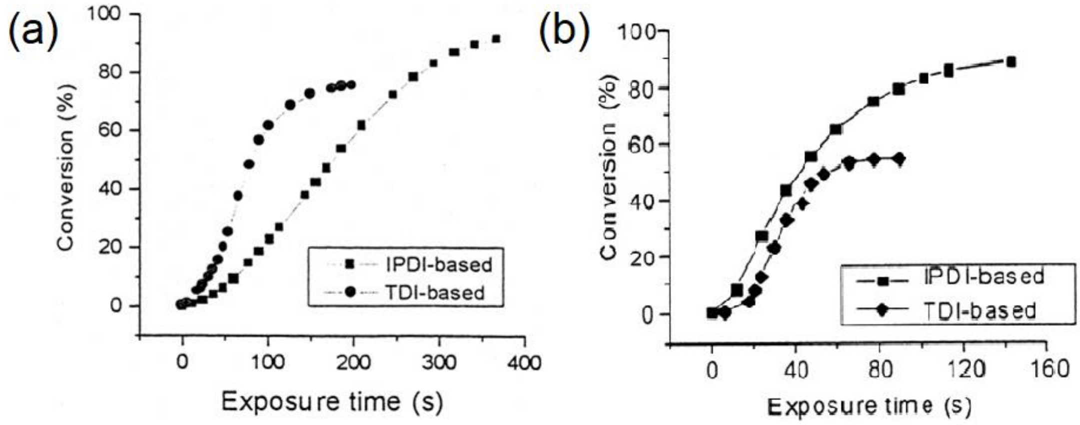

Figure 2. (a) Effect of diisocyanate type on curing kinetics of chain-extended UV-WPU from PEG 400 g/mol and (b) Effect of diisocyanate type on curing kinetics of chain-extended UV-WPU from PEG 2000 g/mol [92]. Adapted with permission from Ref. 91, Yang J, *et al*. (2002) J Appl Polym Sci 84:1818–1831. Copyright © 2002 Wiley Periodicals, Inc.

3.1.2. Polyols

Polyols, the reaction partners for diisocyanate, are mainly dihydroxy terminated long-chain macroglycols with a wide range of molar masses (M_w= 400–6000 g/mol). There are significantly more commercially available polyols (>500) than isocyanates. Among polyols, polyester and polyether ones are the most used to synthesize UV-WPUs. The use of low molar mass polyols results in stiff polymers due to the high concentration of urethane groups. On the other hand, high molar mass polyols produce polymer chains with fewer urethane groups and more flexible alkyl chains. Long-chain polyols with low functionality (1.8–3.0) give soft, elastomeric PU while short-chain polyols of high functionality (greater than 3) provide a more rigid crosslinked product. Different oligomers' choice directly determines the rigidity of the chain and the hydrophobicity, and viscosity of the polyurethane, resulting in different particle shapes and sizes [37]. The hardness, curing rate, and conversion on the photopolymerization increased with the decrease in the polyol's molar mass, mainly because dispersions based on shorter chain polyols have greater reactivity. A higher relative concentration of methacrylate double bonds in the system forms stronger polymer networks [24, 32, 56]. Although a higher crosslink density leads to better physical performance, elongation at break is reduced considerably with crosslinking [24, 50, 118]. High molar masses polyols present larger particle size and lower ionomers weight content in the backbone, leading to higher viscosity systems than polyols of smaller molar masses [106, 111, 154, 155]. Some authors have observed an almost linear correlation between molar mass and average particle size [24, 50, 59, 92]. An example is demonstrated in Figure 3.

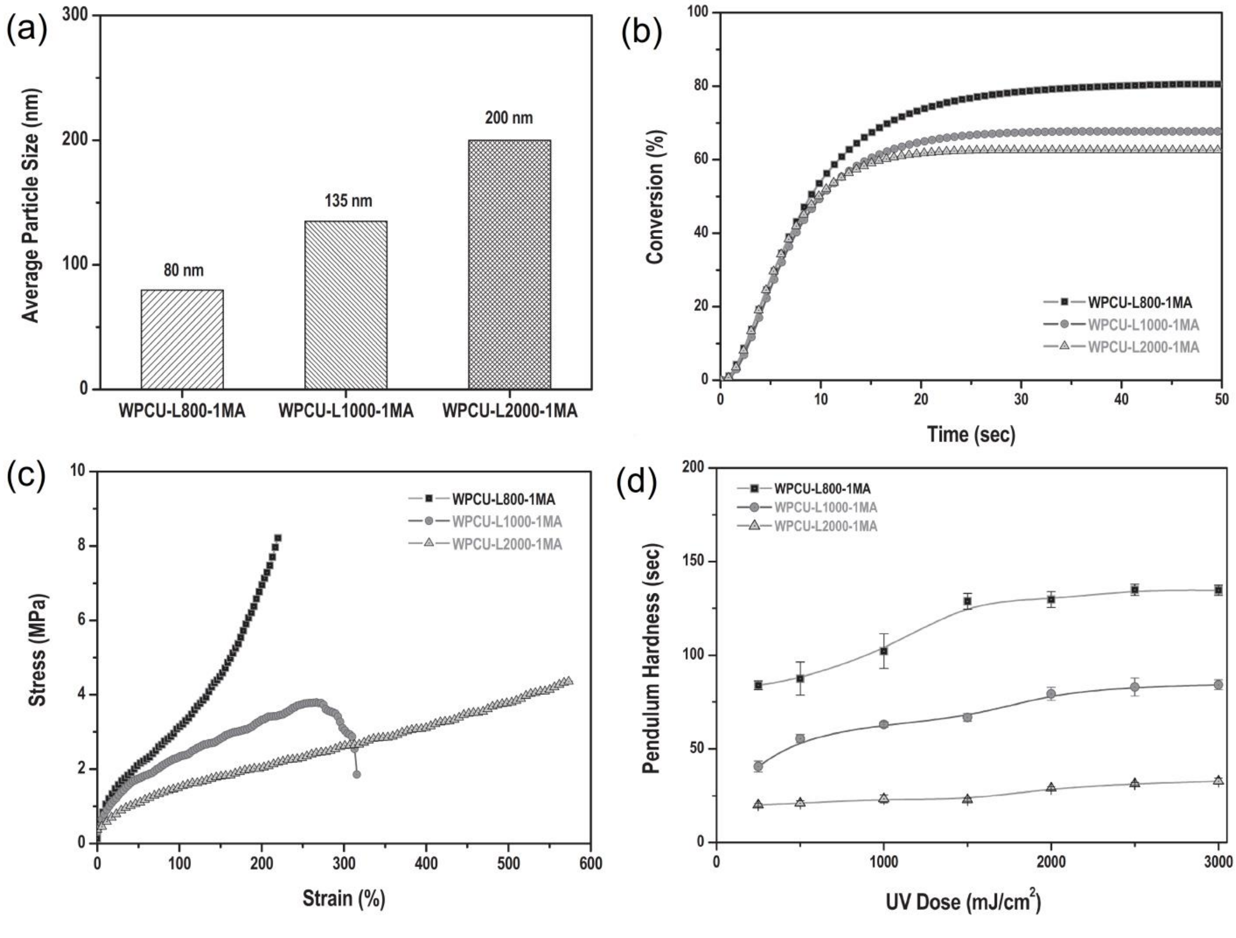

Figure 3. Effect of molar mass on the properties of a coating synthesized using different PCDs ((■) 800 g/mol; (●) 1000 g/mol; (▲) 2000 g/mol). (a) Average particle size of the dispersion. (b) C=C double bond conversion *vs*. time by photo-DSC. (c) Tensile behavior of the cured film. (d) Pendulum hardness of the cured film as function of the UV-dose [24]. Adapted with permission from Ref. 23, Hwang HD, *et al*. (2011) Prog Org Coat 72:663–675. Copyright © 2011 by Elsevier B.V.

Another interesting fact is that, as the segmental chain length decreases, the segment's movement becomes restricted, and the T_g increases. It is well known that polyurethanes possess a two-phase morphology resulting from phase separation between hard and soft segments. The low glass transition temperature (T_{gs}) is attributed to the soft-segment phase, whereas the high glass transition temperature (T_{gh}) is due to the hard-segment phase. UV-WPUs produced with low molar mass polyols showed a single T_g, which meant good miscibility between the hard and soft segments. As the polymer molar mass increases, the phase separation between soft and hard segments becomes more remarkable [92]. Hwang *et al*. [24] used PCDs with chain lengths of 800, 1000, and 2000 g/mol and obtained Tg values of 44.5 °C, 25.5 °C, and -20.5 °C, respectively. The physicomechanical properties, such as pendulum hardness, maximum tensile strength and glass transition temperature are also affected by polyols' chemical structure due to interactions between inter-chains. Ahn *et al*. [40], for example, observed that the aliphatic side chain of polymers such as PPG decreased the cohesion forces between groups, resulting in lower mechanical modulus and glass transition temperature. In contrast, polymers such as poly(tetramethylene adiphate)glycol (PTAd) having ester groups show higher values for these properties than PTMG and PPG since the cohesion of the ester groups is higher than that of the ether groups.

The phase separation between hard and soft segments also affects the thermal decomposition of the material. It is well known that the thermal decomposition of polyurethane chains has at least two stages. The initial stage at approximately 250 °C is associated with the decomposition of the hard segments, represented by the urea and urethane groups. The second stage at approximately 350 °C denotes the soft segment's decomposition, which involves the polyester and polyether [7, 20, 21, 118]. Conventionally, the molar mass of PU is increased by chain extension of isocyanate-terminated prepolymers with short diols. These chain extensions produce many urethane linkages that are vulnerable to thermal decomposition and limit some applications. Etxaniz *et al.* [142] observed that the T_g of a formulation prepared by a dimer fatty-acid based polyol and IPDI shifted to lower temperatures with the increase in the hard segment, due to greater phase separation. Thus, the hard segment's chemical modification is of prime importance to enhance the thermal stability of UV-WPU. This can be done by introducing thermally stable heterocyclic groups in the hard segment [47]. For example, when the imide groups replaced the urethane groups in the hard segment, remarkably enhanced hardness, tensile modulus, strength, and thermal stability were obtained. The augmented mechanical strength of UV-WPU with the imide hard segment is due to the combined effects of increased hydrogen bondings (one imide group has two carbonyl groups), dipole interactions between imide rings, and the rigid structure of the hard segment [47, 61, 72].

The polyol plays an essential role in the structure of the molecular chain due to its polarity which influences the size of the particles and the water absorption of the films. Ahn *et al*. [40] showed that films based on PTAd as soft segments having ester carbonyl hydrogen bonds have higher water swelling than two other types of soft segments, such as PPG, and PTMG. Polyols with regular structures can form crystalline domains more easily, being the cohesive strength between the soft segments so high that it becomes difficult to penetrate water molecules into the membranes [52]. Also, it seems that polyol's miscibility in water is a critical parameter that governs the WPU's particle size. Yoon *et al*. [59] compared three formulations using different polyols, but with the same prepolymer molar mass during synthesis, the particle size increased with the order PPG, PTMG, and PCL. The order depends on the difference in solubility parameter between water and polyol, as noted from 8.63 (PCL), 8.90 (PTMG), 12.6 (PPG), and 23.4 (water) $(\mathrm{cal/cm^3})^{1/2}$.

Vegetable oil is being used to replace petroleum products in the preparation of UV-WPUs, mainly due to its low cost and renewable feedstock [25]. UV-WPUs prepared from castor [13, 104, 134-137], linseed [138], epoxy soybean oil [105], and cardanol [139] polyols showed excellent flexibility, water resistance, hydrolytic stability, shock absorption, and electrical insulation properties. However, the main drawback is their low thermal decomposition temperature. The final double bond conversion of the samples was between 64–80%. Another disadvantage is the high large particle size compared to the WPUs obtained with synthetic polyols using the same content (or higher content). Bio-based polyols act as an internal emulsifier attributed to the lower polarity of the backbone [142]. In recent years, the hyperbranched polymer has gained increasing attention as a novel type of binder material for waterborne UV-curable ink. Compared to its linear counterpart, the hyperbranched polymer displays low viscosity, high activity, good oxygen resistance ability, excellent compatibility due to its highly branched structure, low intermolecular entanglement degree, and a significant number of end functional groups (increasing the crosslinking density) [25, 73, 93, 129, 156, 157]. Due to the nature of compactly packed periphery, high density, cross-linking, and lack of chain entanglements, hyperbranched polyurethanes are usually too brittle to form freestanding and mechanical robust films. Incorporating dendritic hyperbranched WPU into the curing system can increase the crosslink density [11, 25, 93, 129, 131, 132], resulting in films with a highly compact structure due to its functionality. However, although the crosslink density increase has reinforced coatings' rigidity, the decrease in their elongation at break is still noticeable [133, 140].

Another type of UV-curable WPUs can be prepared by blending multifunctional thiol- and ene-terminated polyurethane aqueous dispersions. Thiols have been used to reduce the effects of oxygen inhibition by undergoing chain transfer with the peroxy radicals to produce hydrogen peroxide, and thiyl radicals, which can initiate polymerization. The UV-cured polyurethane films prepared by this method also showed increases of 25% and 10% in Young's modulus and strength at break values, respectively. However, the coating materials obtained usually have low Tg values and poor mechanical properties due to flexible thio-ether bonds, low cross-linking density, and limited availability of rigid thiol monomers. Also, some unreacted thiol groups in cured polymer networks may be unreacted due to the low reactivity of thiols compared to acrylate groups, leading to a dramatic reduction in performance properties [116, 143, 144, 146, 149].

3.2. Influence of the C=C content

There are three most used techniques for incorporating acrylic polymers into WPU dispersions: physical blending, emulsion polymerization, and IPN [26]. The physical blending method involves the independent preparation of the polyurethane and polyacrylate emulsions, followed by their simple mechanical mixing at a certain proportion. This is the simplest way to compound PU and polyacrylate. However, the low compatibility between PU and polyacrylate makes the film susceptible to cracks [158]. In emulsion polymerization, the PU prepolymer's end-capping with hydroxy vinyl monomers (such as hydroxyl acrylates) introduces a double bond into the polymer structure, which is then copolymerized with acrylate monomers. Emulsion polymerization significantly improves water and weather resistances and the transparency of films, being widely used in the synthesis of waterborne coatings [24, 50, 118]. IPN is a compound polymer, wherein at least one of the components is a network crosslinking structure that is not involved in chemical bonding with the other networks. The emulsion composed of polyurethane-acrylate (PUA) should be synthesized from a PU prepolymer previously prepared. Polyurethane and acrylate form separate microphases, with an interfacial physical crosslinking between them, i.e., there is a three-dimensional “mechanical entanglement” at the interface between phases. Most UV-curable waterborne coatings cannot provide proper water and solvent resistance, nor good mechanical properties, due to their low C=C content and low molecular weight. Moreover, the water swell disparity is also affected due to the different crosslinking density and chain mobility. The control of the double bond content of the acrylate incorporated into the PU structure greatly influences the polymer's final properties [6, 23, 31, 54, 137]. This is mainly because the introduction of acrylate in WPU will significantly change its chain structure and crosslinking density. Indeed, a UV-WPU coating with a higher double bond concentration will provide films with a higher crosslink density after curing [106].

Investigating the UV curing kinetics, Zhang *et al*. [6] and Bai *et al*. [31] observed that too high or too low average functionalities were unfavorable for increasing unsaturation conversion. The sample with the highest C=C content (4.5 meq/g) showed the highest initial conversion rate. However, when the radiation time increased, the C=C conversion rate for the sample with 3.6 meq/g C=C became higher than that of the sample with 4.5 meq/g C=C, as shown in Figure 4(a).

This trend can be justified based on the influence of chain mobility. The conversion rate, i.e., the crosslinking rate of C=C bond, decreased with increased radiation time, mainly due to the molecular chain motion restriction at high crosslinking densities [31, 91]. When the average functionality of the UV-WPU is not high, the polymer chains are flexible and active, and the crosslink density can still increase with increasing functional groups. However, when the average functionality of UV-WPU is high enough, the chain movement is restricted, and the remaining active groups are unable to polymerize sequentially, causing the crosslink density to become constant. In this case, the average functionality of UV-WPU will have a minor effect on the crosslink density and its water-resistance [6]. Also, the water swell disparity is much smaller when the functionality is high (Figure 5), which can be attributed to the differences in crosslink density and chain mobility.

The thermal stability of the cured film increased by C=C content. For the samples containing 4.5 meq/g C=C and 1.8 meq/g C=C, decomposition temperatures at T5% of 295 ºC and 270 ºC were observed, respectively. The samples with a higher C=C amount showed a two-stage degradation behavior, which reveals that the decomposition mechanism is dependent on the C=C content [6, 31]. The increase in C=C content favors the increment of hardness, solvent resistance, tensile strength, and initial mechanical modulus of the samples; however, compromises their extensibility [Figure 4(b)]. When the C=C content was high [sample a, Figure 4(b)], the film showed a brittle trend and low extensibility. By reducing the C=C content [samples c and d, Figure 4(b)], the materials presented a yielding pattern with increasing extensibility and reduced tensile strength and initial modulus [31, 118]. Bai *et al*. [31] reported that a proper UV-curable polyurethane dispersion should have a C=C content of over 2.6 meq/g.

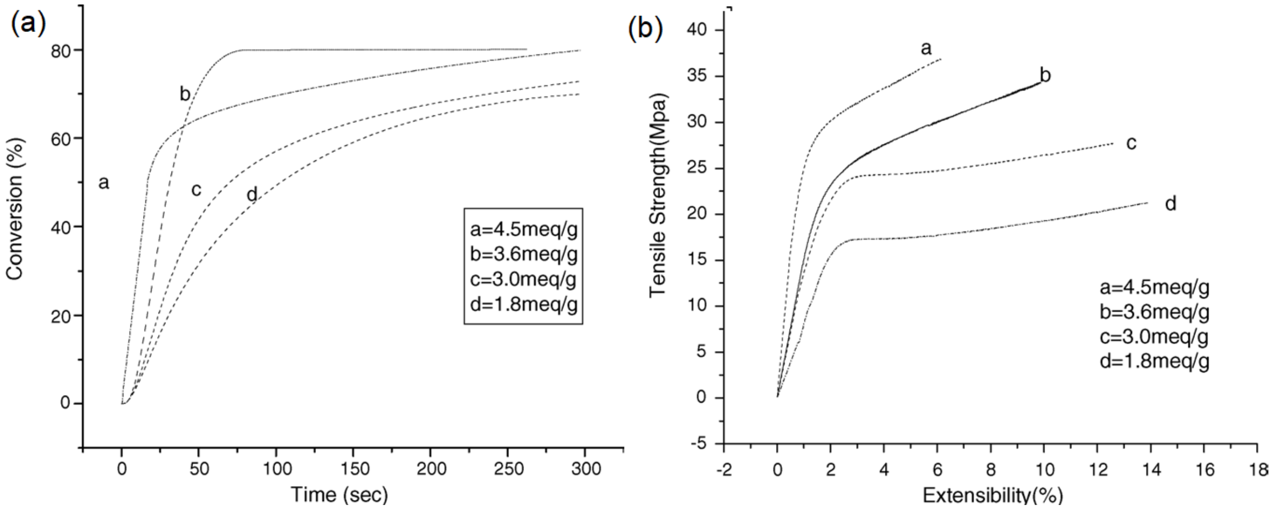

Figure 4. (a) Conversion comparison for samples containing different C=C contents, using 4% Darocur 2959 and 80 mW·cm^{-2} light intensity. (b) Stress–strain curves of UV-cured waterborne

films for the same samples [31]. Adapted with permission from Ref. 30, Bai CY, *et al*. (2006) Prog Org Coat 55:291–295. Copyright © 2005 Elsevier B.V.

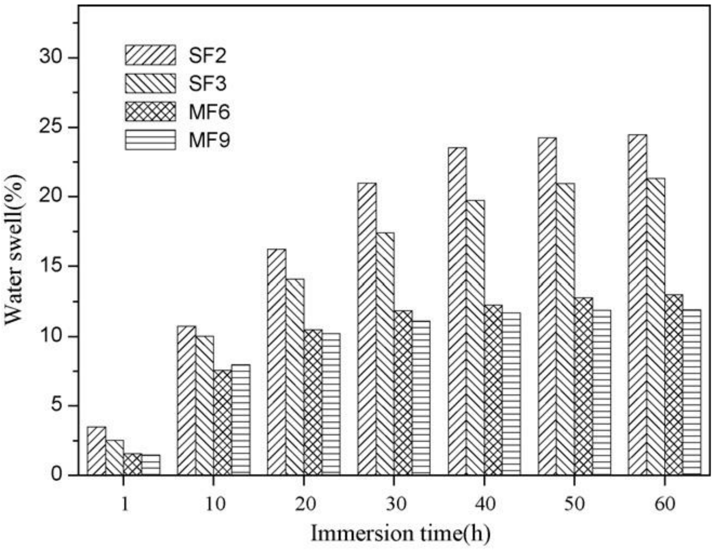

Figure 5. Water swell percentage *versus* immersion time for UV-WPU films with different C=C contents [6]. Reproduced with permission from Ref. 5, Zhang T, *et al*. (2010) Prog Org Coat 68:201-207. Copyright © 2010 Elsevier B.V.

Zhang *et al*. [6] obtained linear or branched chains by varying the terminal acrylate groups (HEMA or PETA) and the chain extenders (ethylene diamine or diethylene triamine). Thereunto, different UV-WPU samples with different average functionalities were synthesized. As a result, an average controllable functionality of the UV-WPU was achieved, reaching up to 9. Consequently, the UV-WPU samples obtained a chemical structure with similar amounts of hard and soft segments, but different crosslinking densities. This difference in the average functionality affected the material's morphology due to different chemical interactions. For the HEMA series samples (functionalities 2 and 3), the hard segments were separated from each other, being considered dispersed in the flexible segments, due to the low values of functionality and crosslinking density. When a tensile force is imposed, the HEMA samples are easily deformed, resulting in protrusions on the fractured surface and great macroscopical flexibility. However, in the PETA series (functionalities 6 and 9), the hard segments can be interconnected, forming a rigid domain system based on sufficient functionalities and crosslinking densities. Thus, PETA samples can hardly be deformed due to their more substantial cohesive energy and covalent bonds. They easily reconvert when the external force is removed, keeping the surface relatively uniform. The replacement of relatively long-distance intermolecular Van der Waals bonds by shorter covalent bonds makes the cured films' shrinkages more significant with the increase in average functionality. This problem can be counteracted by optimizing the curing conditions [6].

Another interesting factor is that acrylate monomers in the WPU formulation can affect the average particle size. When UV-WPUs were produced using the same polyol (PCD 800 g/mol), but with HEA or HEMA acrylate monomers, any significant difference was observed between the particle sizes obtained (78 nm for HEA-based WPU and 80 nm for HEMA-based WPU). However, the average particle size obtained with PETA was much higher (325 nm) than those from the dispersions containing smaller monoacrylate or mono-methacrylate chain end groups. The PETA-based dispersion had bulky tri-acrylate groups at the end of each chain, which increased the dispersion's hydrophobicity, and consequently, altered the particle size [24, 101, 116, 141].

A variation in activity between the tri-acrylate and mono-methacrylate end-cappings was observed. The curing rate and conversion of tri-acrylate functionality are much higher than those samples with mono-methacrylate functionality [33, 46, 116]. Furthermore, the reactivity of vinyl groups is lower than that of acrylate groups [31]. Hydroxy acrylates with methyl groups, such as HEMA and HPMA, produce UV-WPU oligomeric molecules with higher gel proportions than those prepared from hydroxy acrylates without methyl groups (HEA and HPA) [116]. HEA-terminated WPU showed much lower tensile strength than PETA-terminated WPU. HEA gives much more significant swelling than PETA [121]. This phenomenon is because the methyl group is electron-donating. UV-WPUs that contain methyl groups have a higher reactivity and are UV-cured more thoroughly. However, it should be noted that specific properties of UV-cured films, such as hardness and water resistance, are weak when only monofunctional hydroxyl acrylates are used in UV-WPU's synthesis. This is because the double bond content is too low, and each hydroxyl acrylate group contains only one double bond. In this way, only linear macromolecules are formed as UV-cured films. Meanwhile, there is no network crosslinking macromolecules in UV-cured materials [98, 101, 116]. Changes in C=C content had no significant effect on UV-curable WPU dispersions' zeta potential, which suggested that the emulsion had proper stability to resist aggregation [69].

3.3. Chain extender and Reactive diluents

3.3.1. Chain extenders

Chain extenders are used as additives in the production of UV-WPUs to increase the molar mass of polyurethane and improve their properties [92]. The chemical structure and length of the diol chain extender have a significant effect on polyurethanes' crystallinity and hydrogen bonds degree. Diols containing an even number of methylene groups (i.e., butanediol and hexanediol) improve polyurethane crystallinity compared to diols containing an odd number of such groups (such as pentanediol). The chain extenders most used for UV-WPU dispersions are low molar mass difunctional diols (such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, etc.), or cyclohexane dimethanol, diamines, hydroxyl-amines, etc. [101]. The addition of functional chain extenders such as polydimethylsiloxane (PDMS) [33, 120], fluorinated monomer [48, 64, 74, 77, 110, 119, 159, 160], glycidyl azide polymer (GAP), and PTMG [60] can alter the hydrophilicity and free surface energy of the coating, reducing its water absorption. The multifunctional chain extender 1,3-dihydroxy-2-propanone [40] was used as a crosslinking agent to build-up multi-armed polyurethane prepolymers, capable of offering tack-free before cure and peculiar surface and mechanical properties upon curing. Chain extenders with rigid groups such as bisphenol A can significantly improve the coating's hardness and thermal properties. However, benzene rings' introduction may result in the yellowing of coatings, since these functional groups can be easily oxidized into quinones [7, 25, 85].

Hydroxyl-terminated polybutadiene (HTPB) with two end hydroxyl groups can be used to react with isocyanate. As a soft segment, it will introduce more double bonds to polymer chains. Moreover, as a polyurethane chain component, HTPB offers the additional properties of resistances to water and low-temperature. Although the increase of HTPB content in the polymer chain harms the formation of a hydrogen bond, a positive effect is observed in the crosslinking density [23, 52]. This increase in HTPB content produces an increment in tensile strength, but a decrease in the materials' elongation property. PDMS is another option used in UV-WPU matrices. The PDMS has low surface energy, high flexibility, transparency, and excellent thermal, oxidative, and UV stabilities, therefore giving the UV-WPU films some especial properties [33, 44, 52, 54, 66, 120, 123]. However, particularly to the mechanical behavior of the UV-WPU containing PDMS, no significant improvement was observed with the increase in the chain extender content, which was attributed to the high incompatibility between the urethane (or urea) and the PDMS segments from the non-polar nature of the siloxanes. Hydrophobic silicon chains can migrate to the surface layer of the WPU during film formation and UV crosslinking, resulting in many irregular protuberances on the surface of cured films [44, 52, 66].

The incorporation of PDMS in the WPU reduced the initial speed of light curing, although it did not affect the total conversion at the end of the reaction, that is, the PDMS acted in some way as a curing retardant [33, 44, 54]. 3-aminopropyltriethoxysilane (APTES) is a kind of multifunctional oligomer with an effect similar to PDMS; it acts as a chain extender during the preparation of UV-WPUs. APTES can increase the nonlinear structure of dispersions. This multifunctional oligomer can hydrolyze into silanol in the aqueous environment and form Si–O–Si linkages by self-condensation reaction of silanol. The increase in the crosslinking density and hydrophobic Si–O–Si bonds, emerging from the addition of APTES in the cured films, directly reflects the reduction of the materials' surface energy. As Si–O–Si bonds have much lower surface energy than polyurethane, they can migrate to the surface during the formation and UV-curing of films, altering their surface properties [21, 46, 51]. Zhang et al. [51] prepared UV-WPU nanocomposites using a diol with side-chain triethoxysilane HEA-APTES using HEA and APTES. As shown in Fig.6(a), a higher crosslinking density is obtained as HEA-APTES content increases, making the systems more rigid, thus reducing the elongation and increasing the modulus. In Fig.6(b) the films' water absorption was significantly decreased with increasing the HEA-APTES content to 5.0%. This may be ascribed to the formation of a hydrophobic and crosslinked siloxane network structure, which prevented the water molecule from entering the bulk film. However, when the quantity is more than 5wt.%, the films' water absorption was higher than that of neat WPU film. On the one hand, the high content of HEA-APTES led to a decrease in the films' water absorption. Nevertheless, HEA-APTES negatively affected the photo-crosslinking of WUPU films. It seemed that the latter factor had a more substantial effect on the crosslink density and water absorption. As a result, a decrease in mechanical performance is observed in the nanocomposite films.

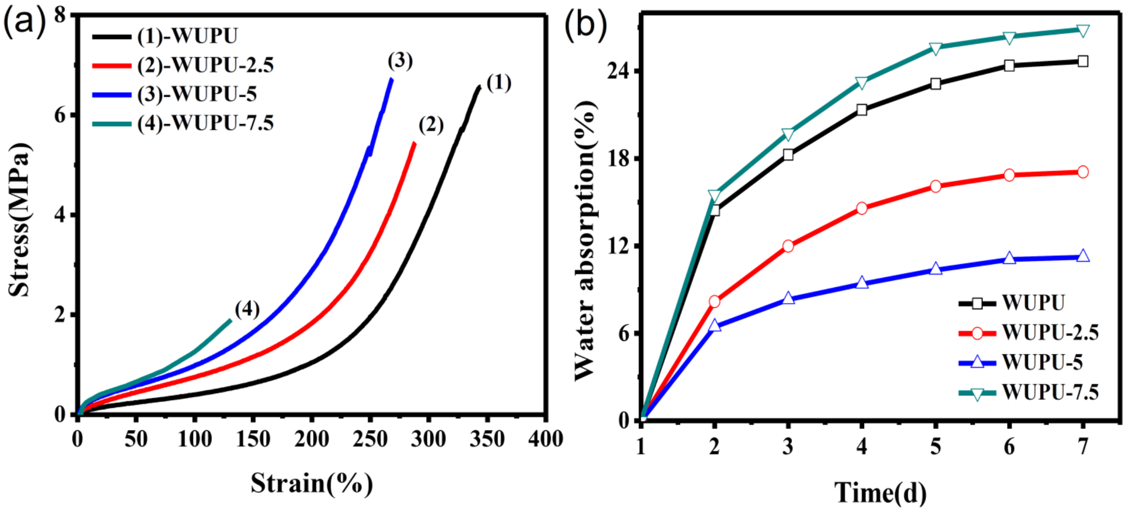

Figure 6. (a) Tensile behavior and (b) water absorption of APTES-HEA-WPU films. WUPU-x, where x is the mass weight fraction of the APTES-HEA [51]. Adapted with permission from Ref. 50, Zhang S, *et al*. (2015) Colloids Surf A Physicochem Eng Asp 468:1–9. Copyright © 2014 Elsevier B.V.

3.3.2. Reactive diluents

Reactive diluents are another kind of additive employed in UV-WPUs production. These additives decrease the curing system's viscosity and help increase the crosslinking density of UV-cured films due to their abundant carbon double bonds [44, 141, 161]. Consequently, some benefits like high curing rate, low energy consumption, high hardness, and enhanced mechanical properties are obtained. Simultaneously, high crosslinking density can prohibit the water molecular penetrating the inside of films and keep hydrophilic groups from moving towards the surface [141]. Reactive diluents as tripropyleneglycol diacrylate (TPGDA) [124, 136], trimethylolpropane triacrylate (TMPTA) [83, 96, 106, 109, 137], pentaerythritol [50], pentaerythritol tetraacrylate (PETTA) [100], dipentaerythritol hexaacylate (DPHA) and dipropylene glycol diacrylate (DPGDA) [137, 141], modified enzymes [134], trimethylolpropane tris(3-mercaptopropionate) (TMPMP) [149] among others can be added during UV-WPUs synthesis.

Li *et al*. [100] used PETA as an end-capper and PETTA as a reactive diluent to form PETA/PETTA composite systems, with a more significant amount of unsaturated double bonds, capable of creating films with higher crosslink density. The incorporation of PETTA to the PU molecule created a dense network structure after curing, causing the systems' pencil hardness to increase from 2H to 3H. The PETA/PETTA system's best mechanical properties were obtained for a PETTA content of 35wt.%. Higher amounts of this reactive diluent produced highly compacted structures with restricted diffusion and motion of PETTA chains or radicals out of networks. Consequently, it brought a reduction of the crosslinking density because of premature termination of polymerization, which was caused by partially unreacted double bonds trapped in polymeric networks. DPHA has higher unsaturation functionality than PETTA and can dramatically increase the crosslinking density in the UV curing process, improving the hardness and water resistance of the resulting films. These properties are fundamental for coatings and paints of consumer electronics, such as mobile phones, CD players, iPods, and others [141].

Xu *et al*. [22] prepared vinyl-terminated PU prepolymer dispersion through a prepolymer-mixing process and then physically blended it with butyl acrylate (BA) and TPGDA reactive diluents. With the increasing of TPGDA content, the hardness of the UV-WPU films increased gradually. This was because the polarity of the TPGDA was somehow compatible with the rigid PU segment. The increase in the content of TPGDA provided greater impact resistance and hardness to the systems, probably due to the higher hydrogen bond degree; however, the excessive increase in acrylate concentration caused these properties to fall [22, 106, 109]. When the BA/TPGDA was added, a good dilute effect on emulsion was obtained, reducing the system's viscosity. On the one hand, the molecular motion ability of the UV-WPU emulsion was enhanced, and the C=C quantity was increased. On the other hand, oxygen could spread more easily through the system, which consumed more free radicals, reducing the chances of light polymerization and increasing curing time. The addition of siloxane groups and silane coupling agents can also reinforce the crosslinking density of the system, thus contributing to increase the hardness of the coating [25, 122].

3.4. Nanoparticles as a reinforcement component

The incorporation of inorganic nanoparticles into a UV-WPU matrix is an effective strategy to enhance some properties and provide specific functionalities to this system [152]. Hardness, tensile strength, water absorption, solvent resistance, and thermal behavior of UV-WPUs can be significantly improved by adding nanoparticles like acryloyl chloride modified lysozyme [134], silver [90, 157], graphene oxide [107, 112, 113], surfactant-modified TiO_2/reduced graphene oxide [45], graphitic carbon nitride [94], and Fe_3O_4 [70, 71]. These nanoparticles also provide excellent antibacterial activity, electrical conductivity, good electronic stability, self-cleaning ability in photocatalysis, and unique magnetic behavior to the coatings. However, the homogeneous distribution and dispersion of these materials in the polymer matrix is always a significant challenge. The simple mechanical mixing of inorganic fillers in the polymer matrix is not always effective in preventing agglomeration and poor distribution, which can negatively affect the resulting composites' properties [71, 78, 103, 115]. Considerable efforts have been concentrated on the refinement of processing techniques (including colloidal-physics [87, 120], and *in situ* polymerization [88] methods), and nanoparticle surface functionalization [70, 71], silanized polyurethane [123], and *in situ* nanoparticle formation by the sol-gel process [76] to control the proper dispersion of nanosized fillers into WPU matrix. The structure and chemistry of these nanoparticles are essential factors that significantly affect their dispersibility in UV-WPU matrices. Fillers with polar functionalities in their structures, such as epoxy, alkoxy, hydroxyl, acids, amine, and others, are highly dispersible since these groups can interact actively with the polar moieties of the matrix.

The addition of antimony-doped tin oxide (ATO) to a UV-WPU matrix using the sol-gel technique contributed to a better dispersion of the nanoparticles than the same composite prepared by physical blending [76, 151]. Besides, the nanoparticle's surface modification was fundamental for achieving good dispersion. The addition of ATO increased the tensile strength of the polyurethane matrix by 317% compared to the unmodified UV-WPU. Furthermore, the ATO-modified UV-WPU coatings showed a higher initial degradation temperature than the neat UV-WPU coatings, demonstrating improved thermal stability due to the high conversion of C=C bonds (~93% in 40 s). Coatings containing 3–4 wt% ATO could absorb near-infrared radiation to effectively prevent heat transmission and heat diffusion, increasing the heat-insulating effect.

The functionalizing agents used in the surface modification of nanoparticles, in general, have C=C double bonds, which crosslink by UV-curing, improving the crosslinking density and, consequently, increasing the material properties [70]. The introduction of a siloxane unit to form a cross-linkable PU/siloxane matrix can improve the mechanical and surface hydrophobic properties of UV-WPU films. Some efficient crosslinkers alternatives have been incorporated to UV-WPU dispersions, including dispersions of silane-modified montmorillonite (O-MMT) [135], hydroxyapatite and clay modified by vinyltrimethoxysilane (VTMS) through sol-gel reaction [49, 78], hollow $Ni_{0.3}Zn_{0.5}Fe_2O_4$ (h-NZFO) nanospheres functionalized with IPDI and trimethylolpropane [71], trimethoxysilane end-capping agent (DAA-GPTMS) derived from diallylamine (DAA), (3-glycidoxypropyl) methyldiethoxysilane (GPTMS) and modified with edge-hydroxylated boron nitride (hBN-OH) nanosheets [75], vinyltriethoxysilane (VTEO)-modified Fe_3O_4 nanoparticles [70] and octavinyl polyhedral oligomeric silsesquioxane (OVPOSS) [79].

Compared to other inorganic nanofillers, silica nanoparticles have been widely used due to their high hardness, relatively low refractive index, and commercial availability. These nanoparticles can be found as colloidal silica [65, 147], aqueous silica sol [88], precipitated or fumed silica [42, 152], nano-silica generated by the sol–gel method [93]. Silica has a silanol group on its surface, capable of interacting by hydrogen-bonding with the carbonyl group of the soft segments and urethane groups of the hard segment of PU [123]. Besides, the nano-silica surface can be functionalized with specific agents to prevent agglomeration and ensure stable covalent bonds between phases. Among these agents, it can be mentioned γ-trimethoxysilylpropyl methacrylate (TMSPM) [99, 125, 147], γ-methacryloxypropyltrimethoxysilane (MEMO) [87, 89, 93, 162], PDMS [120], allyl isocyanate [42], poly (ethylene glycol) monomethyl ether methacrylate (PEGMA) [57], tetraethoxysilane (TEOS), and 3-glycidyloxypropyltrimethoxysilane (GLYMO) [108]. Furthermore, these coupling agents functions effectively as a multifunctional crosslinker and can accelerate the curing speed of UV-WPU coatings [42, 87, 93].

The addition of functionalized silica to the UV-WPU chains contributed to improving the mechanical and thermal properties of the materials. The initial thermal decomposition temperature at T5% of the UV-WPU, especially that of the hard phase, gradually increased with the incorporation of growing levels of silica to the segmented PU [62, 87-89, 99, 103, 150]. The modified silica increases the prepolymer solution viscosity and, consequently, the particle size of the dispersion compared to unmodified silica [51, 62, 88, 99, 120, 150].

Other fillers used are pigments. Pigments and nanoparticles with high UV light are harmful to photopolymerization due to the inhibition of free radicals that lead to binder polymerization, thus decreasing the curing degree in pigmented films [102, 163]. Particles such as carbon black (CB) tend to agglomerate in dispersions and present a higher UV-light absorbency than other pigments, which causes the photoinitiator efficiency to decrease and the unsaturation conversions C=C of UV-WPU to be impaired [102]. On the other hand, zinc oxide (ZnO) nanoparticles have been used as an alternative to organic photoinitiators. ZnO reacts with water under UV irradiation to form hydrogen peroxide, and then active free radicals are generated to initiate the vinyl monomers photopolymerization [164]. An amount of 0.25% wt.% ZnO showed a photoinitiation efficiency equivalent to 3–5 wt% of 2-hydroxyl-2-methyl-1-phenyl-1-propanone (Darocur 1173) [115, 116]. However, the efficiency of this inorganic photoinitiator is limited to the presence of water. All the nanoparticles mentioned before must be added to UV-WPU systems in an ideal concentration. Above, they cause aggregation and heterogeneous distribution in the nanocomposite, compromising the properties of hardness, gel content, and mechanical resistance [45, 70, 76, 108, 135], as shown in Figure 7. Of course, it must be mentioned that introducing inorganic fillers into the resin matrix will roughen the surface of coatings.

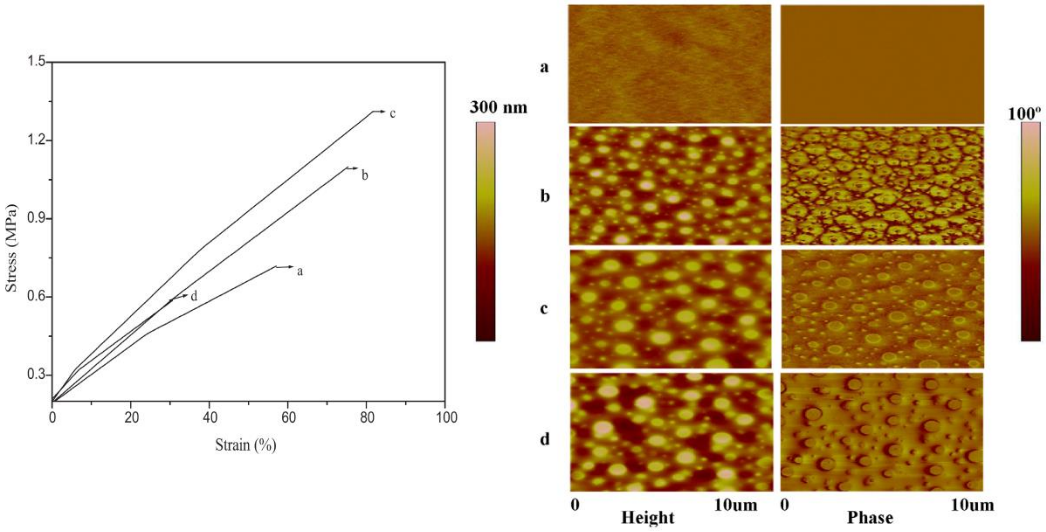

Figure 7. (a) Stress–strain curves for the hybrid films: (a) UV-WPU, (b) UV-WPU-Silica-5, (c) UV-WPU-Silica-10, (d) UV-WPU-Silica-15; (b) AFM images of topography (left) and phase (right) for: (a) UV-WPU, (b) UV-WPU-Silica -5, (c) UV-WPU-Silica -10, (d) UV-WPU-Silica-15 [88]. Adapted with permission from Ref. 87, S. Zhang S, *et al*. (2011) Prog Org Coat 70:1–8. Copyright © 2010 Elsevier B.V.

3.5. Effect of ionic groups content

The production of water-based polyurethanes is related to incorporating a high number of hydrophilic groups in the polymer backbone, which enable solubility in water. For this, it is necessary to add hydrophilic chain extenders and blocked amine-containing ionic groups (such as dimethylol propionic acid with carboxyl groups), that react with the prepolymer. Non-ionic UV-WPU can be prepared similarly when the ionic center is replaced by a lateral or terminal hydrophilic ether chain [96, 148]. Most commercial PU dispersions are only anionically stabilized with a dihydroxycarboxylic compound, such as, for example, DMPA and DMBA [38]. Although hydrophilic groups are essential for ionic dispersion, they retard drying and reduce hydrolytic stability [52, 68, 84, 126]. Therefore, it is essential to minimize the emulsifier's content as much as possible while maintaining a stable dispersion. The emulsifier's ideal amount will depend on the original PU content, phase inversion temperature, and solvent affinity for water. In general, the amount of emulsifier is around 4% wt.% (based on the total solids content). When the hydrophilic group content (–COOH) in the UV-WPU resin is too low, it cannot be emulsified entirely, becoming unstable and partially condensing into blocks [80, 95]. The increase in the amount of DMPA causes a reduction in the particle diameter, due to the higher density of ionic groups and the stabilization mechanism of ionomer dispersions [11, 32, 84, 106]. As more carboxyl groups are incorporated into the UV-WPU structure, some characteristics such as adhesion, gloss, impact strength, and flexibility vary slightly, whereas the pendulum's hardness increases substantially. This can be attributed to more significant interchain interaction through coulombic forces and hydrogen bonding, derived from a higher DMPA content incorporation in the rigid segment [92].

The location of the ionic group and main backbone flexibility also affect the particle size. For example, the dispersion containing ionic groups in the soft segment has a much smaller particle size and higher viscosity than those containing ionic groups in the hard segment. This is because ionic groups can easily tailor the surface during dispersion owing to the easier change conformation in soft segment [24, 33, 50, 61]. In the particle and water interface a double layer is formed by the dissociation of ionic groups. The layer binds to UV-WPU chemically, and the counterion migrates into the water phase around the particle. The interference formed between electric double layers of different particles causes the repulsion between them, contributing to the dispersion stabilization. Adding an inert electrolyte to the ionomer dispersion reduces the range of bilayer repulsion and induces coagulation by providing additional ions at the water phase [11, 34, 92, 126]. Viscosity is a property strongly dependent on the size and conformation of the chains. As the ionic groups in the polymer backbone increase, the mutual repulsion of similar charges causes the chain to expand, resulting in a viscosity increase of the UV-WPU dispersion. Furthermore, interchain associations resulting from hydrogen bonding between urethane and/or ureylene groups make the chains assume a more expanded conformation, which also contributes to the increase in viscosity. However, the intrachain hydrogen interactions formed can favor obtaining compact aggregates of UV-WPU ionomers, thus reducing viscosity. Therefore, the viscosity of the UV-WPU dispersion will be a consequence of the competition between these two phenomena [92].

Some authors have demonstrated that the amount of carboxylic acid introduced into the PU chain to make it water-dispersible may affect the curing kinetics by acting on the viscoelastic properties [101, 165]. It was observed that the final conversion decreased as the acid content was increased. An increase in DMBA content from 4wt.% to 8wt.% caused the gel content to increase from 81.5% to 88.8% and the water absorption decreased from 32.1wt.% to 28.5wt.%. This occurs due to the formation of chain entanglement, hydrogen bonding, and Coulomb interaction in the hard segments. The intermolecular interactions are enhanced, resulting in increased gel content and water resistance. In addition, denser films can be formed due to a decrease in particle size. However, when DMBA content is greater than 8wt.% both the gel content and the water-resistance decrease. The excessive increase in intermolecular interactions amount restricts the molecular movement within the cured film and the reduction in the curing degree directly reflects in the reduction of the gel content and water resistance. Comparing the effects of DMBA and DMPA emulsifiers, Kim *et al*. [50] observed that a dispersion containing a much finer particles was obtained in the presence of DMBA. Because the DMBA has a pendant alkyl group larger than DMPA, it is believed to have caused a more significant steric hindrance to the attack of carboxylic groups by isocyanate groups, leaving more carboxylic groups available for subsequent ionization.

During the first and second stages of UV-WPU formation, it is common to use a solvent to viscosity reduce the reaction medium. The addition of acetone, for example, results in decrease of the viscosity medium, and also self-assembly of isocyanate-terminated prepolymer chains. Hard and soft segments are randomly located while dissolved in acetone. The solvents acetone and MEK are very suitable for controlling the viscosity during the chain extension step. In addition to being inert in the PU synthesis and non-reactive to isocyanates, they are miscible in water and easily removed by distillation due to their low boiling points (~56 °C). An additional advantage of acetone is that it reduces the high reactivity of amine-based chain extenders with isocyanates through the reversible formation of ketamine [10].

3.6. Effect of the neutralization degree

The alkaline compound necessary to neutralize the carboxylic acid groups and obtain a stable aqueous dispersion plays a fundamental role in both the polymerization kinetics and the hydrophilic character of the UV-cured polymer [161]. The neutralization degree influences the particle mechanism formation. When the neutralization degree is below 70%, the particles tend to aggregate and, therefore, do not stably disperse in water. On the other hand, increasing the neutralization degree causes a reduction in the WPU particle sizes. The higher number of dissociated carboxyl groups after neutralization contributes to stabilization. The viscosity of the dispersions also increases with the neutralization degree due to the increase in the hydrodynamic volume of the finer particles [95, 126, 128, 130]. The increase in the neutralization degree also reduces the storage modulus, tensile strength, and glass transition, but contrarily, it increases the elongation at break. The neutralization probably results in decrease of the local ordering of the hard segments regions, enabling the phase mixing due to the reduction of hydrogen bonding degree. This means that some C=O groups previously bonded to the NH of the urethane groups may be switched to bond with $^{+}NR_3H$ (TEA). It seems that TEA works as a plasticizer [127]. As shown in Table 1, TEA is the most used agent to neutralize carboxylic groups and to produce ionic centers to stabilize the polymer particle in water.

Feng *et al.* [116] evaluated the effect of different neutralization degrees on the gel content of UV-WPUs. The gel content gradually decreases as the neutralization degree is increased to 100%. When the neutralization degree is 75%, the gel content is 90.4%. For neutralization degrees higher than 75%, lower gelation rates were observed, which was related to a high content of TEA, and consequently, of active radicals at a short period during UV-curing. As a result, the UV-WPU was quickly UV-cured, leading to a viscous film and the cage effect that affects the subsequent UV-curing process. The increase in the neutralization degree caused a gradual increase in the film's hardness and a progressive reduction in water resistance. However, considering the overall product's properties, UV-WPU dispersions and UV-cured films had the best performance when the neutralization degree was 100%.

3.7. Dispersion process

The next step to neutralize the acid groups formed involves dispersing the WPU in water. In polar solvents, such as acetone, the PU ionomer solution spontaneously disperses when water is added. The transformation of an organic solution into an aqueous dispersion takes place in several steps. According to Dieterich [166], the initial addition of water leads to a sharp drop in viscosity due to the decrease in ionic bonding. The ionic interaction formed by the neutralization of the ionic center is a reversible process, and water reduces these links between the centers and the molecular chains. As more water is added, the hydrophobic chain segment decreases due to the reduction of acetone concentration, and the hydrophobic-induced interaction by the hydrophobic segment increases its viscosity. Further addition of water leads to turbidity and the formation of a dispersed phase, followed by rearrangement to microspheres in which ions are formed superficially in the aggregate particles, resulting in reducing the viscosity [34]. As a result, PU nanoparticles self-assemble into a core-shell structure, where soft hydrophobic segments are surrounded by rigid hydrophilic segments [10]. Since most macromolecular chains are in great length with infinitesimally small cross profile, they curl to form a ball of string morphology [155]. Finally, the solvent used in the synthesis (usually acetone) is removed and a stable suspension, with a zeta potential of -40 to -65 mV, and a particle size of 10–300 nm is obtained. Typically, the finished urethane dispersion has a pH 7–8 and a solids content of 25–40 wt.% [21, 32, 33]. These dispersions remained stable without any change after 6 months of storage at room temperature [54, 106, 137, 143].

Asif *et al*. [126] used deionized water, butyl alcohol, and methyl alcohol as dispersion mediums to investigate the effects of their dielectric constants on particle size with a 100% neutralization degree. The average particle sizes increased as the dielectric constants decreased. The particle size in the different dispersion media followed the order of water <methanol <butanol. The higher the dielectric constant of the dispersion medium, the more significant is the dissociation of carboxyl groups. The concentration of dissociated groups mostly governs the average particle size; thus, higher dissociation is possible in high dielectric constant media (e.g., water).

For these formulations to be applied, formulators in coating industries always balance the viscosity, curing speed, and final properties for a given UV formulation. It is crucial to measure the viscosity of the dispersions as a function of the solids content since, for aqueous UV-curable resins, the water must be evaporated before photo-irradiation. Thus, a higher solid content with the same viscosity is beneficial in terms of energy efficiency.

In WPU dispersions, it is possible to obtain the ideal viscosity for the application, because the viscosity of dispersions is generally independent of the molecular weight of the polymer, it will depend on the particles size and the amount of solids present in the dispersion [126, 127, 167]. The rheological behavior of WPU dispersions belongs to pseudoplastic fluids [11, 82, 92, 130, 145]. A pseudoplastic and thixotropic behavior is interesting for coating applications, especially for spraying. When the coatings are sprayed from the spray-head at a high velocity, the greater shear rate reduces the apparent viscosity of the coatings. Coatings with lower viscosity (or good fluidity) are uniformly dispersed into fine spraying, giving a shiny and generous coat. During storage, the high viscosity of the coatings facilitates transportation efficiency and economic benefit [92].

3.8. Influence of the Photoinitiator

The photoinitiator is extremely important in UV-radiation curing as it controls both the initiation rate and, the penetration of the incident light (cure depth). For water-based systems, the photoinitiator must be uniformly distributed in the film after the drying stage. For most photoinitiators, this can be achieved only by incorporating it into the WPU resin before the dispersion in water. The photoinitiator molecules will remain in the micelles until their coalescence by water removing, being then randomly distributed in the dry coating. So, the compatibility between the photoinitiator and WPU dispersions is required to properly cure the films [66, 92, 165]. The photoinitiator choice depends directly on its solubility in the medium, compatibility with resins, and, of course, the matching between its absorption peak and the waveband of the radiation source [32]. The photoinitiator will form active free radicals after energy absorption in the ultraviolet region, causing the addition polymerization of C=C bonds in monomers or oligomers. Fig. 8 shows several photoinitiators' influence on a WPU coating [165].

Some photoinitiators, such as hydroxyphenyl ketones (Irgacure 2959 and Darocur 1173), are partially soluble in water and can be incorporated into the aqueous dispersion to a certain concentration (1–5 wt.%) [68, 165]. Fast and extensive curing can be achieved by using 4 wt.% of Darocur 1173. This photoinitiator appears to be particularly well suited when low temperatures are required for the drying and curing processes (~55 °C). For faster drying steps, under higher temperatures, this liquid photoinitiator is partially lost, and, in this case, solid hydroxyphenyl ketone (Irgacure 2959) is used, which has a higher thermal resistance. Masson *et al.* [165] confirmed that the photoinitiator content of the sample based on Irgacure 2959 remained essentially constant upon heating at 80 °C up to 1 h.

Another critical factor is that the amount of photoinitiator affects the final properties of the UV-WPU. Generally, the best properties are obtained with 3–4 wt% of the photoinitiator concerning the solids content [73, 118, 167]. The relationship between photoinitiator concentration and curing rate can be expressed by the general free radical polymerization rate equation (1) [91]:

$$V_P = k_{\mathrm{p}}(\mathrm{fk_d/k_t})^{0.5}[\mathrm{M}][\mathrm{I}]^{0.5} \tag{1}$$

where V_P represents polymerization rate, *[M]* is the monomer concentration, *[I]* represents the photoinitiator concentration, k_d is the disproportionation termination rate constant of the termination reaction, and $\mathrm{k_t}$ represents the rate constant of the termination reaction. According to this equation, the polymerization reaction rate is proportional to the square root of the photoinitiator content. Consequently, within a specific range of curing time and concentration, the higher the photoinitiator concentration, the higher the crosslinking degree. However, as the photoinitiator content is above 5wt.%, the C=C conversion is slightly reduced with further increasing of photoinitiator. According to Lambert-Beer law, the light intensity behaves like a decreasing exponential as a function of the photoinitiator content increase [91].

The higher the photoinitiator content, the higher the amount of UV light absorbed, reflected, or scattered. This will not only reduce the radiation intensity distinctly but also generate abundant active free radicals on the UV-WPU film surface, leading to its rapid curing of C=C bonds. Meanwhile, the network structure reticulated on the film's surface can hinder the incidence of UV light, which reduces the absorption of this radiation by the bottom layer of UV-WPU materials. As a result, the gel content decreases slightly as the photoinitiator is in excess [66, 91, 101]. Also, the high concentration of photoinitiator will produce an excess of free radicals, which can easily combine each other, interrupting the chain growth and decreasing the curing rate [22, 86, 111]. While the excess of photoinitiator leads to high cost, the insufficient amount of it generates a lower number of free radicals than necessary for the reaction, resulting in a low conversion of double bonds. Furthermore, excessive photoinitiator could lead to a high cost [22, 111].

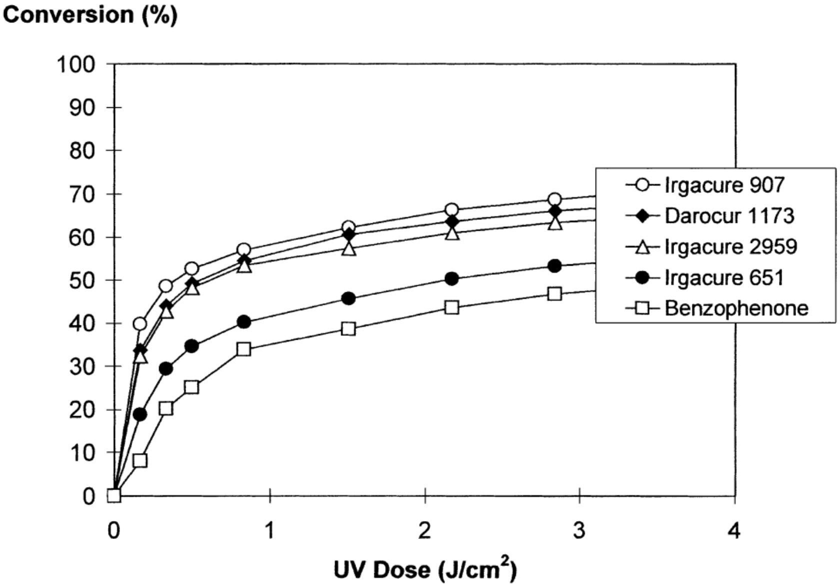

Figure 8. Influence of the photoinitiator on the UV-curing of a WPU coating. Temperature: 25°C; light intensity=60 mW/cm^{-2}; [photoinitiator]=1 wt.% [165]. Reproduced with permission from Ref. 164, Masson F, *et al*. (2000) Prog Org Coat 39(2–4) 115–126. Copyright © 2000 Elsevier Science S.A

3.9. Curing process

Waterborne UV-curable coatings are crosslinked through a two-step process: water evaporation, and UV-curing. In any industrial application of waterborne UV-curable coatings, the drying step will be the parameter that will control the curing line's speed since it is the slowest process [127, 165]. In the water flash-off step, the physical entanglements occurred due to the approximation between the WPU nanoparticles to give a tack-free dried film [22]. The drying conditions (water drying rate and temperature) have significant effects on the surface properties and coatings' morphology. Insufficient or speedy drying can cause cracking, flaking, and bubble formation on the cured coating [24, 168]. In the second UV-curing step, radicals formed by activated photoinitiators break the acrylate double bond resulting in a crosslinking structure [24, 106]. Several factors determine the UV curing behavior, including the wavelength and intensity of radiation, the species and concentration of photoinitiator, reaction temperature, the viscosity of the acrylate formulation, the reactivity of functional groups, and others [22, 33]. The difference in heat capacity between cured and non-cured materials, for example, decreased as a function of the photoinitiator concentration, which means that the crosslinking degree is higher for systems containing a lower photoinitiator content. This is because an increment in the photoinitiator concentration increases the termination reactions, leading to a reduction in the crosslinking degree [32].

The increase in temperature results in increase of the reaction rate due to higher segmental mobility of the polymer chains, making the unsaturation sites more accessible for polymerization (Figure 9) [32, 142]. Masson *et al*. [165] demonstrated that a single pass under the UV lamp at a 20 m/min. speed was sufficient to polymerize 90% of the acrylate double bonds when the sample temperature was 100 °C, compared to only 30% at ambient. Based on these results, it is recommended to irradiate the hot sample immediately after performing the drying step, if acceptable for the substrate [32, 161, 165]. Faster and more complete polymerization can also be achieved by adding a diacrylate monomer to the dispersion to act as a reactive plasticizer. The maximum rate of polymerization shifts gradually for longer times as both photoinitiator content and temperature decrease. Thus, it is evident that at the end of the reaction, diffusion controls the reaction. The curing rate and the conversion increase with increasing the functionality of the end-capping groups, because coatings with higher functionality are easily activated and continue the reaction [24]. The exposure time to ultraviolet radiation, that is, the curing time also has a significant effect on the crosslinking of the material. When the curing time is short, the double bonds are not available entirely. When the curing time is prolonged, the curing degree remains unchanged [22].

Bai *et al.* [31] evaluated the effect of light intensity on the material's polymerization rate. The conversion of C=C bonds was low when the light intensity was 80mW/cm^2 and increased as the light intensity increased until a specific maximum value. With the increase in light intensity, the number of radicals generated is higher, contributing to the inhibition of the negative effect of oxygen. However, when the light intensity is high enough, the radical-radical termination rate becomes faster than that of chain propagation, so the conversion is reversed or, at least, kept constant.

In general, the polymerization rate profiles of UV-curable prepolymers exhibit several typical features, which are autodeceleration, structural heterogeneity, and unequal functional group reactivity. During curing, the initial portions of curves involve a rapid increase in rates, while the second phases of polymerization involve a less fast increase and have generally been referred to as autoacceleration, that is, the polymerization rate increases despite the consumption of prepolymers. During autoacceleration, the mobility of radicals decreases dramatically, which leads to a reduction in the termination rate, as this step becomes controlled by diffusion. Finally, the polymerization reaction reaches a maximum rate and then begins to decrease. In this region (called autodeceleration) the vitrification crosslinking restricts and eventually stops the propagation. In these polymers, the bulk mobility of radicals is severely hindered, leading to a diffusion-limited termination mechanism [127]. According to Jansen *et al*. [169], acrylated prepolymers capable of hydrogen bonding exhibited 3–6 times higher polymerization rates than their non-hydrogen bonding counterparts.

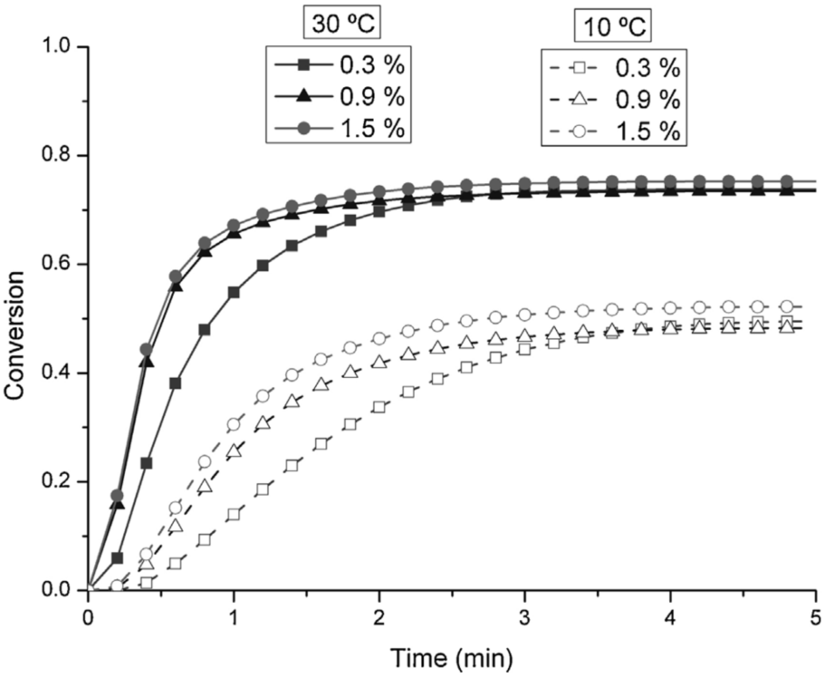

Figure 9. Curing conversion of UV-WPU sample at 10 and 30 °C, using different photoinitiator amounts [32]. Reproduced with permission from Ref. 31, Llorente O, *et al*. (2016) Prog Org Coat 99:437–442. Copyright © 2016 Elsevier B.V.

Dual curing systems (UV/air and air/UV) have also been explored [138, 139]. Such systems exhibited higher hardness than both coatings cured only by UV radiation, as can be seen in Fig. 10. In the structure of the dual-curing coating films, it was possible to detect the occurrence of both curing mechanisms: bulk free-radical polymerization and oxygen-dependent oxidation polymerization. The authors [138, 139] stated that air-drying results in the formation of a skin layer with a higher crosslinking density. In air/UV dual-cured coatings, the initial air-drying to form a layer with a high crosslinking density acted as a barrier for the diffusion of oxygen to the inner layer of the film. This process was followed by rapid UV post-curing, which was the primary curing mechanism at the inner layer. The inner layer comprised more unsaturated double bonds, and a higher crosslinking density was therefore obtained after UV post-curing.

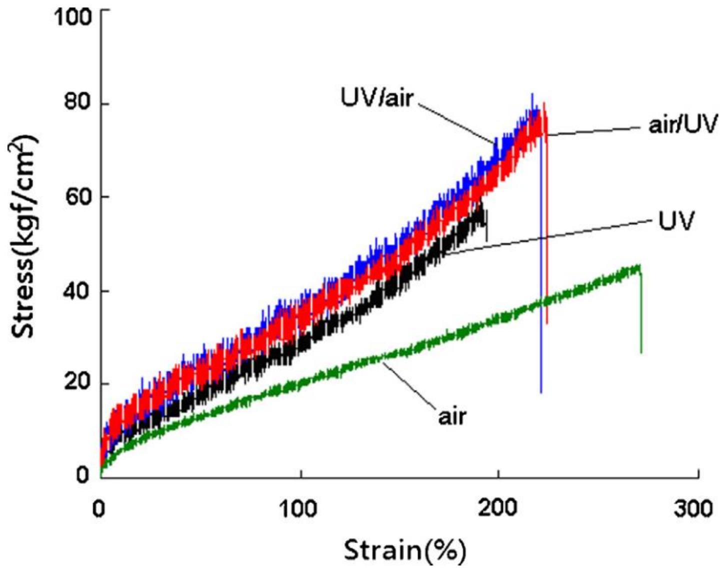

Figure 10. Stress-strain curves of UV-WPU coatings prepared using different curing processes [138]. Reproduced with permission from Ref. 137, Chang, *et al* (2013) Prog Org Coat 76(7-8):1024–1031. Copyright © 2013 Elsevier B.V.

3.10. Applications

Waterborne UV-curable coatings have the performance and environmental requirements necessary for industrial applications as substrate protectors, such as wood, metal, automotive parts, synthetic leather, fabrics, and paper [43, 91, 110, 138, 153, 163, 165]. They can also be applied in the form of ink for flexographic printing packaging materials, magazines, and miscellaneous pieces of printing sectors [93]. For outdoor applications, these coatings may require light stabilizers, mainly UV absorbers, and HALS radical scavengers, to improve their weathering resistance and ensure efficient protection of the organic substrate against sunlight [153]. Mao *et al*. [91] applied UV-WPUs to coat cotton fabrics and noted that they have outstanding stability to UV light, although the color of the coated cotton fabrics turned slightly dim with prolonged UV curing time. The color fastness of the UV-WPUs-coated cotton fabrics can be improved to 4–5 grade with increasing the UV radiation and C=C content. Consequently, the UV-curable polymeric dyes with higher functionality are amazing to be applied in textiles and other fields. The simple mixture of castor oil-based cationic WPU and acryloyl chloride modified lysozyme, followed by UV-curing, provided the coatings antibacterial properties [134]. Compared to thermally curable coatings, UV-curing technology is considered environmentally friendly, since the formulations release minimal amounts of VOCs and use less energy. Although the UV-curing process has been thoroughly investigated, as well as the resulting crosslinked polymers' properties, there is little information about the weathering resistance of waterborne UV-cured coatings.

The application of UV-cured polymer coatings is limited to flat objects with small and simple shapes, such as tabletops, doors, and wooden panels. The coating of a substrate with a complex configuration may result in shadow zones unreached by the UV radiation, which would lead to its incomplete curing. Or pieces of thick layers could have their internal layers curing compromised, due to the limited light penetration. The oxygen inhibition resulting from molecular oxygen scavenging radicals is a significant limitation as it reduces the overall efficiency of UV-curable coatings. Other limitations can be detected for conventional UV-cured coatings, like non-uniform crosslinked films, and high internal stress.

Different methods have been developed to avoid the harmful effect of oxygen inhibition. These methods comprise purging inert gases, providing physical barriers, increasing light intensities [170], and photoinitiators content~~s~~, adopting dual-curing hybrid photopolymerization [53, 138], and adding hydrogen-donating chemicals such as tertiary amine [171] or thiol [149], which consume oxygen during curing. Thiol–ene photocurable reaction, also known as click reaction, has been used in conventional and waterborne radiation-curable coatings, due to its lower oxygen inhibition, uniform curing, and low-stress development.

Organic coatings or paints give the aesthetic appearance and protect against corrosion. The aesthetic properties of coatings, such as color and brightness, can be manipulated as desired, but they must be committed to preserving the surface against environmental influences, including moisture, radiation, biological deterioration, or damages from mechanical and chemical origin. This refers to both interior and exterior applications. Typical corrosion-resistant coatings protect metallic surfaces mainly by two mechanisms: acting as a physical barrier to isolate the substrate from a corrosive environment, or containing inhibiting agents (usually pigments) in their composition, which interact with a vehicle component and inhibit corrosion [1]. There must be a viscous flow of polymer chains near the coating surface so that it tacks to the substrate. In terms of tack and chain mobility, UV-WPU coatings with cyclic structures are less efficient than those with linear architectures and similar molar masses. Tack free before curing is an essential property for a resilient flooring application, for example, since its coated surface can be embossed without sticking to the embossing roll [40, 46, 50].

4. FUTURE PERSPECTIVES

The reduced consumption of fossil fuels like coal and natural gas in different areas is a current trend nowadays. In the synthesis and manufacturing of polymeric materials, the replacement of petroleum-derived materials by renewable energy sources is an emergent and promising field.

UV-curable waterborne polyurethane coatings bring some attractive benefits to the polymer field, such as the waterborne technology that reduces/eliminates the need for solvents, fast and low energy UV-curing, and the tailorable chemistry of polyurethanes. Hence, these systems are capable of providing cleaner power, appreciable convenience, along with significant time-saving. Other advantages include the extended durability, increased service life, easy application, cleaning of painting equipment, drip lowered on vertical surfaces, short drying time, flexibility, and prices versus income. However, commercialization and market growth are strongly dependent on the characteristics of low water resistance and weather resistance. For this, the combination of waterborne PU with other monomers can solve this problem. Studies from the waterborne PU market anticipate a rise through the impetus caught by the global construction industry, especially expected to be prominent in the emerging economies [172]. The Asia Pacific (including China, India, Malaysia, and Indonesia) is the most promising region globally for the inclusion of waterborne PU. Similar high growth rates can be seen in the Latin American area. It is also expected to have very high growth in North America and Europe, resulting in a very positive growth rate for the construction industry in these regions […].

[We have to highlight the positive points of these systems, but what are the remaining process and final properties inconveniences ??? What solutions should research aim for? What still has to improve on these materials??].

5. CONCLUSION

The UV-curable WPU will continue to find broad application in industry and academic field. It guarantees high productivity, excellent quality, and low environmental impact. The process involves some stages: polymer spheres dispersed in water, water evaporation, tightly packed polymer particles (remaining an amount of water), particle deformation – coalescence and forms a dry film, UV irradiation, and UV cured film. The advantages of PU waterborne is to reduce or eliminate solvent; the benefits of UV is a quick cure, low energy cure vs thermal ovens, and the advantages of PU is tailorable chemistry to design performance. The result of such materials is a tremendous diversity of possible polymers, thus enabling a vast range of variations and enhancement of material properties and applications. The basic understanding of these materials' chemistry and mechanistic aspects has reached a level where tailor-made formulations suitable for a particular application may be designed. There is, however, an enduring need to refine these systems to improve their physical properties so that their potential application areas are extended. […].

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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AUTHORSHIP CONTRIBUTIONS

L.D and O.B. had the idea to organize this review to support L.D.'s PhD’s thesis. L.D., H.L.O. and F.T.G.D. designed the databases search for articles and constructed the discussion of the paper. O.B. and M.S. made a critical correction of the document. All authors read and approved the final manuscript.

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Table 1. Composition and properties of the UV-cured WPU selected in the databases search.

Polyol (g/mol)	**Isocyanate**	**Catalyst**	**Emulsifier**	**Chain extender/ reactive diluent**	**Solvent**	**Acrylic prepolymer**	**Nanofillers**	**Neutralizing agent**	**Inhibitor**	**Photoinitiator (wt%)**	**UV light intensity/Curing time**	**Solid content (wt.%)**	**Particle size (nm)**	**Gel content (%)**	**Hardness**	**Tensile strength (MPa)**	**Elongation at Break (%)**	**Thermal degradation at $T_{10\%}$ (°C)**	**Water absorbability/(%)**	**Potential application**	**Ref.**
CO_2-polyol	MDI	–	DMPA	–	MEK	PETA/ HEA	–	TEA	–	(3%) Irg.2959	0.5-2017 mW/cm^2	–	30–96	66–88	–	29–67	9.6–150	–	8–14	–	[9]
DAP (1000–2000)	IPDI	DBTDA	DMPA	BDO	acetone	HEMA	–	TEA	–	(0.3%) Irg.184	200 W 5 min	35%	365–746	58–62	–	–	–	–	–	–	[142]
Desmo 1019–55	IPDI	DBTDL	DMPA	–	acetone	TriSH or DiAE	–	TEA	–	(1–1.5%) Irg.2959	600 mW/cm^2	40%	100–200	99	(Pencil) 7H	23.8	40.5	–	–	–	[143, 144]
DME	IPDI	DBTDL	DMPA	TMPMP	acetone	HEMA	–	TEA	–	(2%)BPO/HCPK	1000 W	30%	380	91–97	(Pencil) 4H–6H	10–19	76–176	263–291	2.3–3.5	Coating	[149]
ETP	IPDI, HMDI	DBTDL	DMPA	Non-ionic diol	DMF, acetone	HEA or HEMA	SiO_2-MSMA	TEA	–	(3–5%) Irg.2959, Irg.500	1000–2200 W 10 min	33–40%	46–86	92–94	(Pencil) H–5H	–	–	230–316	18–28	–	[147, 148]
HBP (H10–H40)	IPDI, TDI	DBTDL	SAN, DMPA or MA	–	THF or dioxane	HEMA, HEA or HPA	LDH or TMSPM	TEA	HQ or MEHQ	(1–2%) Irg.2959, Dar1173, Run1103	80 W/cm 20–250 s	30–40%	30–458	49–97	(Pencil) 2B–4H	8–22	35–91	200–310	6–35	Coating	[11, 125-133]
PBA (2000)	IPDI	DBTDL	DMPA	TMP	acetone	HEMA, HEA or PETA	SiO_2	TEA	HQ or MEHQ	(3–4%) Irg.184 Irg.2959	200 W 2 min	15–45%	34–82	94–96	(Shore A) 82–91	4.2–28	180–206	250–280	3.3–6.2	–	[9, 103, 145]
PCD (500–2000)	IPDI, TDI, IAAE/ HMDI	DBTDL	DMPA or DMBA	PDMS, silicone, PEG400, PFPE, TPGDA, PCL/PDMS/PCL or HTPB	MEK or acetone	TMPMe HEMA, HBA, HEA or PETA	SiO_2	TEA	HQ or MEHQ	(3–4%) Dar1173 Irg.2959 Irg.500 Micure HP-8	40–3000 mw/cm^2 20–250 s	15–35%	40–740	62–98	(Pencil) H–4H or (Shore S) 43–57	3–34	20–620	260–350	1.3–28	Coating	[24, 33, 52, 103, 118-124]
PCL (500–2000)	IPDI	DBTDL or Bicat-8113	DMPA or DMBA	DETA, IPDA, PDMS, PETTA, DMEA, MDEA, MPEG, CO,AESO, GAA,EDA	acetone or ethyl acetate	TMPMe HEMA, PEDA, HEA or PETA	SiO_2 with TMSPM, carbon black, gelatin with VTMS or β –CD	TEA or AC	HQ or MEHQ	(1–5%) Dar1173 Irg.2959 Chem-73W-CR	8 W/2 h or 100–3000 W; 0.1–6 min	15–35%	14–150	22–97	(Pencil) HB–3H or (Shore A) 75–91	0.1–38	6–560	200–310	2–36	Coating, textiles printing and surface sizing agents	[6, 20, 31, 52, 59, 97-105]
PEA (2000)	TDI	–	DMPA	TMPTA	NMP	HEMA	SiO_2-DMCS	TEA	–	Irg.2959	1000 W	32%	–	–	Pendulum 0.53–0.62	14–16	77–85	–	–	–	[152]
PEG (400–2000)	IPDI, TDI, HDI	DBTDL	DMPA	TMPTA, TPGDA, MPTES, DEOA, TMP,GMA VHSO, BA, EG, APTES, DETA,	MEK, NMP, DMF or acetone	HEA, HEMA, PETA, DPPA	SiO_2, (SiO_2 with MEMO or MPTS), Me-β-CD, $AgNO_3$ or g-C_3N_4	TEA	HQ or MEHQ	(1–6%) Dar1173, Irg.500, Irg.2022, Irg.2100, Irg.2959, Irg.184, TPO or HCPK	15–1000W, 1–30min or 125–400 mW/cm^2 180 s	30–50%	54–2000	54–98	(Pencil) HB–5H or (Shore A) 65–90	0.4–17	20–483	200–350	1.3–12	Textile industry, antibacterial coating, screen printing ink or food packaging	[7, 21, 73, 83-96]

				MMA, and E51																	
PET	IPDI	T-12	DMPA	–	acetone	HEMA	SiO_2-TEOS	TEA	HQ	(3%) Irg.2959	1000 W 8 min	56%	74–489	–	(Pencil) H–5H	–	–	250–290	8–28	–	[150]
PIDG (2000)	IPDI	DBTDL	DMPA	BDO and EDA	acetone	PETA	ATO-MPS	TEA	–	(3%) Irg.2959	8W/cm 40 s	30%	–	92.7	–	18–38	116–142	–	–	–	[151]
pNGA (600)	IPDI	–	DMPA	DMEAE PET3MP	MEK	PEAE	–	TEA	–	Not specified	20 min	28%	56–126	–	–	–	–	–	–	–	[146]
Polyether diol (1120–3000)	IPDI, TDI	DBTDL	DMBA, DMPA	St-BA, TPGDA, TMPTA, glycerol, HFBMA or BA	acetone, DMF or NMP	HEA, HEMA, PETA, HPA or HPMA	ZnO, GO or SiO_2-GLYMO or TEOS	TEA	HQ or MEHQ	(0–4%) Dar1173, Irg.184, Dar.651 or TPO	800-1000 W 0.1–30 min	20–30%	32–260	42–98	(Pencil) B–H or (Shore A) 51–98	0.7–11.6	10–399	150–310	0.8–22	Coating and electromagnetic shielding	[22, 106-117]
PPG (400–2000)	IPDI, TDI, HDI, HMDI	DBTDL or DBTDA	DMPA or DMBA	MLGLY, DA_2OH, PMDA, OF-diol, E51, HTPB, TMP,EDA, FDO,BDO, CO, DEG or HZM	MEK or acetone	HEA, HEMA, PETA, DAA-GPTMS	Fe_3O_4-VTMS, h-NZFO, hBN-OH, ATO, HAP with VTMS, SiO_2 or OVPOSS	TEA	HQ or MEHQ	(0.3–5%) Dar1173, Irg.2959, Irg.500, Irg.184, or TPO	1–125 mW/cm^2 2–15min or 8–1000 W; 0.5–120 min	20–48%	26–311	43–98	(Pencil) 3B–4H or (shore A) 52–95	0.6–200	1.5–630	240–290	2–45	Coating and microwave absorbing	[12, 23, 32, 40, 52, 59, 65, 67-82]
PTAd (1000)	HMDI	DBTDL	DMPA	DA_2OH	–	HEA	–	TEA	–	(3%) Dar1173	Not specified	30%	–	–	(Shore A) 59	38	80	–	14	–	[40]
PTMG (250–2000)	IPDI, HDI, TDI, HMDI	DBTDL	DMBA, DMPA or AC	DA_2OH, MDEA, PDMS, APTES, PMDA, DHPDMS TMPME, HEG,SMA MMA, BA, BDO, Gly, TETA, PE, TMP or HFIP	acetone, DMAC, MEK or NMP	HEA, HEMA, PETA, GAP or PEDA	SiO_2, Na^+ montmorillonite with VTMS, C-TiO_2/rGO, (SiO_2 with PEGMA or allyl isocyanat)	TEA	HQ or MEHQ	(1–4%) Dar1173, Irg.2959, Irg.184, Irg.500, Cyr6974, BPO or TPO	8–2000 W 1–120 min	20–50%	97–387	73–97	(Pencil) B–2H or (Shore A) 43–96	0.3–49	90–1120	200–340	0.6–61	Coatings and Self-cleaning coating	[26, 40-66]
PTHF (1000)	IPDI	DBTDL	DMPA	TMP	acetone	HEMA	–	TEA	–	(3%) Dar1173	65 min	30%	–	89–94	(Pencil) 2–3H	–	–	–	6–12	–	[73]
Vegetable oil (castor, linseed or cardanol)	IPDI, HDI	DBTDL	DMPA, MDEA	BDO, TPGDA, TMPTA, DPGDA or HDDA	MEK or acetone	HEA or HEMA	O-MMT or lysozyme	TEA or AC	HQ or MEHQ	(2–3%) Dar1173, Irg.2959 or BPO/ HCPK	40–1000W; 0.1–10 min	20–45%	61–5001	53–94	(Pencil) 2H–7H	0.8–21	6–525	187–300	0.8–19	Coating	[134-139]
HMBT/ PEUDA	IPDI	DBTDL	DMPA	TMPTA, HDDA	acetone	HEA	–	TEA	MEHQ	(3%) Irg.2959	300W/in 0–250 s	30%	41–69	18–80	Pendulum 35-128	–	–	260–290	4–23	Coating	[140]
PEO/PPO/ PEO (2000)	IPDI	DBTDL	DMPA	–	acetone	HEMA	SiO_2	TEA	HQ	(3–4%) Irg.2959	200 W 2 min	30%	31–34	–	–	0.4–0.9	300–400	–	–	–	[65]
PEA/PPO (400–2000)	IPDI/ MDI	DBTDL	DMPA	DPHA, DPGDA	–	PETA or HEA	–	TEA	–	(3%) Irg.184	1000 W 15 s	42%	64–104	–	(Pencil) 4H–4H	–	–	250–315	2.5–25	Coating	[141]

AC: acetic acid; AESO: acrylated epoxidized soybean oil; APTES: 3-aminopropyltriethoxysilane; ATO: antimony doped tin oxide; BA: butyl acrylate; BDO: 1,4-butane diol; BPO: benzophenone; CO: castor oil; DA2OH: 1,3-dihydroxy-2-propanone; DAA-GPTMS: derived from diallylamine with methyldiethoxysilane; DAP: Dimer fatty acid-based polyol; Dar1173: (Darocur) 2-hydroxy-2-methylpropiophenone; Dar651: (Darocur 651) Benzil dimethyl ketal; DBTDA: dibutyltin diacetate; DBTDL: dibutyltin dilaurate; DEG: diethylene glycol; DEOA: diethanolamine; Desmo1019-55: poly(hexylene adipate-isophthalate) polyester diol; DETA: diethylene triamine; DHPDMS: dihydroxybutyl terminated polydimethylsiloxane; DiAE: 2,2-bis(prop-2-enoxymethyl)butan-1-ol; DMAC: N,N-Dimethylacetamide; DMBA: 2,2-bis(hydroxymethyl)butyric acid; DMCS: dimethyl dichlorosilane; DME: dimer acid-modified epoxy polyol; DMEA: N,N-dimethyl ethanolamine; DMF: N, N-dimethyl formamide; DMPA: 2,2-bis(hydroxymethyl) propionic acid; DPGDA: dipropylene glycol diacrylate; DPHA: dipentaerythritol hexaacylate; DPPA: dipentaerythritol pentaacrylate; EDA: ethylene diamine; EG: ethylene glycol; ETP: ester-type polyol; E51: bisphenol-A-based epoxy resin; FDO: fluorinated macromolecular diols; GAA: guanidinoacetic acid; GAP: glycidyl azide polymer; g-C3N4: graphitic carbon nitride; Gly: glycidol; GLYMO: 3-glycidyloxypropyltrimethoxysilane; GMA: glycidyl methacrylate; GO: graphene oxide; HAP: hydroxyapatite; HBA: 2,2-bis (hydroxymethyl) butyl acrylate; hBN-OH: hydroxylated hexagonal boron nitride; HBP: hyperbranched aliphatic polyester; HCPK: 1-hydroxycyclohexyl phenyl ketone; HDDA: hexanediol diacrylate; HDI: 1,6-hexamethylene diisocyanate; HEA: 2-hydroxyethyl acrylate; HEG: 1,6-hexylene glycol; HEMA: 2-hydroxyethyl methacrylate; HFBMA: 2,2,3,4,4,4-hexafluorobutyl methacrylate; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol; HMBT: 1,6-Hexamethylene bis(thioglycolic acetate); HMDI: 4,4'-methylenebis(cyclohexyl isocyanate); h-NZFO: Ni0.3Zn0.5Fe2O4 nanospheres; HPA: 2-hydroxypropyl acrylate; HPMA: hydroxypropyl methacrylate; HQ: hydroquinone; HTPB: hydroxyl-terminated polybutadiene; HZM: hydrazine monohydrate; IAAE: isocyanate-functionalized aliphatic acrylic ester; IPDA: isophoron diamine; IPDI: isophorone diisocyanate; Irg.184: (Irgacure) 1-hydroxycyclohexyl phenyl ketone; Irg.2959: (Irgacure) 2-hydroxy-4′-(-2-hydroxyethoxy)-2-methylpropion-phenone; LDH: layered double hydroxide; MA: maleic anhydride; MDEA: N-methyl diethanolamine; MDI: methylene diphenyl 4,4-diisocyanate; MEHQ: 4-methoxyphenol or p-hydroxyanisole; MEK: methyl ethyl ketone; MEMO: methacryloxy (propyl) trimethoxysilane; MLGLY: hydrophilic maleic anhydride–glycerol oligomer; MMA: methyl methacrylate; MPEG: methoxypolyethylene glycols; MPS: 3-methacryloxypropyltrimethoxysilane; MPTES: 3-mercaptopropyltriethoxysilane; MPTS: methacryloxypropyltrimethoxysilane; MSMA: 3-(trimethoxysilyl) propylmethacrylate; NMP: N-methyl-2-pyrrolidone; OF-diol: perfluorooctanoate glycerate; O-MMT: organic montmorillonite; OVPOSS: octavinyl polyhedral oligomeric silsesquioxane; PBA: polybutane adipate diol; PCD: polycarbonate diol; PCL: polycaprolactone diol; PDMS: polydimethylsiloxane; PE: pentaerythritol; PEA: poly(neopentyleneglycol adipate); PEAE: pentaerythritol allyl ether; PEDA: pentaerythritol diacrylate; PEG: poly (ethylene glycol); PEGMA: poly (ethylene glycol) monomethyl ether methacrylate; PEO-PPO-PEO: Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide); PET: polyester (adipic acid and neopentyl glycol); PETA: pentaerythritol triacrylate; PETTA: pentaerythritol tetraacrylate; PET3MP: pentaerythritol tetrakis(3-mercaptopropionate); PEUDA: propionic ester-based urethane diacrylate; PFPE: hydroxy-terminated perfluoropolyether; PIDG: polyisophthalic diglycol; PMDA: pyromellitic dianhydride; pNGA: poly(neopentyl glycol adipate); PPG: polypropylene glycol; PTAd: poly(tetramethylene adiphate)glycol; PTHF: polytetrahydrofuran; PTMG: polytetramethylene glycol; Run1103: (Runtecure) 1-(4-Hydroxy-2-methylphenyl)propan-1-one; SAN: succinic anhydride; SMA: surface modifying agent; St-BA: styrene butyl acrylate; TDI: toluene diisocyanate; TEA: triethylamine; TEOS: tetraethoxysilane; TETA: triethylene tetramine; THF: tetrahydrofuran; TMP: trimethylolpropane; TMPME: trimethylolpropane monoethylene ether; TMPMP: trimethylolpropane tris(3-mercaptopropionate); TMPTA: trimethylol propane triacrylate; TMSPM: trimethoxysilyl-propyl methacrylate; TPGDA: tripropyleneglycol diacrylate; TPO: 2,4,6-trimethylbenzoyldi-phenyl phosphine oxid; TriSH: 2,2-bis(3-sulfanylpropanoyloxymethyl)butyl-3-sulfanylpropanoate; VHSO: vinyl hydroxyl silicone oil; VTMS: vinyltrimethoxysilane; β –CD: β-cyclodextrin; Me-β-CD: methylated-β-cyclodextrin.