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Waterborne Epoxy Based Coating Materials

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Abstract

Epoxy resins were commercially introduced as binders in protective organic coatings due to their outstanding processability, great adherence to many substrates, excellent chemical, and corrosion resistance properties. Besides the concern about volatile organic compounds (VOCs), efforts have been made towards the development of waterborne epoxy (WBE) based corrosion resistant materials and coatings which are low energy-curing and less toxic during the application process. Literature survey reveals that WBE has immense potential, significance, and applications in the field of paints and coatings. The aim of this book review is to represent the synthesis of WBE, curing agents used for WBE, current and past use of conventional WBE based systems and their use as binders in protective coatings.

Keywords: waterborne epoxy; eco-friendly; synthesis; curing agent; coatings.

1. Introduction

An increasing awareness of environmental and health protection, higher solvent prices and emission of VOCs has led to increased emphasis on the development of new coating technologies [1-3]. The efforts in this area have been to develop the environment-friendly methods and processes to replace the traditional reactions, which involve the application of organic solvents that consume much energy and generate undesirable by-products and/or waste in the form of VOCs [4, 5]. Therefore, the current trend in the coating industry is towards the eco-friendly coatings like powder coatings, solventless coatings, UV curable coatings and waterborne coatings [6]. The first step in this process has been the introduction of water-based coatings in the 1950s leading to the recent development of so-called low VOC and zero VOC content [7-9]. Since 1970, there has been a further trend away from solvent- borne coatings because of higher solvent prices and particularly the need to reduce VOC emissions to meet air quality standards [10].

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Epoxy is one of the most important materials used in surface coatings [11]. Epoxy resins find an important role as binders in protective coatings due to their magnificent performance in terms of corrosion protection, chemical resistance, and great adherence to many substrates [12, 13]. The diglycidyl ether of bisphenol-A (DGEBA) is produced by reacting epichlorohydrin with bisphenol-A in the presence of a basic catalyst. Figure 1: shows the chemical structure of DGEBA (Epoxy). Epoxy resins are characterized as compounds or mixture of compounds that contain one or more epoxy or oxirane or ethoxyline group, which is a three-membered oxide ring. They are polymerized through these epoxide groups or hydroxyl groups in the resin using a cross-linking agent to form a tough three-dimensional network [14]. In addition, cured epoxy resins have good mechanical and electrical properties, superior dimensional stability and good resistance to heat and chemical attack [15, 16].

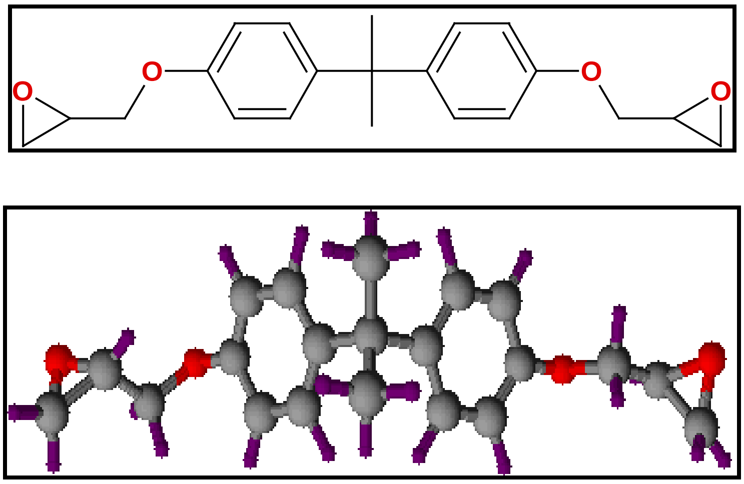

Figure 1: Chemical structure of epoxy

WBE was commercially introduced about 40 years ago, mainly as an environment-friendly coating system to replace the solvent borne epoxies particularly in countries with strong environmental and work safety regulations [17, 18]. Literature survey reveals that WBE has immense potential, significance, and applications in the field of surface coatings [19, 20, 21]. WBE resin systems find innumerable industrial applications like civil engineering, adhesives, structural end-uses, fiber sizing, glass, synthetic and carbon fibers, tie-coats, primers and laminates, textiles, sealants, insulating materials, electronic photo imaging, and coatings; floor, corrosion resistant [22-24]. WBE has been prepared by emulsion polymerization and water reducible processes by the incorporation of vinyl monomers via. grafting copolymerization technique [25-29]. Epoxy can be heated with different hydrophilic groups such as polyethylene glycol or polyethylene oxide instead of carboxylic acid salts. These epoxy coatings range from industrial baking finishes that deliver the maximum performance in solvent and chemical resistance for maintenance systems in corrosive environments and also include the can linings, overprint, varnishes, durable laminates, lightweight foams and porting compounds for all varieties of electrical and electronic apparatus and chemically resistant floor and wall coatings [30, 31]. The mechanical properties of waterborne epoxies may also improve in combination with polyacrylate and polystyrene resins. This combination finds applications in high-performance paints [32].

The preceding sections describe the synthesis, curing agents, and waterborne epoxy based various polymeric systems, along with their preparation and applications used as surface coatings.

1.1. Synthesis of Waterborne Epoxy

WBE has been prepared by emulsion polymerization and water reducible processes by the incorporation of vinyl monomers via. grafting copolymerization technique [33-35]

1.1.1. Emulsion Polymerization

It is well known that for emulsion polymerization, hydrophobic monomer, emulsifier, and hydrophilic initiator are the main constituents could be used in the water phase Figure 2: Polymers such as acrylonitrile, butadiene, styrene, polystyrene, poly-methyl-methacrylate, etc. can be easily prepared via emulsion polymerization processes [36, 37]. These polymers have applications in adhesives, paints, coatings, diagnostic tests, drug delivery systems, thermoplastics and synthetic rubbers [38-40]. The potential application for the enhancement of emulsion polymerization is to produce polymers with unique properties and environmental concern to substitute solvent-based systems by waterborne products. The term emulsion polymerization encompasses several related processes: **(1)** conventional emulsion polymerization, **(2)** inverse emulsion polymerization, **(3)** mini-emulsion polymerization **(4)** dispersion polymerization and microemulsion polymerization [41]. As it is well known, it was difficult to polymerize the acrylic monomer in the presence of the epoxy resin. Thus, the emulsion polymerization method was used to synthesize epoxy resin/ acrylic composite latexes [42-44]. Wet-Roos and his colleagues [45] synthesized an epoxy-acrylic composite latex by emulsion polymerization that involved emulsifying epoxy resin with monomers. A self-emulsified waterborne epoxy curing agent of the nonionic type was prepared by Zhou and his colleagues [46] using diglycidyl ether of polyglycol (DGEPG), triethylene tetramine (TETA) and liquid epoxy resin as raw materials, which showed good property of emulsifying liquid epoxy resin. Epoxy groups were often used as a cross-linking agent in the heat curing process of conventional latexes with carboxyl groups [47].

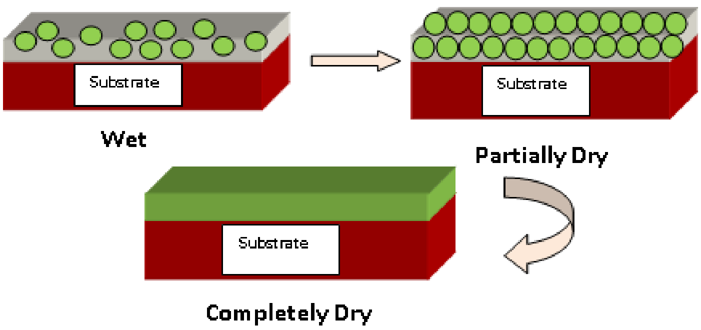

Figure 2: Emulsion coating

1.1.2. Water-reducible or water dispersible processes

Water dispersible resins are generally produced via polycondensation or polymerization reactions in presence of a blend of the organic medium which contains organic co-solvents like alcohols, glycol ethers or other oxygen containing solvents that are soluble or miscible with water [48]. Cosolvents can enhance the several basic properties of coatings such as film formation, pot life, gloss, and film coalescence [49]. Cosolvents that are most commonly used in WBE coatings are given in Table 1. To achieve water dispersibility, chemical modification is done to introduce polar groups to the polymer backbone, usually; anionic or cationic charges such as carboxyl/amino groups as shown in Figures: 3 and 4. After most of the solvent has been removed, a tertiary amine/acids necessary for neutralization of resins is added. Thus, water or water miscible co-solvent is added to reduce the coating formulations [20, 50]. The use of water as a dispersion medium can overcome these disadvantages and decrease the content of VOCs in the preparation of waterborne epoxy-acrylic resins. Hence, WBE systems have been developed due to the pressure of environmental concern [30]. Woo and Toman [26] synthesized water-reducible epoxy-acrylic composite copolymers, which incorporated hydrophilic groups into the molecular chains of the epoxy resin to make them water dispersible.

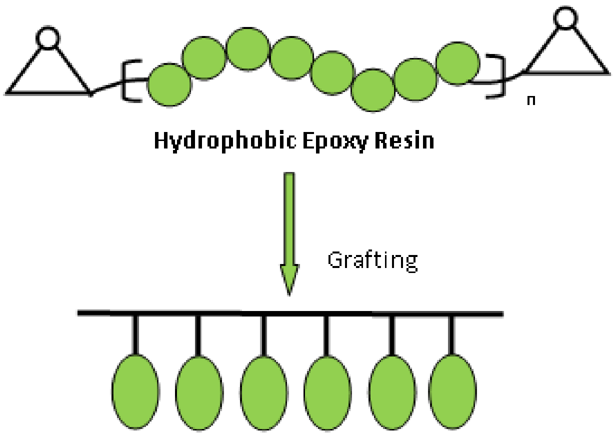

Figure 3: Water dispersible grafted epoxy

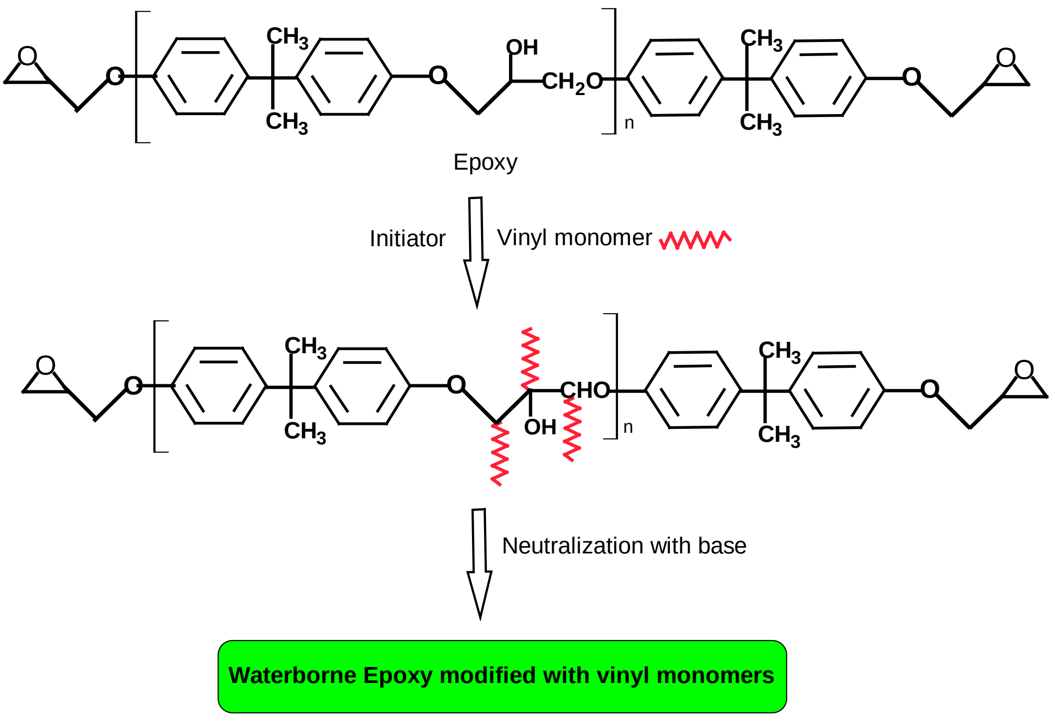

Figure 4: Synthesis of vinyl monomer modified waterborne epoxy

Table 1: List of waterborne epoxy co-solvents

S.No.	Name of co-solvent	B.p.(^oC)
1.	Ethylene glycol monobutyl ether	171
2.	Diethylene glycol monobutyl ether	231
3.	Ethylene glycol monoisopropyl ether	142
4.	Tripropylene glycol monomethyl ether	242
5.	Dipropylene glycol monomethyl ether	231
6.	Ethylene glycol monoethyl ether	135
7.	Diacetone alcohol	166
8.	Propylene glycol monomethyl ether	119
9.	Ethylene glycol monomethyl ether	124
10.	Diethylene glycol monoethyl ether	196

2. Curing agents used in Waterborne Epoxy

Curing agents have been widely used in low molecular weight epoxy oligomer to form three-dimensional crosslinked thermoset networks. The cured epoxy showed excellent heat resistance, durability, adhesiveness and better mechanical and thermal properties. Epoxy resins can be cured or crosslinked by many types of curing agents such as amines, amides, acids and anhydrides to prepare a majority of thermosetting plastics, chemical-resistant linings, concrete coatings, adhesives, composites and surface coatings [51, 52]. Epoxy resins cured with aromatic amine generally provide enhanced environmental (hydrolytic) stability, outstanding heat resistant and mechanical properties [53]. 4,4’-diaminodi-phenyl methane, m-phenylene diamine and 4,4’-diaminodiphenylsulfone are principal commercial aromatic amine curing agents [54]. Recently, researchers have already developed some silicone-contained amine in low cost [55, 56]. Besides the concern about VOC, efforts have been made towards the development of low energy-curing, coating resistant materials and coatings which are less toxic during the application process and environment compatible. For ambient temperature cured systems, the fundamentally multifunctional amine base systems can be used as crosslinking agents in epoxy resins [57]. The first commercially available waterborne curing agents were essentially unmodified polyamides. For water dispersibility, the epoxy resins are either partially neutralized with carboxylic acids or by the inclusion of non-ionic surfactant [58, 59]. The epoxides undergo curing reactions with hydroxyl groups with phenols or ureas and producing improved water stability, dry speed, gloss, hardness, and chemical resistance of coatings [60]. Epoxy and acrylic resins or epoxy/acrylic graft copolymers [61], cross-linked with amino resins (melamine–formaldehyde and urea–formaldehyde resins), and related cross-linkers, where curing of coatings occurs at ambient temperature. Melamine-formaldehyde resin is an important component of the thermosetting type of synthetic resins. They are widely used as a cross-linking agent with alkyd, polyester, polyurethanes and epoxy resins in the coating industry [62]. Literature reveals that epoxy based waterborne formulations in combination with amine curing agents (Figure 5:) exhibit a wide range of uses and properties in two component adhesives, composites and primer/maintenance coatings [63, 64]. The cross-link density afforded by the combination of polyfunctional resin and polyfunctional curing agent provide faster drying times, as well as improved corrosion resistance properties [65]. Hawkins and his colleagues [66] used organic acids in epoxypolyamine curing agents to make them distributed in water. The coatings have shown improved chemical resistance and flexibility of the cured film, however, performances of cured film are not satisfactory due to the acid neutralization. In order to obtain improved coatings, Schneider and his colleagues [67] have developed a silane-based crosslinker which showed excellent flexibility, chemical resistance and thermal stability of the film. Waler and his colleagues [68] have also reported the waterborne curing agent by using liquid epoxy resin and polyamine which showed poor intermiscibility with epoxy resin. An amidoamine curing agent was prepared by Elmore and his colleagues using carboxyl terminal polyether alcohol as termination agent for epoxy-polyamine adduct [69]. A self-emulsified waterborne epoxy curing agent of the nonionic type was reported by Zhou and his colleagues [46] using diglycidyl ether of polyglycol, triethylene tetramine and liquid epoxy resin as raw materials, which has good property of emulsifying liquid epoxy resin. Chen and his colleagues [70] used a series of epoxy silane as active additives for reactive polymer emulsions. Xinyan Xiao and his colleagues[71] prepared UV (ultra-violet) curable waterborne epoxy acrylate/silica sol hybrid materials.

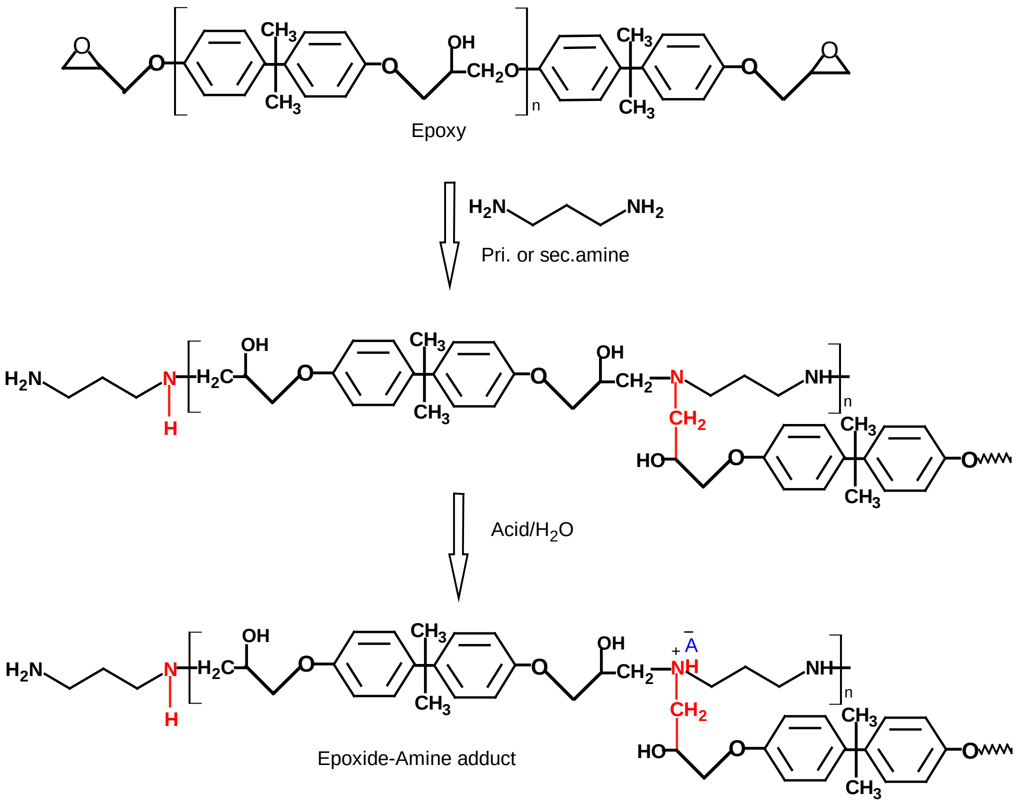

Figure 5: Amine terminated waterborne epoxy

3. WBE based polymeric systems

WBE based systems have been widely used as novel environmentally friendly organic coatings materials in industrial and high-performance architectural applications. Many attempts have been made to formulate WBE as polymeric coatings [12, 72].

3.1. Graft copolymer based WBE systems

WBE systems have been produced by the introduction of graft copolymers comprising acrylic acid, methylmethacrylate, methacrylic acid, styrene, ethyl acrylate, acrylonitrile or mixtures of these into epoxide molecules [73, 74]. Various commercially available methods are employed to incorporate carboxyl vinyl polymer into the epoxy resin. Among these is the water reducible epoxy–acrylic composition. Waterborne epoxy–acrylic copolymer is formed from the epoxy resin by the grafting of addition polymer onto aliphatic backbone carbons of the epoxy resin as shown in Figure 6: [75].

Coatings with excellent properties have been obtained from epoxy-acrylate, which showed good water resistance, good adhesive effect, and high mechanical strength. Hence, epoxy-acrylate have been widely used in the field of corrosion resistant materials and coatings [76].

In another preferred method, self-emulsifiable mixtures are prepared by esterifying epoxy resin with carboxyl acrylic polymer in an organic solvent medium in the presence of a tertiary amine.Then the adduct reacts with a base and renders it self-dispersible into the water in neutralized form [77].WBE have also been synthesized by free-radical grafting method, that provides high molecular weight complex copolymers which lower the proportion of curing agent and provides tougher and more impact resistant cured coatings [78]. Kanako and coworkers have synthesized WBE esters based on non-polar/polar acrylic monomers [79]. Epoxy graft poly(St-acrylate) composite latex was also prepared by A Klein [35] and coworkers. The coatings have shown immense potential in the field of functional steel coatings.

3.2. Polyurethane (PU) based WBE systems

PU is a thermoplastic rubber composed of repeating hard and soft segments, it thus possess good mechanical properties such as medium tensile strength and high elongation. It is widely used in synthetic leather, fibers, and adhesives [80]. PU have found extensive applications in the coatings industry mainly because they exhibit excellent abrasion resistance, toughness, low-temperature flexibility, chemical and corrosion resistance, and a wide range of mechanical strength [81].

Figure 7: shows the formulation of low VOC, high performance, two component isocyanate crosslinked WBE coatings. Preparation of epoxy based waterborne polyurethanes has been extensively reported in the literature [82].Waterborne UV-curable polyurethane-acrylate, bisphenol-S epoxy acrylate and methyl acryloyl propyl polyhedral oligomeric silsesquioxanes were synthesized by Jungang Gao and his colleagues [83]. The nanocomposites produced were cured by both UV-light irradiation and thermal free radical polymerization.

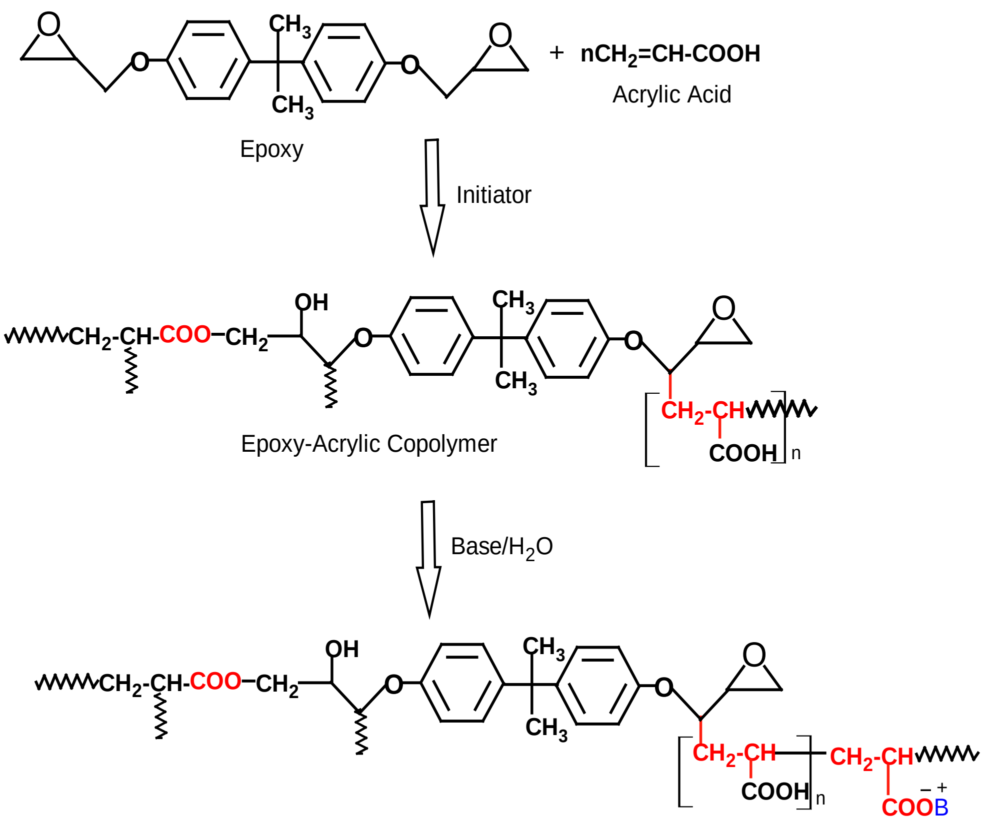

Figure 6: Acrylic acid grafted waterborne epoxy

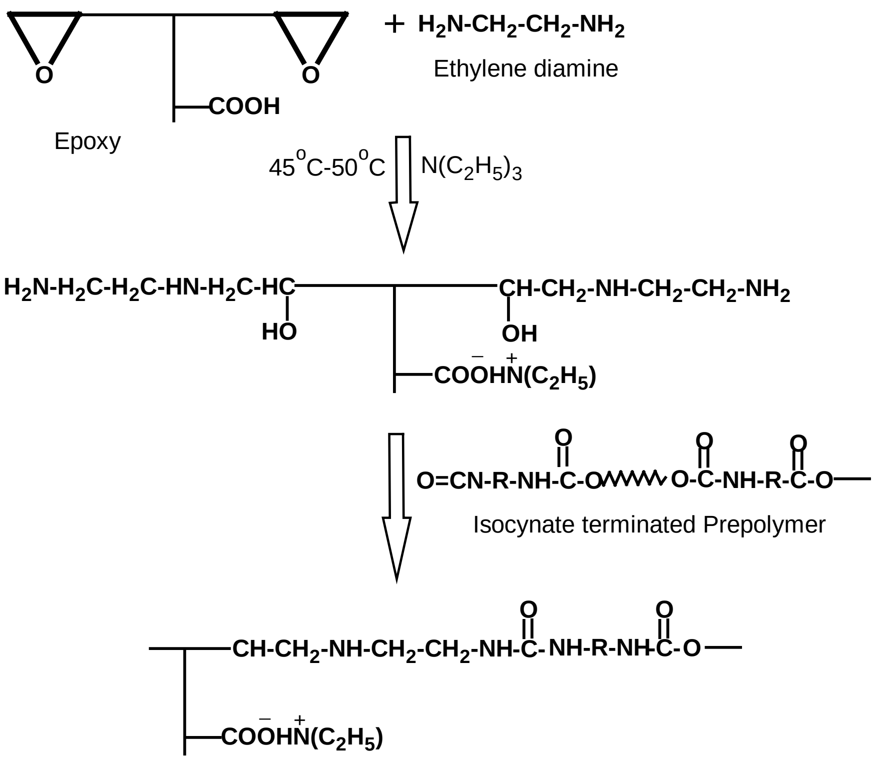

Figure 7: Polyurethane based waterborne epoxy

3.3. WBE based esters

Waterborne epoxy esters are obtained by an esterification reaction between epoxy resins and mono and poly anhydrides/acids or with a mixture of acids and anhydrides. The coatings produced were cured at ambient temperature or as baked coatings. These showed glossy, smooth and continuous film [84, 85]. Waterborne epoxy esters (Figure 8:) were also developed from epoxy resins treated with a mixture of oil fatty acids such as linseed oil or dehydrated castor oil fatty acids mixed with mono carboxylic acids [79]. WBE esters can be prepared by condensing itaconic or fumaric adduct of unsaturated fatty acids with epoxy resin [86]. Another way of synthesizing water soluble maleinized epoxy resin fatty acid esters is to partially esterify the epoxy resin with dehydrated castor oil (DCO) or tall oil fatty acids and to subsequently esterify with a hydrolysed adduct of maleic anhydride and unsaturated fatty acid [87, 88]. WBE esters can also be synthesized from phenolic resols, epoxy resin, and a mixture of linseed oil, DCO, and maleic anhydride. These products are solubilized in butyl cellosolve and neutralized with triethyl amine prior to dilution in water [85, 89]. The aqueous coating composition can be obtained by esterifying epoxy resins with carboxylated acrylic polymer in the presence of polyfunctional tertiary amine catalyst and then neutralizing the residual carboxyl groups [75]. Pyromellitic dianhydride modified epoxy ester studied by Ramesh and his colleagues [79] have shown better film properties.

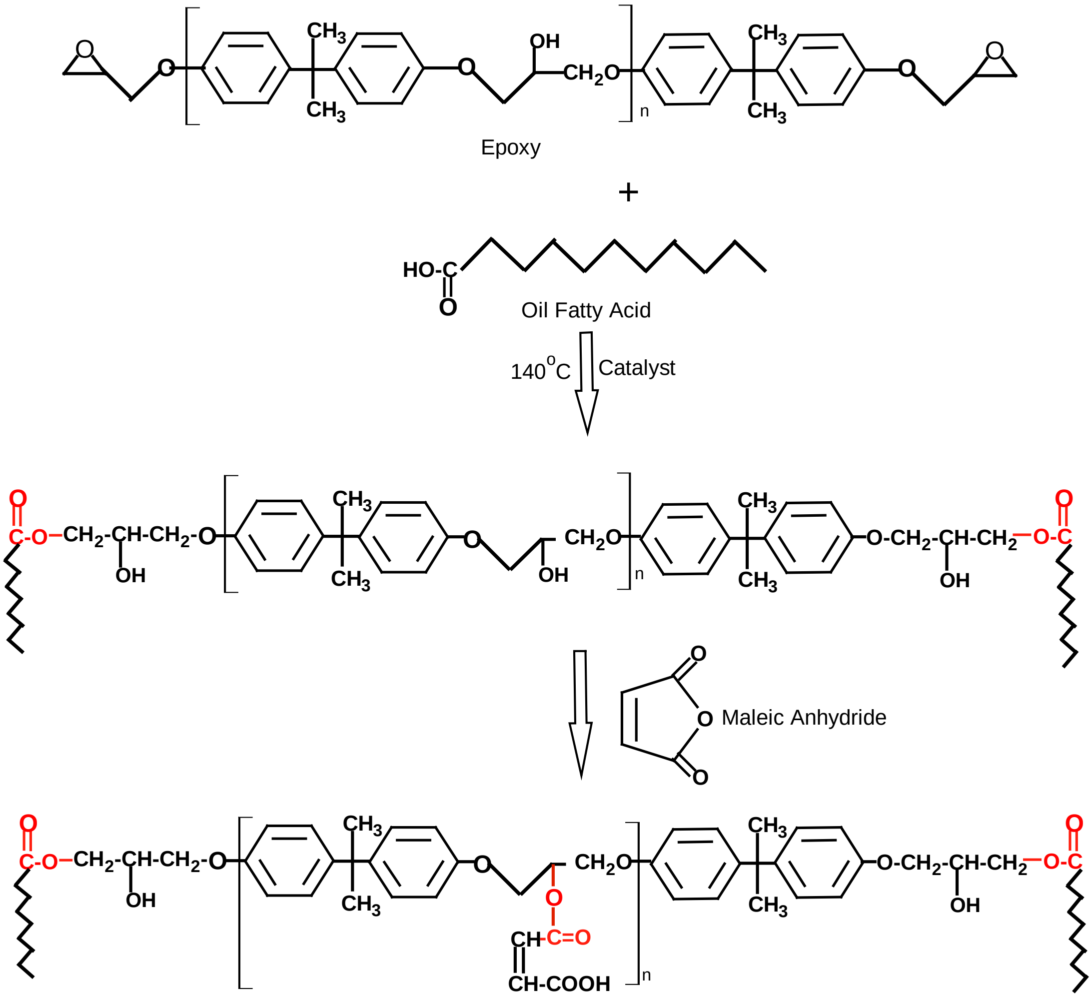

Figure 8: Waterborne epoxy ester

3.4. WBE based ethers resins

WBE based ethers were synthesized through the condensation polymerization of unsaturated fatty alcohol or ally1 alcohol. They contain repeating ether linkages in their backbone and possess improved coating properties. Ether linkages are known to confer good adhesion, flexibility and chemical resistance to the resin. They find important application as binders in paints and coatings [16, 18]. The partial ally1 ethers of epoxy resins can also be modified with maleinized adducts of linseed fatty acids [90]. Figure 9: shows the epoxy groups etherified with alkanol amides and/or oxalolines of unsaturated fatty acids treated with maleic anhydride give water soluble products on neutralization with amines.

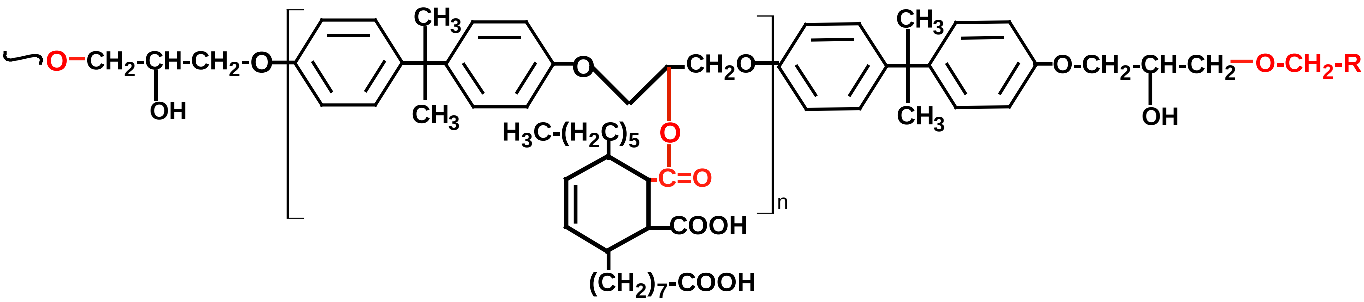

Figure 9: Waterborne epoxy ether

3.5. WBE based nanocomposites

Nanocomposites based on WBE emulsion and suspension has attracted the interest of many industrial and academic researchers in the last two decades due to their unique chemical and physical properties [91]. In the last few decades, the majority of polymers or copolymers nanocomposites have been synthesized and studied for anticorrosion and abrasion resistance properties over various metallic substrates [92]. Nanoparticles are being incorporated into waterborne polymer matrices as filler to improve the mechanical, rheological, anticorrosive, and light-resistance properties, especially nano metal oxides such as TiO_2, Fe_2O_3, ZnO, SiO_2, Al_2O_3, $CaCO_3$ and zirconia have been used as nanofiller for corrosion protection on mild steel [93]. In recent years, more attention has been paid to the preparation of low VOC epoxy coatings because of environmental protection and health hazards [64, 94]. The successful method to prevent corrosion is to improve the barrier property of the epoxy coatings to decrease the permeability of water and oxygen, which fuel the corrosion process [95]. Therefore, coating properties of WBE can be improved by the inclusion of nanoparticles in these coatings (Figures 10 and 11:). Nanoclay is one of the most promising materials since this material exhibits significant improvement in anticorrosion performance and barrier property of WBE coatings [96, 97].

Organophilic montmorillonites were used for waterborne and solvent type epoxy coating materials. Kowalczyk and Spychaj [98] report the effect of organically modified montmorillonites in the epoxy coating on a steel substrate. Montmorillonite clay was also used by Hang and his colleagues [99] as filler for solvent epoxy coatings. It was found that with the addition of 2% nano clay in an epoxy resin there was a significant improvement in the anticorrosive and barrier properties of the coating compared with the neat coating. Waterborne epoxy–clay nanocomposites were prepared by Jin Suk Chung [32] and co-worker, which revealed encapsulation of organoclays in epoxy latex particles via phase inversion emulsification. Wang and his colleagues [100] have studied the preparation and thermal stability of UV cured epoxy-based coatings modified with octamercaptopropyl polyhedral oligomeric silsesquioxanes (POSS). Lai and his colleagues [95] investigated the anticorrosion performance of water-based polyacrylate latex materials by adding Na^+ montmorillonite. N.Girouard [24] and co-workers provide the mechanical and thermal properties of cellulose nanocrystals based composites with WBE matrix.

Gao and his colleagues [76] have synthesized the waterborne UV curable epoxy acrylate coatings modified with methyl acryloyl propyl-POSS and investigated the cure kinetics of the coating by differential scanning calorimetry. Gao and his colleagues have also provided the similar work on waterborne epoxy acrylate (EA) coating modified with methyl acryloyl propyl polyhedral oligomeric silsesquioxanes (MAP-POSS). The MAP-POSS and EA resin have shown better compatibility and can co-cure with free radical copolymerization. Jin Suk Chung and his colleagues [32] have developed waterborne epoxy–clay nanocomposites by encapsulation of organoclays in epoxy latex particles via phase inversion emulsification. Recently, thermoset nanocomposites were prepared from waterborne terpene–maleic ester type epoxy resin modified by inclusion of cellulose nanowhiskers [101].

Novel UV curing transparent hybrid materials were synthesized by Xinyan Xiao and his colleagues using self-synthesized waterborne acrylate epoxy and nano-silica sol [71].

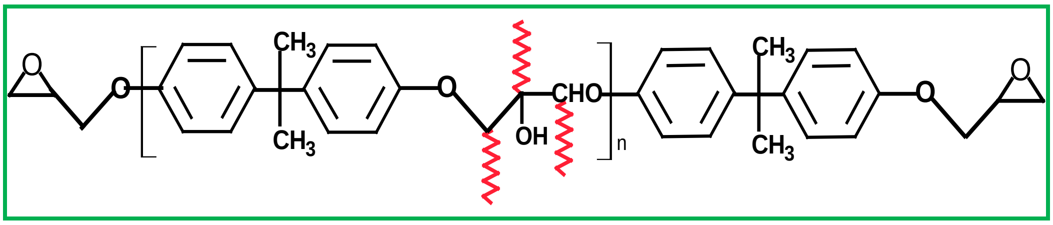

Figure 10: Nanoparticles in epoxy matrix

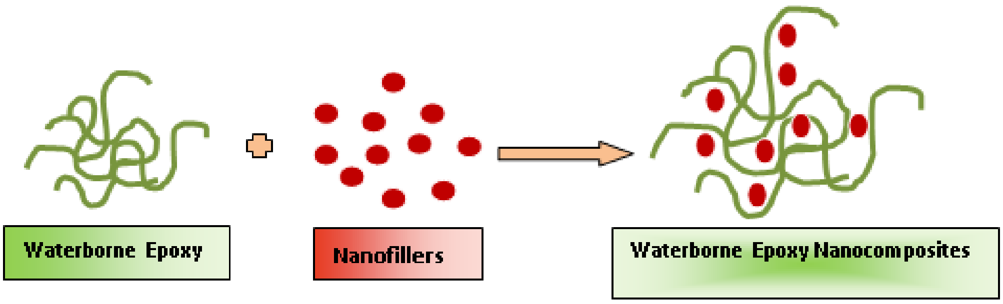

Figure 11: Formation of waterborne epoxy nanocomposite

4. Applications of WBE

- WBE resin systems have been widely used as corrosion protective surface coating materials because to their outstanding processability, great adherence to many substrates, excellent chemical and anticorrosive properties as well as excellent abrasion and impact resistance [102, 103].
- WBE systems today are used in industries such as automotive, electrical, electronics and marine [104].
- WBE resins are extensively used in automotive industries as anti-rust protective coatings [105].
- WBE have also been utilised in a wide variety of applications in the area of electronics such as encapsulation, thin film coating, and packing of electronic circuits [106].
- WBE systems also impart superior adhesion to almost all the substrates such as timber, metal, and plastics and promote its use in the marine industry [64].
- WBE coatings are also used as hygiene coatings in food factories, abattoirs, dairies, etc. [34].

- WBE systems also provides superior adhesion in floor coating, specially interior concrete, primers for metal, epoxy cement concrete (ECC), and fibre sizing [107].

5. Conclusion

WBE based polymeric systems have provided the opportunity to reduce or replace the traditional polymeric systems that involve the use of organic solvents which consume much energy and cause VOCs emissions. Using the most recent WBE systems, waterborne epoxy coatings can be formulated which match or exceed the performance of solvent-based coatings at low or zero solvent content and adour. This study reviewed various methods to formulate WBE based polymeric coatings. The coating performance and barrier properties of WBE coatings can also be improved by the inclusion of nanoparticles of different chemical nature and morphology of inside the epoxy matrix. The development of highly durable, corrosion resistant waterborne coating formulations is still a challenge for the researchers as well as industrialist. Furthermore, the non-ionic surfactants will be utilized to enhance the compatibility as well as stability with components that are mixed into resin systems including fillers, defoamers and coupling agents. To obtain ambient curing and optimum coating properties phenolic modifiers were also used. Due to their high performance, unique handling characteristics, and low VOC content, these waterborne epoxy resin systems are expected to be commercially utilized in a wide variety of applications for civil engineering, adhesive, and structural end-uses as well as in other non-traditional applications. [34, 64, 102, 103]

References

[1] M. de Meijer, "Review on the durability of exterior wood coatings with reduced VOC-content," Progress in organic coatings, vol. 43, pp. 217-225, 2001.

[2] P. Geurink, T. Scherer, R. Buter, A. Steenbergen, and H. Henderiks, "A complete new design for waterborne 2-pack PUR coatings with robust application properties," Progress in organic coatings, vol. 55, pp. 119-127, 2006.

[3] H. Tanabe and H. Ohsugi, "A new resin system for super high solids coating," Progress in organic coatings, vol. 32, pp. 197-203, 1997.

[4] E. A. Murillo and B. L. López, "Novel waterborne hyperbranched acrylated-maleinized alkyd resins," Progress in Organic Coatings, vol. 72, pp. 731-738, 2011.

[5] Y. Nakayama, "Polymer blend systems for water-borne paints," Progress in organic coatings, vol. 33, pp. 108-116, 1998.

[6] F. Galliano and D. Landolt, "Evaluation of corrosion protection properties of additives for waterborne epoxy coatings on steel," Progress in Organic Coatings, vol. 44, pp. 217-225, 2002.

[7] H. D. Hwang, J. I. Moon, J. H. Choi, H. J. Kim, S. Do Kim, and J. C. Park, "Effect of water drying conditions on the surface property and morphology of waterborne UV-curable coatings for engineered

flooring," Journal of Industrial and Engineering Chemistry, vol. 15, pp. 381-387, 2009.

[8] S. Xinrong, W. Nanfang, S. Kunyang, D. Sha, and C. Zhen, "Synthesis and characterization of waterborne polyurethane containing UV absorption group for finishing of cotton fabrics," Journal of Industrial and Engineering Chemistry, vol. 20, pp. 3228-3233, 2014.

[9] A. Schieweck and M. C. Bock, "Emissions from low-VOC and zero-VOC paints–Valuable alternatives to conventional formulations also for use in sensitive environments?," Building and Environment, vol. 85, pp. 243-252, 2015.

[10] K. D. Weiss, "Paint and coatings: a mature industry in transition," Progress in polymer science, vol. 22, pp. 203-245, 1997.

[11] E. Zhavoronok, I. Senchikhin, V. Vysotskii, and V. Roldugin, "Effect of the nature and associate structure of an epoxy oligomer on the rate of its curing with diamine," Polymer Science, Series B, vol. 59, pp. 421-429, 2017.

[12] F. L. Jin, X. Li, and S. J. Park, "Synthesis and application of epoxy resins: A review," Journal of Industrial and Engineering Chemistry, vol. 29, pp. 1-11, 2015.

[13] S. Zheng, J. Pascault, and R. Williams, "Epoxy polymers: new materials and innovations," Pascault, JP, Williams, RJJ, Eds, 2010.

[14] J. P. Pascault, H. Sautereau, J. Verdu, and R. J. Williams, Thermosetting polymers vol. 477: Marcel Dekker New York, 2002.

[15] I. K. Hong, Y. S. Yoon, and S.-B. Lee, "Selection of thinner for epoxy type resins for neon transformer housing," Journal of Industrial and Engineering Chemistry, vol. 18, pp. 1997-2003, 2012.

[16] W. Jiang, F.-L. Jin, and S.-J. Park, "Thermo-mechanical behaviors of epoxy resins reinforced with nano-Al2O3 particles," Journal of Industrial and Engineering Chemistry, vol. 18, pp. 594-596, 2012.

[17] S. Zafar, F. Zafar, U. Riaz, and S. Ahmad, "Synthesis, characterization, and anticorrosive coating properties of waterborne interpenetrating polymer network based on epoxy-acrylic-oleic acid with butylated melamine formaldehyde," Journal of applied polymer science, vol. 113, pp. 827-838, 2009.

[18] E. Potvin, L. Brossard, and G. Larochelle, "Corrosion protective performances of commercial low-VOC epoxy/urethane coatings on hot-rolled 1010 mild steel," Progress in organic coatings, vol. 31, pp. 363-373, 1997.

[19] D. Klein and K. Jörg, "Two-component aqueous epoxy binders free of volatile organic content (VOC)," Progress in organic coatings, vol. 32, pp. 119-125, 1997.

[20] Z. Zhaoying, H. Yuhui, L. Bing, and C. Guangming, "Studies on particle size of waterborne emulsions derived from epoxy resin," European Polymer Journal, vol. 37, pp. 1207-1211, 2001.

[21] S. Zafar, U. Riaz, and S. Ahmad, "Water-borne melamine–formaldehyde-cured epoxy–acrylate corrosion resistant coatings," Journal of applied polymer science, vol. 107, pp. 215-222, 2008.

[22] S. Liu, L. Gu, H. Zhao, J. Chen, and H. Yu, "Corrosion resistance of graphene-reinforced waterborne epoxy coatings," Journal of Materials Science & Technology, vol. 32, pp. 425-431, 2016.

[23] G. m. Wu, Z. w. Kong, J. Chen, S.-p. Huo, and G.-f. Liu, "Preparation and properties of waterborne polyurethane/epoxy resin composite coating from anionic terpene-based polyol dispersion," Progress in Organic Coatings, vol. 77, pp. 315-321, 2014.

[24] S. Xu, N. Girouard, G. Schueneman, M. L. Shofner, and J. C. Meredith, "Mechanical and thermal properties of waterborne epoxy composites containing cellulose nanocrystals," Polymer, vol. 54, pp. 6589-6598, 2013.

[25] F. H. Walker, J. B. Dickenson, C. R. Hegedus, and F. R. Pepe, "Cationic polymerization of emulsified epoxy resins," Progress in organic coatings, vol. 45, pp. 291-303, 2002.

[26] J. T. Woo and A. Toman, "Water-based epoxy-acrylic graft copolymer," Progress in organic Coatings, vol. 21, pp. 371-385, 1993.

[27] L. Chen, L. Hong, J.-C. Lin, G. Meyers, J. Harris, and M. Radler, "Epoxy-acrylic core-shell particles by seeded emulsion polymerization," Journal of colloid and interface science, vol. 473, pp. 182-189, 2016.

[28] R. Parmar, K. Patel, and J. Parmar, "High-performance waterborne coatings based on epoxy-acrylic-graft-copolymer-modified polyurethane dispersions," Polymer International, vol. 54, pp. 488-494, 2005.

[29] K. Zhang, H. q. Fu, H. Huang, and H. q. Chen, "Waterborne Epoxy-Acrylic Dispersions Modified by Siloxane," Journal of Dispersion Science and Technology, vol. 28, pp. 1209-1217, 2007.

[30] H. Sun, W. Ni, B. Yuan, T. Wang, P. Li, Y. Liu, et al., "Synthesis and characterization of emulsion-type curing agent of water-borne epoxy resin," Journal of Applied Polymer Science, vol. 130, pp. 2652-2659, 2013.

[31] K. D. Suh, Y. S. Chon, and J. Y. Kim, "Preparation of UV curable emulsions using PEG-modified urethane acrylates and their coating properties III: Effects of epoxy acrylate," Polymer bulletin, vol. 38, pp. 287-294, 1997.

[32] V. H. Pham, Y. W. Ha, S. H. Kim, H. T. Jeong, M. Y. Jung, B. S. Ko, et al., "Synthesis of epoxy encapsulated organoclay nanocomposite latex via phase inversion emulsification and its gas barrier property," Journal of Industrial and Engineering Chemistry, vol. 20, pp. 108-112, 2014.

[33] A. Wegmann, "Novel waterborne epoxy resin emulsion," JCT, Journal of coatings technology, vol. 65, pp. 27-34, 1993.

[34] G. Pan, L. Wu, Z. Zhang, and D. Li, "Synthesis and characterization of epoxy-acrylate composite latex," Journal of Applied polymer science, vol. 83, pp. 1736-1743, 2002.

[35] E. Tang, F. Bian, A. Klein, M. El-Aasser, S. Liu, M. Yuan, et al., "Fabrication of an epoxy graft poly (St-acrylate) composite latex and its functional properties as a steel coating," Progress in Organic Coatings, vol. 77, pp. 1854-1860, 2014.

[36] A. R. Mahdavian, M. Ashjari, and A. B. Makoo, "Preparation of poly (styrene–methyl methacrylate)/SiO2 composite nanoparticles via emulsion polymerization. An investigation into the compatiblization," European Polymer Journal, vol. 43, pp. 336-344, 2007.

[37] R. Wei, Y. Luo, and Z. Li, "Synthesis of structured nanoparticles of styrene/butadiene block copolymers via RAFT seeded emulsion polymerization," Polymer, vol. 51, pp. 3879-3886, 2010.

[38] K. R. Christopher, A. Pal, G. Mirchandani, and T. Dhar, "Synthesis and characterization of polystyrene-acrylate/polysiloxane (PSA/PSi) core shell polymers and evaluation of their properties for high durable exterior coatings," Progress in Organic Coatings, vol. 77, pp. 1063-1068, 2014.

[39] N. Pokeržnik and M. Krajnc, "Synthesis of a glucose-based surfmer and its copolymerization with n-butyl acrylate for emulsion pressure sensitive adhesives," European Polymer Journal, vol. 68, pp. 558-572, 2015.

[40] J. C. Garay-Jimenez, D. Gergeres, A. Young, D. V. Lim, and E. Turos, "Physical properties and biological activity of poly (butyl acrylate–styrene) nanoparticle emulsions prepared with conventional and polymerizable surfactants," Nanomedicine: Nanotechnology, Biology and Medicine, vol. 5, pp. 443-451, 2009.

[41] S. Tolue, M. R. Moghbeli, and S. M. Ghafelebashi, "Preparation of ASA (acrylonitrile-styrene-acrylate) structural latexes via seeded emulsion polymerization," European Polymer Journal, vol. 45, pp. 714-720, 2009.

[42] J. M. Asua, "Miniemulsion polymerization," Progress in polymer science, vol. 27, pp. 1283-1346, 2002.

[43] J. Ugelstad, F. K. Hansen, and S. Lange, "Emulsion polymerization of styrene with sodium hexadecyl

sulphate/hexadecanol mixtures as emulsifiers. Initiation in monomer droplets," Die Makromolekulare Chemie: Macromolecular Chemistry and Physics, vol. 175, pp. 507-521, 1974.

[44] F. K. Hansen and J. Ugelstad, "Particle nucleation in emulsion polymerization. IV. Nucleation in monomer droplets," Journal of Polymer Science: Polymer Chemistry Edition, vol. 17, pp. 3069-3082, 1979.

[45] D. De Wet-Roos, J. Knoetze, B. Cooray, and R. Sanderson, "Emulsion polymerization of an epoxy-acrylate emulsion stabilized with polyacrylate. i. influence of salt, initiator, neutralizing amine, and stirring speed," Journal of applied polymer science, vol. 71, pp. 1347-1360, 1999.

[46] J. l. Zhou and W. p. Tu, "Synthesis of nonionic type self-emulsified waterborne epoxy curing agent and its properties," Journal of Chemical Engineering of Chinese Universities, vol. 20, p. 94, 2006.

[47] H. Kawahara, S. Matsufuji, T. Goto, Y. Okamoto, H. Ogura, H. Kage, et al., "Epoxy resin/acrylic composite latexes: reactivity and stability of epoxy groups with carboxyl groups," Advanced Powder Technology, vol. 12, pp. 521-532, 2001.

[48] M. Durand, V. Molinier, T. Féron, and J.-M. Aubry, "Isosorbide mono-and di-alkyl ethers, a new class of sustainable coalescents for water-borne paints," Progress in Organic Coatings, vol. 69, pp. 344-351, 2010.

[49] C. L. Rodriguez, J. Weathers, B. Corujo, and P. Peterson, "Formulating water-based systems with propylene-oxide-based glycol ethers," Journal of Coatings Technology, vol. 72, pp. 67-72, 2000.

[50] S. Gupta and M. Shukla, "Water soluble epoxy resins for cathodic electrodeposition coatings," Pigment & resin technology, vol. 21, pp. 4-7, 1992.

[51] M. F. Mustafa, W. D. Cook, T. L. Schiller, and H. M. Siddiqi, "Curing behavior and thermal properties of TGDDM copolymerized with a new pyridine-containing diamine and with DDM or DDS," Thermochimica Acta, vol. 575, pp. 21-28, 2014.

[52] M. Liu, X. Mao, H. Zhu, A. Lin, and D. Wang, "Water and corrosion resistance of epoxy–acrylic–amine waterborne coatings: Effects of resin molecular weight, polar group and hydrophobic segment," Corrosion Science, vol. 75, pp. 106-113, 2013.

[53] M. Ghaemy, M. Barghamadi, and H. Behmadi, "Cure kinetics of epoxy resin and aromatic diamines," Journal of Applied Polymer Science, vol. 94, pp. 1049-1056, 2004.

[54] X. Xiong, R. Ren, S. Liu, S. Lu, and P. Chen, "The curing kinetics and thermal properties of epoxy resins cured by aromatic diamine with hetero-cyclic side chain structure," Thermochimica Acta, vol. 595, pp. 22-27, 2014.

[55] P. Murias, H. Maciejewski, and H. Galina, "Epoxy resins modified with reactive low molecular weight siloxanes," European Polymer Journal, vol. 48, pp. 769-773, 2012.

[56] H. Ren, W. Chen, and L. Fan, "Study on the cure kinetics of a silicone-modified waterborne epoxy curing agent by the advanced isoconversional method," Polymer-Plastics Technology and Engineering, vol. 49, pp. 836-840, 2010.

[57] X. Yang, W. Huang, and Y. Yu, "Synthesis, characterization, and properties of silicone–epoxy resins," Journal of Applied Polymer Science, vol. 120, pp. 1216-1224, 2011.

[58] M. Kathalewar and A. Sabnis, "Effect of molecular weight of phenalkamines on the curing, mechanical, thermal and anticorrosive properties of epoxy based coatings," Progress in Organic Coatings, vol. 84, pp. 79-88, 2015.

[59] A. Wegmann, "Freeze-thaw stability of epoxy resin emulsions," Pigment & resin technology, vol. 26, pp. 153-160, 1997.

[60] S. Han, H. Gyu Yoon, K. S. Suh, W. Gun Kim, and T. Jin Moon, "Cure kinetics of biphenyl epoxy-phenol novolac resin system using triphenylphosphine as catalyst," Journal of Polymer Science Part A: Polymer Chemistry, vol. 37, pp. 713-720, 1999.

[61] L. Liu, J. Li, X. Zhang, and K. Jin, "The preparation of a three-layer “core–shell” structured epoxy-acrylate emulsion," RSC Advances, vol. 4, pp. 47184-47190, 2014.

[62] K. Mequanint and R. Sanderson, "Nano-structure phosphorus-containing polyurethane dispersions: synthesis and crosslinking with melamine formaldehyde resin," Polymer, vol. 44, pp. 2631-2639, 2003.

[63] S. Cheraghi, H. J. Naghash, and M. Younesi, "RETRACTED: Synthesis and characterization of two novel heterocyclic monomers bearing allylic function and their applications in the epoxy-acrylic-amine waterborne coatings," ed: Elsevier, 2015.

[64] M. Bagherzadeh, F. Mahdavi, M. Ghasemi, H. Shariatpanahi, and H. Faridi, "Using nanoemeraldine salt-polyaniline for preparation of a new anticorrosive water-based epoxy coating," Progress in Organic Coatings, vol. 68, pp. 319-322, 2010.

[65] S. Ahmad, S. Ashraf, G. Kumar, A. Hasnat, and E. Sharmin, "Studies on epoxy-butylated melamine formaldehyde-based anticorrosive coatings from a sustainable resource," Progress in organic coatings, vol. 56, pp. 207-213, 2006.

[66] C. Hawkins, A. Sheppard, and T. Wood, "Recent advances in aqueous two-component systems for heavy-duty metal protection," Progress in organic coatings, vol. 32, pp. 253-261, 1997.

[67] W. Schneider, "Ambient temperature curing waterborne epoxy systems," Materials performance, vol.

30, pp. 28-32, 1991.

[68] F. H. Walker, "Amide-containing self-emulsifying epoxy curing agent," ed: Google Patents, 1997.

[69] L. Guangqi, S. Jianzhong, and Z. Qiyun, "Synthesis and characterization of waterborne epoxy curing agent modified by silane," Chinese Journal of Chemical Engineering, vol. 15, pp. 899-905, 2007.

[70] M. J. Chen, F. D. Osterholtz, A. Chaves, P. E. Ramdatt, and B. A. Waldman, "Epoxy silanes in reactive polymer emulsions," Journal of Coatings Technology, vol. 69, pp. 49-55, 1997.

[71] X. Xiao and C. Hao, "Preparation of waterborne epoxy acrylate/silica sol hybrid materials and study of their UV curing behavior," Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 359, pp. 82-87, 2010.

[72] J. Woo, V. Ting, J. Evans, R. Marcinko, G. Carlson, and C. Ortiz, "Synthesis and characterization of water-reducible graft epoxy copolymers," Journal of Coatings Technology, vol. 54, pp. 41-55, 1982.

[73] F. Chu, T. F. McKenna, Y. Jiang, and S. Lu, "A study of the preparation and mechanism of the ambient temperature curing of acrylic latex with epoxy resins," Polymer, vol. 38, pp. 6157-6165, 1997.

[74] S. X. Li, W. F. Wang, L. M. Liu, and G. Y. Liu, "Morphology and characterization of epoxy-acrylate composite particles," Polymer bulletin, vol. 61, pp. 749-757, 2008.

[75] S. Sun, P. Sun, and D. Liu, "The study of esterifying reaction between epoxy resins and carboxyl acrylic polymers in the presence of tertiary amine," European polymer journal, vol. 41, pp. 913-922, 2005.

[76] J. Gao, H. Lv, X. Zhang, and H. Zhao, "Syntheshis and properties of waterborne epoxy acrylate nanocomposite coating modified by MAP-POSS," Progress in Organic Coatings, vol. 76, pp. 1477-1483, 2013.

[77] S. Mishra, J. Singh, and V. Choudhary, "Synthesis and characterization of butyl acrylate/methyl methacrylate/glycidyl methacrylate latexes," Journal of applied polymer science, vol. 115, pp. 549-557, 2010.

[78] J. P. Kennedy, "Free radical and ionic grafting," in Journal of Polymer Science: Polymer Symposia, 1978, pp. 117-124.

[79] D. Ramesh and T. Vasudevan, "Synthesis and physico-chemical evaluation of water-soluble epoxy ester primer coating," Progress in Organic Coatings, vol. 66, pp. 93-98, 2009.

[80] Y. Liu, C. P. Wu, and C. Y. Pan, "Effect of chemical crosslinking on the structure and mechanical properties of polyurethane prepared from copoly (PPO–THF) triols," Journal of applied polymer

science, vol. 67, pp. 2163-2169, 1998.

[81] Z. Ge and Y. Luo, "Synthesis and characterization of siloxane-modified two-component waterborne polyurethane," Progress in Organic Coatings, vol. 76, pp. 1522-1526, 2013.

[82] L. Chen and S. Chen, "Latex interpenetrating networks based on polyurethane, polyacrylate and epoxy resin," Progress in Organic Coatings, vol. 49, pp. 252-258, 2004.

[83] J. Gao, F. L. Zhu, J. Yang, and X. Liu, "Synthesis and curing kinetics of UV-curable waterborne bisphenol-Sepoxy-acrylate/polyurethane-acrylate/methylacryloylpropyl-POSS nanocomposites," Journal of Macromolecular Science, Part B, vol. 53, pp. 1800-1813, 2014.

[84] K. Raghupathy and S. Guruviah, "Water-Borne Air-Drying Coatings Based on Epoxy Ester for Protection of Metals," Bull. Electrochem., vol. 5, pp. 511-512, 1989.

[85] A. P. Singh, G. Gunasekaran, C. Suryanarayana, and R. B. Naik, "Fatty acid based waterborne air drying epoxy ester resin for coating applications," Progress in Organic Coatings, vol. 87, pp. 95-105, 2015.

[86] D. Shikha, P. Kamani, and M. Shukla, "Studies on synthesis of water-borne epoxy ester based on RBO fatty acids," Progress in organic coatings, vol. 47, pp. 87-94, 2003.

[87] N. Krishnamurti, M. Shirsalkar, and M. Sivasamban, "Water soluble epoxy resin fatty acid esters," Paint and Resin, vol. 59, p. 30, 1989.

[88] J. T. Derksen, F. P. Cuperus, and P. Kolster, "Renewable resources in coatings technology: a review," Progress in Organic Coatings, vol. 27, pp. 45-53, 1996.

[89] V. D. Athawale and R. V. Nimbalkar, "Waterborne coatings based on renewable oil resources: an overview," Journal of the American Oil Chemists' Society, vol. 88, pp. 159-185, 2011.

[90] K. Krishnamurti, "Water-soluble epoxy resins for surface coatings," Progress in Organic Coatings, vol. 11, pp. 167-197, 1983.

[91] M. M. Ruiz, J. Y. Cavaillé, A. Dufresne, C. Graillat, and J. F. Gérard, "New waterborne epoxy coatings based on cellulose nanofillers," in Macromolecular Symposia, 2001, pp. 211-222.

[92] Y. Bautista, M. Gómez, C. Ribes, and V. Sanz, "Relation between the scratch resistance and the chemical structure of organic–inorganic hybrid coatings," Progress in Organic Coatings, vol. 70, pp. 358-364, 2011.

[93] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, and R. Kumar, "Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—a review," Progress in Polymer

Science, vol. 38, pp. 1232-1261, 2013.

[94] T. Fu, C. Wen, J. Lu, Y. Zhou, S. Ma, B. Dong, et al., "Sol-gel derived TiO2 coating on plasma nitrided 316L stainless steel," Vacuum, vol. 86, pp. 1402-1407, 2012.

[95] M.-C. Lai, K.-C. Chang, J.-M. Yeh, S.-J. Liou, M.-F. Hsieh, and H.-S. Chang, "Advanced environmentally friendly anticorrosive materials prepared from water-based polyacrylate/Na+-MMT clay nanocomposite latexes," European Polymer Journal, vol. 43, pp. 4219-4228, 2007.

[96] A. Usuki, N. Hasegawa, M. Kato, and S. Kobayashi, "Polymer-clay nanocomposites," in Inorganic polymeric nanocomposites and membranes, ed: Springer, 2005, pp. 135-195.

[97] M. Bagherzadeh and T. Mousavinejad, "Preparation and investigation of anticorrosion properties of the water-based epoxy-clay nanocoating modified by Na+-MMT and Cloisite 30B," Progress in Organic Coatings, vol. 74, pp. 589-595, 2012.

[98] K. Kowalczyk and T. Spychaj, "Epoxy coatings with modified montmorillonites," Progress in Organic Coatings, vol. 62, pp. 425-429, 2008.

[99] T. T. X. Hang, T. A. Truc, T. H. Nam, V. K. Oanh, J.-B. Jorcin, and N. Pébère, "Corrosion protection of carbon steel by an epoxy resin containing organically modified clay," Surface and Coatings Technology, vol. 201, pp. 7408-7415, 2007.

[100] X. Wang, X. Wang, L. Song, W. Xing, G. Tang, W. Hu, et al., "Preparation and thermal stability of UV-cured epoxy-based coatings modified with octamercaptopropyl POSS," Thermochimica acta, vol. 568, pp. 130-139, 2013.

[101] G.-m. Wu, D. Liu, G.-f. Liu, J. Chen, S.-p. Huo, and Z.-w. Kong, "Thermoset nanocomposites from waterborne bio-based epoxy resin and cellulose nanowhiskers," Carbohydrate polymers, vol. 127, pp. 229-235, 2015.

[102] M. N. Katariya, A. K. Jana, and P. A. Parikh, "Corrosion inhibition effectiveness of zeolite ZSM-5 coating on mild steel against various organic acids and its antimicrobial activity," Journal of industrial and Engineering Chemistry, vol. 19, pp. 286-291, 2013.

[103] Y. Hao, F. Liu, and E.-H. Han, "Protection of epoxy coatings containing polyaniline modified ultra-short glass fibers," Progress in Organic Coatings, vol. 76, pp. 571-580, 2013.

[104] W. Sun, X. Yan, and X. Zhu, "The synthetic kinetics and underwater acoustic absorption properties of novel epoxyurethanes and their blends with epoxy resin," Polymer bulletin, vol. 69, pp. 621-633, 2012.

[105] W. Lenhard, U. Neumann, and W. Collong, "Amino resin curable water reducible epoxy systems for automotive refinishing paints," Progress in organic coatings, vol. 32, pp. 127-130, 1997.

[106] M. Yao, E. Tang, C. Guo, S. Liu, H. Tian, and H. Gao, "Synthesis of waterborne epoxy/polyacrylate composites via miniemulsion polymerization and corrosion resistance of coatings," Progress in Organic Coatings, vol. 113, pp. 143-150, 2017.

[107] A. Wegmann, "Chemical resistance of waterborne epoxy/amine coatings," Progress in Organic Coatings, vol. 32, pp. 231-239, 1997.

6. Recommadations

WBE based polymeric systems have provided the opportunity to reduce or replace the VOCs. Various methods have been developed to formulate WBE based polymeric coatings. The coating performance and barrier properties of WBE coatings can also be improved by the inclusion of nanoparticles. WBE systems can be commercially employed in a wide variety of applications especially in the field of architectural and industrial coatings.