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# Progress in waterborne polymer dispersions for coating applications: commercialized systems and new trends

Kyle Pieters and Tizazu H. Mekonnen \*

The environmental impact and safety of products have become increasingly prominent in recent years, with stringent legislation expected to persist. Polymeric coatings are pervasive in modern life, serving to impart desirable properties and protection to a wide range of surfaces. Traditionally dispersed in volatile organic solvents harmful to the environment and workers, modern coatings are shifting towards waterborne, minimizing harmful environmental emissions. Waterborne coatings have seen substantial commercial uptake in large sectors such as architectural and automotive coatings. Nevertheless, their performance still lags behind conventional systems, and, currently, some products lack commercially viable waterborne alternatives. This review focuses on the current state of commercialized waterborne polymer systems, scrutinizing their performance, composition, and market penetration. Additionally, it explores future trends aimed at addressing existing challenges and pioneering novel coating technologies, with an emphasis on achieving fully sustainable systems.

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## Sustainability spotlight

Existing waterborne polymeric coatings are essential to modern lifestyle but their manufacture frequently results in harmful emissions to workers and the environment. A shift from more harmful chemicals to safe and environmentally friendly water is necessary for fully sustainable coatings. In this review, progress on waterborne coating systems is reported with currently commercialized products highlighted and scrutinized. The future for waterborne coating systems is analyzed, with a focus on current impediments to wider adoption, as well as making fully sustainable systems using biobased and biodegradable polymers. Waterborne coating systems advance each of the following important UN sustainable development goals: good health and well being (SDG 3), industry, innovation, and infrastructure (SDG 9), responsible consumption and production (SDG 12), and climate action (SDG 13).

## 1. Introduction

Polymerically coated surfaces have become ubiquitous in modern life. From house paint to food packaging, kitchenware to synthetic leathers, a myriad of products leverage the properties imparted by the polymeric coating in tandem with the substrate to provide improved material appearance, functionality, or performance.<sup>1–5</sup> At the same time, these coatings must remain competitive with alternative options in terms of cost, availability, environmental impact, and other pertinent indicators.<sup>1,6</sup>

Even as a thin surface coating, polymers offer substantial advantages over non-polymeric materials. A broad range of tunable materials enables the selection of a polymer system that fulfills a wide range of color ranges, textures, and appearances, ranging from metallic luster to imitation leather, matte finish and more.<sup>7–9</sup> Moreover, these surfaces can be tailored to exhibit

high performance in areas, such as water and vapor barrier properties (high barrier or selectively porous membranes), UV and corrosion resistance, electrical conductivity, flexibility, and impact strength, thereby enhancing the properties of or safeguarding the underlying substrate.<sup>1</sup> Furthermore, polymer coatings facilitate the generation of smart surfaces, providing functionalities, such as antimicrobial surfaces, actuators, and active packaging.<sup>10–13</sup>

There are multiple methods available for coating polymers onto surfaces, including extrusion, powder coating, and liquid carriers. Drawbacks associated with extrusion and other hot melt methods include high processing temperatures and handling costs due to the highly viscous polymer melt.<sup>14,15</sup> For some materials, like poly(hydroxybutyrate-valerate) (PHBV) and polylactic acid (PLA), extrusion methods can yield brittle films,<sup>16,17</sup> while liquid-borne coating method allows for flexible film formation.<sup>6</sup> Powder coating enables the application of thin, uniform coatings without requiring an evaporation step, although it necessitates an initial melting stage for powder formation and encounters challenges such as powder agglomeration and moisture control.<sup>18</sup> Other liquid-free coating

Department of Chemical Engineering, Institute of Polymer Research, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, N2L 3G1, Ontario, Canada.  
E-mail: tmekonnen@uwaterloo.ca



methods, such as press, supercritical fluid, and cold spray coating are also used in specialized applications.<sup>19,20</sup>

When using a liquid carrier, the polymer is either dissolved in or dispersed within a suitable solvent, which is subsequently evaporated after surface coating.<sup>21</sup> Liquid carriers are chosen to enable evaporation at lower processing temperatures compared to other film preparation methods involving polymer melting.<sup>21</sup> Coating polymers from within a liquid medium offers a broad range of application methods, such as spraying, dipping, rod coating, and more.<sup>3</sup> Liquid coating is also preferred when functionality or multicomponent systems are involved, as it allows for self-stratification of different components.<sup>22</sup>

Waterborne systems are preferred over organic solvents whenever possible due to their superior environmental friendliness and enhanced safety features, including reduced fire, explosion, and worker physiological risks.<sup>23,24</sup> It is important to note that within this review work, 'solvent' or 'solventborne' refer to organic liquids that can act as hazardous pollutants. Initially, waterborne systems gained popularity because of their ability to achieve sufficiently high solid weight percentages (wt%) while substantially reducing targeted emissions.<sup>23</sup> Higher solids percentage results in smaller equipment sizes, faster drying time, and reduced storage and transportation costs.<sup>25</sup> Achieving higher solids percentages in dispersions is possible because the system is no longer constrained by the amount of polymer that can dissolve in the solvent or form *via* reaction, as the viscosity remains relatively low as desired.<sup>26,27</sup> Rather than viscosity being dictated by the hydrodynamic interactions between the dissolved polymer and the solvent, the viscosity is largely dictated by particle size, and any added rheological modifiers.<sup>6,26,28,29</sup> While waterborne and high solids content were initially synonymous with one another,<sup>23</sup> some applications of waterborne polymer systems now do not necessarily require high solids content to be industrially practical.<sup>4,30</sup>

However, designing waterborne systems is still limited by several drawbacks. Chiefly, many polymer systems do not dissolve or disperse well in water and instead prefer organic solvents.<sup>31</sup> Additionally, water-phase polymerization of monomer to obtain waterborne polymers is not possible for many preformed polymers, including biopolymers, many of which are of interest for sustainable coatings.<sup>21</sup> As a result, substantial resources must be allocated to create a suitable dispersion. Additionally, while higher wt% means lower storage and shipment costs than organic solvent systems, dry systems offer even better cost-effectiveness in this regard. Storage and shipment can also be complicated by the poor stability arising in many waterborne systems.<sup>32</sup> Organic solvents are also still frequently required as part of the overall process.<sup>6,23</sup> Lastly, the evaporation temperature for water is often higher than its organic solvent counterparts.<sup>26</sup> A summary of these benefits and remaining drawbacks is provided in Fig. 1.

While there are multiple methods available, the predominant approach for obtaining waterborne polymer dispersions of preformed polymers (not emulsion polymerizable) is through phase inversion.<sup>21</sup> In this process, the preformed polymer is dissolved in a suitable organic solvent, which is immiscible in water. Subsequently, water and a surfactant are added to the

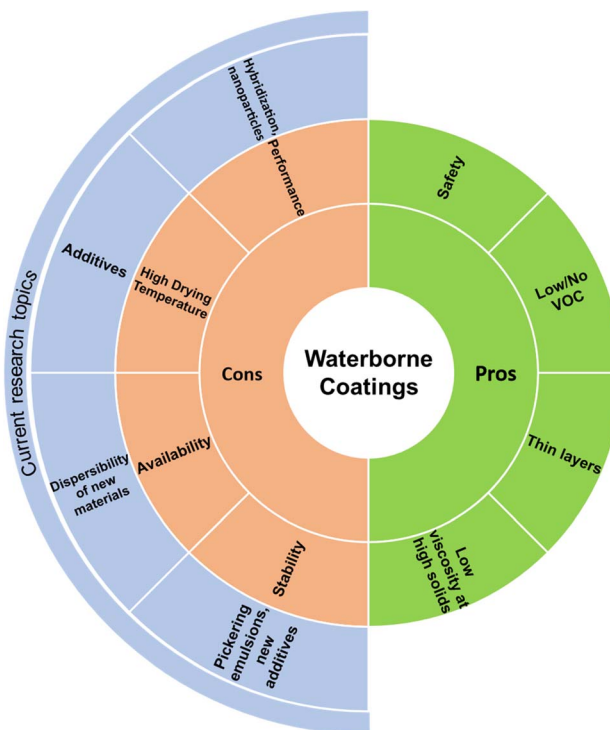


Fig. 1 Benefits and drawbacks to waterborne coating systems compared to existing alternatives.

solution alongside an energy input. The organic solvent is then evaporated, leaving the polymer dispersed in water.<sup>6</sup> Although an organic solvent is still used in this process, the quantity required can be significantly reduced compared to non-waterborne processes. Moreover, it can be better controlled and recovered during the preparation process, and in some cases, it may be eliminated entirely with alternative preparation methods.<sup>23,33</sup>

The waterborne dispersion is subsequently cast onto a substrate, and as water evaporates, the polymer particles undergo merging to form a homogeneous coated surface.<sup>21</sup> Initially, as water evaporates, the dispersed polymer spheres pack closely together due to the decreasing volume and start to deform to fill in void spaces. With sufficient temperature (above the minimum film forming temperature, or MFFT), the spheres coalesce, with the polymer chains interpenetrating and forming a continuous film.<sup>21,26,34,35</sup> It is important to note that this process is specific to dispersed polymer systems, which require spherical particle deformation and coalescence, rather than dissolved polymer systems.<sup>26</sup> These steps are illustrated in Fig. 2. While the process involved for dispersed systems is more complex, it can be beneficial in tuning film morphology.<sup>36</sup> Different dispersed particles exhibit greatly varying coalescence behavior, as opposed to dissolved systems, where behavior is nearly uniform.<sup>36</sup>

Currently, waterborne dispersions are used in place of solventborne in some of the largest use case coatings industries, including the biggest, architectural applications.<sup>23,37</sup> Advances in waterborne technology have also allowed their use for wood



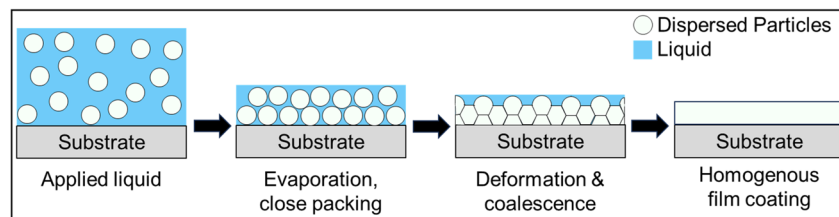


Fig. 2 Process of film formation from liquid polymer dispersions.

coatings, automotive, and more.<sup>38,39</sup> As the technology continues to advance, replacement of conventional coatings for applications, such as paper packaging,<sup>21</sup> availability of water-insoluble polymers like polyhydroxyalkanoates,<sup>35</sup> novel applications including smart packaging,<sup>40</sup> and stabilization methods such as Pickering emulsions<sup>41</sup> will all continue the expansion of the waterborne coatings industry.

This review paper sets out to showcase the most recent challenges and developments in waterborne polymer coatings. The latest progress in improvements to stability, breadth of materials, and industrial viability is critically reviewed. As well, current industrial uptake and the future of waterborne system advancement and adoption is thoroughly discussed.

## 2. Established waterborne polymer systems

Waterborne coatings have gained significant traction across various commercial applications, offering a multitude of benefits. They provide grease/moisture barrier properties in packaging products, mitigate moisture and microbial attack in wood finishes, and enhance corrosion resistance in metal substrates. Notably, waterborne coatings constitute the largest global class of coatings,<sup>42</sup> and they substantially reduce the volatile organic compounds (VOC) content compared to solventborne coatings, thereby benefiting both workers and the environment.<sup>23,24</sup> Additionally, dispersion coatings can utilize less solid material than dry coating methods like extrusion.<sup>35</sup> Although formulating waterborne coatings to match the stability and performance as conventional coatings presents challenges,<sup>32</sup> ongoing advancements are steadily enhancing their efficacy. Consequently, the market adoption of waterborne coatings is projected to continue rising in the foreseeable future.<sup>43</sup>

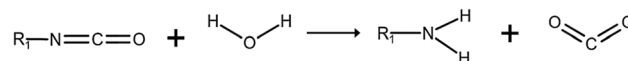
### 2.1. Wood coatings

Uncoated wood, whether indoors or outdoors, is highly vulnerable to environmental damage and degradation. Factors, such as moisture, radiation, microorganisms, temperature variations, mechanical stresses, and chemical exposure can easily compromise its integrity.<sup>44,45</sup> The frequency and intensity of these stressors in a given environment dictate the degree of protection which must be imparted by the selected coating.<sup>44</sup> The biopolymers constituting wood (polysaccharides, lignin, phenolics) are particularly susceptible to degradation caused by

ultraviolet (UV) and biological attack.<sup>45</sup> Due to the high incidence of fungal growth, moisture control is of utmost importance.<sup>45,46</sup> While some wood treatments involve chemical modification of the wood or the addition of fillers, wood coatings remain the standard for providing protection.<sup>47,48</sup>

In addition to imparting protection, wood coatings are commonly used to enhance the visual appearance of the product, and must meet consumer expectations in terms of aesthetics.<sup>44,49</sup> This can pose challenges, especially for applications requiring extensive protection, such as exterior products, and even more so when a clearcoat finish is desired to preserve the natural beauty of the wood.<sup>49</sup> Clearcoats typically allow UV transmittance through the coating to the wood substrate, leading to photodegradation and coating delamination.<sup>49</sup> In such cases, the coating alone may not suffice, necessitating the combination with pretreatments or other measures to stabilize the wood.<sup>49</sup> Extensive research has been conducted to develop successful clearcoats that do not require additional treatments, such as using silicone coatings with metal additives. However, the protective and longevity performance of these clearcoats has yet to match that of opaque alternatives.<sup>38,49</sup>

In general, waterborne wood coatings for exterior applications are based on polyurethane, acrylic, or alkyd based polymers.<sup>38</sup> Polyurethane coatings exhibit strong weathering and mechanical degradation resistance.<sup>38</sup> Since polyurethane is incompatible with water, various waterborne dispersing methods are employed to generate waterborne systems.<sup>50</sup> As well, the fundamental polyurethane formation reaction of a polyol with a polyisocyanate should not be performed in the presence of water as the water and isocyanate reaction will react as shown in Scheme 1.<sup>51</sup> Common industrial methods include forming a hydrophilic pre-polymer that is then polymerized in water or conducting the formation in acetone and then transferring to water when removing the acetone.<sup>50</sup> Less commonly, hot-melting or using a ketimine–ketazine process are reported.<sup>50</sup> Other waterborne polyurethane (WPU) polymerization methods under development include homogenous solution (HSP), reversible addition–fragmentation chain transfer (RAFT), miniemulsion (MEPP), and atom transfer radical (ATRP).<sup>52</sup> While the pre-polymer and acetone methods remain the most widely used, advantages of the other processes include benefits



Scheme 1 Undesired reaction between polyisocyanates and water.



such as being a single-step procedure in the case of the mini-emulsion process and the hot-melt process being solvent-free.<sup>50,52</sup>

Acrylic solutions offer strong UV resistance, dry quickly, and possess good adhesion to wood.<sup>38</sup> However, they may contain micropores, which allow fungal penetration and degradation of the wood, and often require additional measures to prevent fungal growth.<sup>38,53</sup> Acrylic coatings are typically produced through emulsion co-polymerization to form a stable colloidal dispersion in water.<sup>44</sup> Alternatively, solution, bulk, and suspension polymerization are used to a limited degree industrially, with miniemulsions also being employed for some waterborne acrylic hybrids.<sup>54,55</sup> Waterborne self-emulsifying hybrid acrylics are under development which are solvent-free, but do not appear to be industrially employed.<sup>56</sup> Lastly, alkyd resins for wood coatings offer distinct benefits, including a glossy appearance and potential for auto-oxidative curing.<sup>38</sup> Alkyd dispersions in water can be formed either *via* direct emulsification or through phase inversion methods.<sup>57</sup>

Alkyd and acrylic resins are often combined to mitigate individual disadvantages, typically utilizing water-soluble alkyds for wood coating applications.<sup>38,44</sup> For example, the acrylic backbone generally provides superior physical toughness and durability to the resulting coating, while the alkyd resin promotes chemical resistance and visual appeal.<sup>56</sup> For interior applications, where the degradative stresses on wood are much lower, protective performance is of reduced concern.<sup>30,58</sup> The same polymers serve as the basis of interior wood waterborne coatings, albeit with simpler formulations required.<sup>59</sup> Multi-coat systems are prevalent, including combinations like acrylic primers and polyurethane top-coating, or hybridized versions thereof.<sup>60</sup> Coating additives encompass components acting as colorants, fillers, thickeners, dispersants, UV absorbers, and more depending on the desired properties.<sup>45</sup> Biopolymers, such as lignin, chitin, and zein all have potential to displace some current conventional wood coatings with biodegradable alternatives.<sup>45</sup> However, material availability, costs, and more complex formulations act as barriers to commercial adoption.<sup>61</sup>

Wood coatings are typically applied *via* spraying, brushing, or dipping methods.<sup>46</sup> Subsequently, the coating undergoes curing, which can involve applying heat to facilitate surface coalescence, using UV light or another reaction initiator when the system is not yet fully polymerized such as some polyurethanes, or drying at ambient conditions.<sup>44,50,62</sup> In addition to these conventional surface coating methods, there are alternative pressurized and non-pressurized methods available for achieving deeper penetration, such as the Bethell process and Gedrian's Bath.<sup>46</sup> However, these methods tend to be costly, and are generally reserved for chemical treatment and nanoparticle impregnation rather than combined with surface coating applications.<sup>46</sup>

Unfortunately, waterborne wood coatings still exhibit numerous drawbacks. In exterior applications, water barrier properties are of utmost concern to avoid fungal growth, yet waterborne coatings tend to have higher hydrophilicity than conventional coatings.<sup>63</sup> Conversely, for interior applications,

mechanical resistance is the most desired property, and waterborne coatings often fall short.<sup>61</sup> These challenges are further complicated by wood's inherent properties, such as its porosity, which leads to dimensional changes as moisture levels fluctuate. Consequently, coatings must be flexible and possess strong surface adhesion to prevent deterioration and decay over time.<sup>46</sup> Nevertheless, significant strides, including nanoparticle incorporation and other modifications to existing coatings or the development of novel waterborne formulations, have enabled the mitigation of these issues, offering a promising future for the continued utilization of improved waterborne wood coatings.<sup>46,61</sup>

## 2.2. Paints

Paints encompass a vast category, characterized by diverse purposes, polymers, substrates, and coating methods. However, their primary function is always to enhance appearance and, in commercial contexts, to provide some level of protection to the underlying substrate.<sup>64,65</sup> Consequently, paints typically contain colorants alongside polymeric resin and other additives.<sup>65-67</sup> Architectural paints dominate market segment size, comprising over 50% of worldwide volume, and include both indoor and outdoor paints with ~75% of the coatings being waterborne.<sup>39,42,68</sup> Other significant applications include automotive, coil, and marine coatings, all of which are discussed in this work. Although numerous additional paint applications exist, such as toys and home appliances, they occupy smaller market shares and research interests, often exhibiting substantial technological overlap with the aforementioned segments.<sup>69</sup> For many years, the paint industry raised environmental and occupational concerns due to high VOC emissions. However, a combination of innovation and legislation has significantly reduced emissions, favoring lower VOC options like waterborne paints.<sup>23,39,70</sup>

**2.2.1. Automotive paints.** Automotive paints represent some of the most complex coatings, with multiple distinct layers required to meet the stringent appearance, lifespan, and environmental resistance requirements which are demanded by consumers.<sup>66,71</sup> Automotive coatings are highly competitive among companies with consumers holding high expectations, and having been subject to substantial environmental and worker safety regulations.<sup>42,72-74</sup> These factors have contributed to automotive coatings having substantial significance to the overall coatings industry (outsized beyond market share) as it has been involved in many industry innovations, from formulations to application methods.<sup>71,73</sup> Relevant to this work, waterborne exterior automotive paints began to be introduced in the 1980s for basecoats, with waterborne primer and clearcoats following in the 1990s.<sup>39</sup>

Broadly, automotive coatings can be divided into exterior and interior applications, with exterior coatings necessarily undergoing much greater environmental stress.<sup>66</sup> Exterior metal automotive parts involve multiple layers of coating, including an initial corrosion resistant layer known as the electrodeposition coat (E-coat), followed by a primer, basecoat, and a clearcoat, applied in this order, as shown in Fig. 3.<sup>42,75</sup>



Dry thickness (μm)	Name	Purpose	Waterborne Market share
40–50	Clearcoat	Appearance protection, gloss	<1%
10–30	Basecoat	Color and effect	>80%
25–40	Primer	Bind E-Coat to Basecoat	>10%
20	E-Coat	Corrosion protection	100%
Pre-treated substrate			

Fig. 3 Layers of a typical automotive exterior paint stack, with estimates of global waterborne market share within each standard automotive exterior coating layer.<sup>39,72,75–78</sup>

Additional coating layers are also applied to areas for specific purposes, such as anti-chip coatings on the hood and lower body between the e-coat and primer layers, and additional rustproofing and sound deadening of the underbody.<sup>71</sup> Exterior plastic parts, such as bumpers and mirror shells, are frequently coated to match the appearance of their metallic counterparts, and can be coated independently of the metal components (offline), or mounted and then metal and plastic parts coated all at once (inline/online depending on at which layer the plastic and metal components are combined).<sup>79</sup> In either case, the basecoat and clearcoat products are identical, as is the application equipment, such that the components appear identical.<sup>79</sup> Rather, the primary difference between components is in the primer layers and initial treatment steps. For electrostatic basecoats (uncommon) only, an offline or inline (mounted after E-coating) plastic component must be coated with an electrically conductive primer or have electrical conductivity integrated into the substrate.<sup>79</sup> Online coated systems (mounted prior to pretreatment) must be capable of withstanding temperatures of 160–190 °C used for E-coat drying, limiting some plastics from being mounted early in the process.<sup>79,80</sup> While not itself a layer, there is also an initial pretreatment step. Pretreatment ensures that the surface is smooth and free of contaminants and dust, and possesses desired surface energy and tension, allowing for better coating adhesion and smooth film formation.<sup>79,81</sup> Pretreatment requirements are even more stringent when waterborne coatings are involved, with the current industry standard being a multi-zone water power wash and dry to avoid the introduction of organic solvents.<sup>71,79,82</sup> For plastic components, the pre-treatment stage may also include the use of an adhesion promoting layer, as coating adhesion is frequently the most challenging part of using coated plastic components.<sup>80</sup>

**2.2.1.1. Electrodeposition coat (E-coat).** Following pretreatment, the first coating layer applied is designed to provide corrosion resistance and is known as the electrodeposition coat or E-coat.<sup>71</sup> Modern E-coats overwhelmingly provide protection

via barrier properties (as opposed to sacrificial or inhibitor coatings) whereby the coating blocks water, salt, and oxygen from reaching the underlying metal surface.<sup>83</sup> This layer also serves to enhance chip-resistance and contributes to the overall durability of the coating stack, often working in conjunction with the primer.<sup>72,83</sup> Initially, anodic electrodeposition was used for coating application, but modern processes overwhelmingly use cathodic electrodeposition whereby the metal is negatively charged and the paint is positively charged.<sup>71</sup> The coating is applied *via* a dip tank, for which the car body passes through a tank (~90 °F) containing majority deionized water (80–90%), paint solids (10–20%), and some solvent.<sup>71</sup> The car body then enters a bake oven at 160–190 °C for 10 minutes to allow evaporation, crosslinking, and uniform film formation.<sup>71,79,80</sup> Solvent content is very low, below 0.5%, thus this layer is typically considered environmentally friendly from an emissions perspective.<sup>71,83</sup> Final coated thicknesses are around 20 μm, with the process standardized and highly reliable to the point where many manufacturers have only a single electrocoating tank/line feeding all further downstream coating lines.<sup>83</sup> A further benefit of the dip tank method is that internal surfaces which would otherwise be difficult to reach are also coated.<sup>71,84</sup> These tanks are very large, with a material turnover rate (theoretical rate of tank contents by feed material) of two weeks to six months.<sup>83</sup>

The paint solids makeup is typical of a waterborne paint, being majority (70%) comprised of a waterborne resin and a cross-linker, with the remainder being pigment grinding and stabilizing resin, pigments, and extenders and additives, such as dispersants, stabilizers, and cross-linking catalysts.<sup>83</sup> The resin composition is typically an epoxy blend (such as bis-phenol) which further incorporates polyesters, polyacrylates, and polyurethanes, with rubber also occasionally included to further improve energy absorption and thus chip resistance.<sup>83,85–89</sup> While any crosslinking functional group could be used, for best solubility and consistent film formation, primary amine substitution is highly preferential.<sup>83,85</sup> Similarly, many crosslinking agents are available, however modified polyisocyanates are currently heavily favored by industry due to their high reactivity and capability to fine-tune final film properties.<sup>85,90</sup> Waterborne epoxy dispersions are principally prepared commercially using either chemical modification or phase inversion techniques.<sup>91–93</sup> Phase inversion waterborne epoxy is more widely applied due to being more easily performed, but yields products with worse size distributions and stability than more carefully controllable modification reactions.<sup>91</sup> Automotive Original Equipment Manufacturer (OEM) coating is oligopolistic, with BASF, PPG, and Axalta (Dupont pre-2013 (ref. 94–96)) providing nearly all exterior coatings, and with these products highly engineered specifically for automotive applications.<sup>39</sup>

For E-coating, their respective products are CathoGuard® (BASF), ENVIRO-PRIME® & POWERCRON® (PPG), and Aqua-EC™ (Axalta).<sup>97–99</sup> The chemical reactions at the electrodes produce oxygen and hydrogen, which can present as bubbles in the film if the bath and/or drying temperatures are insufficient to allow for their release.<sup>83</sup> Other common defects include craters, pinholes, boil outs, hash marks, and “water spots”,



which can be removed by sanding.<sup>71,83</sup> Overall, drawbacks to the waterborne approach currently employed are relatively few. Among these, the primary issues are preventing bacterial growth in the large open water tanks used for coating, the necessity and intensity of the pretreatment steps, and the high energy associated with baking the E-coat layer.<sup>72,83,85</sup> As the percentage of metal components replaced with polymer composites as the substrate for exterior automotive applications continues to grow, the demand for and purpose of this layer may change significantly.<sup>71,80</sup>

**2.2.1.2. Primer.** A primer (or primer surfacer) is the next layer applied, and primarily serves to ensure a high-quality bond between the E-coat and the topcoat (basecoat + clearcoat).<sup>100</sup> Secondly, the primer acts as another layer of chip resistance, and enhances the overall paint appearance by providing a smooth coating surface for finishing.<sup>71</sup> Lastly, the primer acts to block UV from reaching and delaminating the E-coat, as the topcoat thicknesses and compositions are usually insufficient for this purpose due to the focus being on final appearance.<sup>100</sup>

Solventborne, waterborne, and powder primers are available, with solventborne still dominant worldwide but with waterborne standard in Europe and powders heavily used in the United States, due to stricter environmental and safety regulations in these markets phasing out solventborne options.<sup>89,100</sup> Regardless of format, the polymer content is usually acrylic, polyurethane, or polyester crosslinked with alkyoxylated melamine.<sup>84</sup> Powders have the advantages over waterborne of having near zero volatile content, as well as waste from overspray being able to be recycled.<sup>74</sup> On the other hand, waterborne systems are more easily retrofitted into existing manufacturing plants,<sup>101</sup> as well as having thinner films and lower material usage.<sup>74</sup> Color of the primer is chosen to roughly match the color of the basecoat, such that a chip which penetrates to the primer is less visible.<sup>84,102</sup> Depending on the type of primer and application method, typical thicknesses range from 25–40  $\mu\text{m}$ .<sup>72,84</sup>

Recently, there have been successful efforts to remove the primer layer entirely by shifting its responsibilities to other layers. Beyond material savings and emission reductions from the coating layer itself, this has the further benefit of reducing the number of “bakes” or curing steps which occurs from the current standard of 3 bakes down to 2. Note that despite 4 layers, there are only 3 bakes since with the standard process the topcoat consisting of base and clearcoats is always applied wet-on-wet then cured with a single bake.<sup>103</sup> The standard 4-coat-3-bake (4C3B) process as well as primerless deviations is shown in Fig. 4. There would be substantial environmental benefit from development of widely applicable waterborne systems requiring fewer coating and baking steps.<sup>103</sup>

A primerless system incorporating isocyanate into the basecoat to impart better chip and UV resistance has been used by Volkswagen (VW) and BMW at various plants in Mexico, Spain, the United States, the United Kingdom, and more.<sup>66,104</sup> Daihatsu and Mercedes-Benz have also used a 3-coat-2-bake (3C2B) which retains drying between layers, while Mazda and Ford have employed a 4C2B solventborne system retaining the primer where each layer is applied wet-on-wet.<sup>74</sup> However, these methods described have not gained worldwide adoption as they generally sacrifice the majority of the chip and UV resistance aspects imparted by the conventional primer and are thus ill-suited for high corrosion risk geographic areas, as well as having a lower lifespan before UV-caused delamination will occur.<sup>89</sup> As such, while as much as 50% of vehicles in economically developing regions are made without the primer layer for cost purposes,<sup>66</sup> the focus here is on waterborne primerless systems which can compete with conventional systems in terms of performance. More recently, Honda has introduced a 3C2B system to a plant in Brazil, in which two waterborne basecoats and clearcoat are all applied and then cured in a single bake.<sup>89,103</sup> This method retains the increased durability and quality imparted by the primer layer, but shifts the responsibility to the first basecoat layer.<sup>89</sup> Defect control also

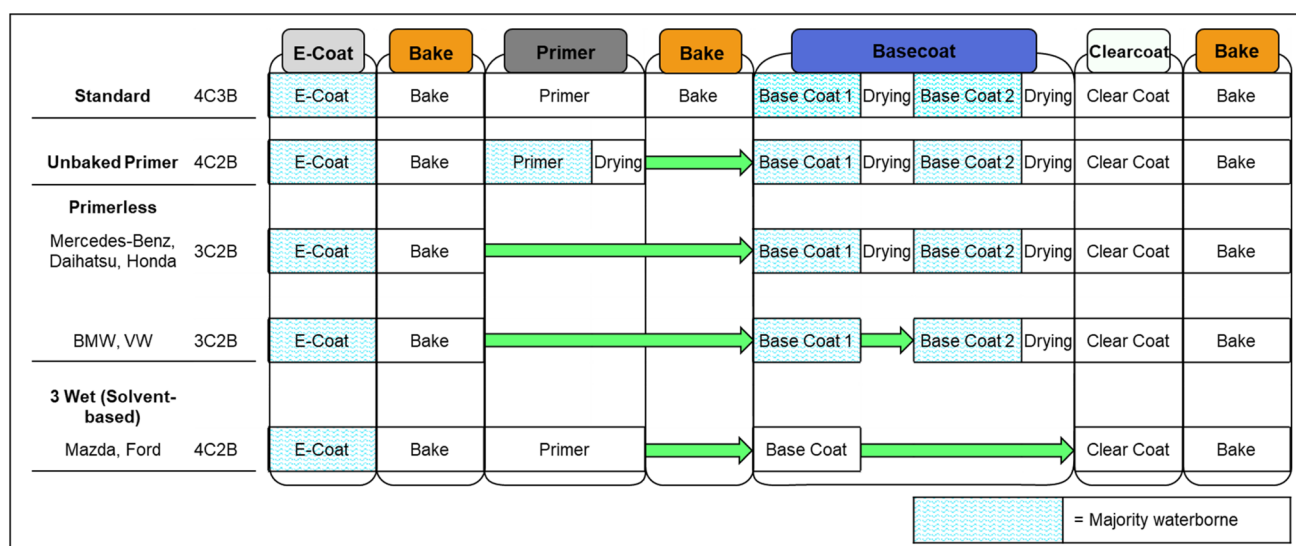


Fig. 4 Standard automotive coating process and variations thereof. Steps where waterborne coatings are the dominant choice are highlighted.



becomes more difficult as the three successive waterborne layers compounds the risks of popping and sagging occurring.<sup>89</sup> In the standard process depicted in Fig. 4, basecoat 1 and basecoat 2 are the same coating just applied multiple times (e.g. 2× with bell applicators or bell followed by pneumatic spray).<sup>66</sup> As a result, the Honda process does have four formulaically distinct coatings similar to the standard process.<sup>89</sup> Further, the responsibilities of the standard primer have been shifted nearly exclusively to the new basecoat 1 layer, while conventional basecoat responsibility for color development is now solely provided by basecoat 2.<sup>103</sup> Therefore, the distinction between the primer in the standard process and basecoat 1 employed in the Honda process is not clear, and the author feels the Honda process could fairly be regarded as a 4C2B system with a single-application basecoat replacing the conventionally double-applied basecoat. Regardless, it should be recognized that the Honda technology depicted in Fig. 4 is distinct from that of Mercedes-Benz and Daihatsu, as while the process steps are the same the more recent Honda technology incorporates greater vehicle protection measures.<sup>103</sup> Similarly, the BMW process listed works similarly to that of Honda, shifting the responsibilities of the primer to a new basecoat 1 distinct from basecoat 2, making it also effectively a 4C2B system.<sup>104</sup> Also, the numbering conventions differ between publications and manufacturers, likely in part due to it being beneficial to claim any reduction in the number of coats or bakes. There are also references to 3C1B systems which ignore the 1C1B aspect of the initial E-coat, however in this paper that is always counted as a discrete step.<sup>105</sup>

Toyota has also published research into applying the primer, basecoat, and clearcoat followed by a single bake for the three layers.<sup>105</sup> Toyota notes that the appearance of the single bake systems is conventionally inferior to that of the traditional 4C3B system, and so has been confined largely to economy-class vehicles.<sup>105</sup> To improve surface smoothness of the basecoat (and thus the basecoat/clearcoat interface) as well as the final coating appearance and quality, the glass transition temperature ( $T_g$ ) of the acrylic resin should be reduced, and melamine substituted with an isocyanate hardener.<sup>105</sup>

**2.2.1.3. Basecoat.** The main purpose of the basecoat is to provide the desired color and visual appearance effects to the vehicle.<sup>72,106</sup> Because of the high quantity of pigments and additives, basecoats are the most expensive layer in the vehicle paint stack.<sup>84</sup> Basecoats typically have a thickness of 10–20  $\mu\text{m}$ .<sup>72,84</sup> However, the thickness is dependent on the colour and incorporated effects, and how well they exhibit black-white hiding.<sup>66</sup> Silver and white tend to be thinner, while chromatics such as red may be as high as 30  $\mu\text{m}$ .<sup>66</sup> Monocoat systems (single topcoat layer rather than separate basecoat and clearcoat) were the standard until 1970, and remain available in limited capacity.<sup>66,107,108</sup> However, they have been phased out in North America and other markets where the improved durability and appearance of the 2C1B topcoat outweighs the increase in cost.<sup>66,109</sup>

White is by far the most popular color worldwide as it was utilized for 35% of new vehicles in 2021, the locally leading color in nine out of 10 identified major market regions, and the

global lead for the past eleven years.<sup>110,111</sup> Despite this, white's share has been slowly declining as chromatic (non-white, black, gray, or silver) colors have increased in popularity, albeit still representing <20% of the market.<sup>110,111</sup> Black and gray tie for 2<sup>nd</sup> place with 19% each, with the only market where white is not in 1<sup>st</sup> place being Europe, where it is in 2<sup>nd</sup> place behind gray; at 27% for gray and 23% for white.<sup>110</sup> It should be noted that the large coating companies, BASF and Axalta, both classify silver as a separate category from gray; at nearly 10% of new global vehicles the combination of silver and gray would be solidly above black for 2<sup>nd</sup> place, although black retains an outsized share in the luxury vehicle segment.<sup>110,111</sup> While white leads in nearly all regions, its largest lead is also home to the highest automotive production volume, with just under 50% of vehicles in Asian regions having white coatings.<sup>110,111</sup> TiO<sub>2</sub> (titanium white) is overwhelmingly used as the white pigment, both for automotive and other applications, and in fact nearly 95% of global titanium production is for titanium white.<sup>66,112,113</sup> However, due to photocatalytic degradation caused by unmodified TiO<sub>2</sub>, the TiO<sub>2</sub> particles are coated with layers of both SiO<sub>2</sub> and AlO<sub>3</sub> to prevent photooxidation of the coating matrix.<sup>66,114</sup> There are over 40 000 distinct automotive base coatings which have appeared on the market, with over 1000 released annually.<sup>66</sup> The color and desired visual effect largely impacts the selection of pigments and additives rather than the resin, with insoluble pigments as opposed to soluble dyes being overwhelmingly chosen for automotive applications due to their superior lightfastness.<sup>66</sup>

Waterborne basecoats use an acrylic and/or polyester as the main binder, as a partially cross-linked core-shell emulsified polymer.<sup>66,84</sup> Co-binders are additional polyesters or polyurethanes, while melamine provides more cross-linking upon baking.<sup>66,84</sup> Shear-thinning behavior is critical (as with most paints), and for waterborne basecoats this is generally achieved by incorporating silicates.<sup>66,115</sup> Thixotropic behavior not only prevents defects, such as sagging, but is also necessary for proper flake orientation during drying (also aided by high volume shrinkage caused by the evaporation), and preventing settling in supply tanks.<sup>66,84,116</sup> However, the low-shear viscosity cannot be too high or else proper levelling of the film will not occur, so the choice and quantity of additives must be done with great care.<sup>116</sup> Solid basecoats can be applied as a single coat while more complex paint effects, such as metallic paints, require two coats to properly achieve the desired visual effect.<sup>74</sup> In the past 10 years, waterborne basecoats have overtaken solventborne options within major markets, driven by environmental regulations.<sup>117–119</sup>

Waterborne basecoats remain a significant source of emissions, as VOC content is typically still 10–15%.<sup>66,72,120</sup> While the shift to waterborne paints (and other improvements) has cut automotive VOC emissions to less than 10% of the level seen in the 1970's, development of waterborne basecoats without the need for an appreciable VOC content is critical to eliminating remaining emissions.<sup>72</sup>

**2.2.1.4. Clearcoat.** Clearcoats are the final layer applied, and act to both protect the appearance of the vehicle and impart a glossy visual effect.<sup>84,106</sup> Typical thicknesses are 40–50  $\mu\text{m}$ ,



applied *via* spraying.<sup>72,84</sup> The clearcoat is applied directly onto the basecoat, without an intermediary baking step.<sup>84</sup> However, there is a brief drying/flashing stage which dries the basecoat to be as high as 90% solids content.<sup>72,78</sup>

The clearcoat must be durable against multiple adverse conditions, including temperature, UV, abrasion, impacts, airborne pollutants, and acid rain.<sup>84,121</sup> As a result, durable resins must be chosen, and all formulations include ultraviolet light absorbers (UVAs) and hindered amine light stabilizers (HALS) to assist with longevity.<sup>84</sup> Waterborne clearcoats generally use polyester-acrylate resin which is crosslinked with melamine and/or blocked isocyanate.<sup>66,122</sup> Since the late 1990s, top clearcoats have employed nanosilica to improve scratch resistance and gloss retention.<sup>75</sup>

While waterborne clearcoats were first available in 1990, as of 2008 they constituted <1% of the global clearcoat market, and remain similarly low today.<sup>66</sup> Instead, solventborne clearcoating remains dominant, with powder coating capturing a small (<5%) portion, but edging out waterborne coatings as the environmentally friendly clearcoat option chosen by industry.<sup>66,78</sup> Isocyanate is difficult to incorporate into waterborne systems without incurring unwanted reactions or extremely short pot life, and has been among the key limitations on waterborne clearcoat development.<sup>123,124</sup> The high thickness of the clearcoat layer has been noted as another key issue, as a waterborne clearcoat will then require substantial energy and time for evaporation, as well as increased risk of improper curing.<sup>125,126</sup> Despite this, waterborne clearcoats are available on the market, and see moderate adoption in the refinishing segment.<sup>125,127</sup> However, regardless of whether waterborne or powder clearcoats are chosen, widespread OEM adoption will only occur if forcibly imposed *via* stricter emission regulations.<sup>119,125</sup>

**2.2.1.5. Automotive interiors.** Interior automotive surfaces employ a variety of coatings to bestow specific appearances and textures, as well as improve durability.<sup>42</sup> Waterborne polyurethane (WPU) is the most employed, being used for synthetic leather surfaces, nonwoven fiber protection, and as a clear coating.<sup>5,128</sup> WPU is also extensively employed throughout other parts of automobiles, for example as adhesives and foams.<sup>129</sup> As a coating, WPU is known to provide excellent mechanical properties, as well as vital resistance to UV and weatherability.<sup>128</sup> Coated fibers such as those constituting floor mats are dip coated, while synthetic leathers are coated then dried (and surface coagulated) *via* a variety of proprietary methods such as applying acids or heat depending on the formulation and desired appearance.<sup>5,130</sup> The microsphere structure of the resulting surface plays a strong role in the resulting appearance, with a smoother surface appearing glossier while a rougher surface appears matte (approximately linear relationship).<sup>5,131–133</sup> Control of the surface morphology can be performed through control of crosslinking, such as through additives, as crosslinking increases roughness and thus decreases gloss, and *vice versa*.<sup>5,9</sup> Surface heterogeneity also plays a large role in gloss determination.<sup>134</sup> For automotive leathers, the WPU chosen is generally based on an aliphatic diisocyanate for superior long-term durability.<sup>135</sup> The selection

of polyol (WPU's are obtained by reaction of polyol and diisocyanate) is more varied depending on the specific desired effects, with polyester, acrylic, polyether, and polycarbonate-based polyols all seeing use.<sup>135,136</sup> The surface coating will also incorporate acrylic emulsions, as well as typical additives such as pigments and rheological modifiers.<sup>135</sup> These WPU synthetic leather surfaces are also used for other products, such as furniture, clothing, and accessories, however the high weatherability and durability requirements for automotive applications makes the application of particular interest, as successful coatings can then generally be applied to other products with lesser requirements.<sup>5</sup>

**2.2.1.6. Other waterborne automotive coatings.** There is interest in converting the remaining solventborne coatings still in use to waterborne counterparts, such as for engine coatings.<sup>137</sup> As well, there is continued innovative improvement of systems such as waterborne flaky aluminum pigments in order to suppress existing issues with corrosion (novel double-layered surface decoration),<sup>138</sup> addition of nanoparticles to existing dispersions for improved performance,<sup>139,140</sup> improvement of WPU self-healing properties,<sup>141</sup> and invention of smart coatings which can react to varied environmental stimuli.<sup>71</sup> Lastly, it should be noted as well that the information presented is specifically for OEM coatings rather than refinish coatings unless otherwise specified. Refinish coatings must cure at temperatures between ambient and 60 °C, and do not have access to intensive coating processes, making waterborne applications inconsistent and expensive.<sup>119,123,142,143</sup> As a result, while the polymer composition of the coatings remains very similar, resin with a lower glass transition temperature may be used in order to achieve better curing.<sup>142</sup> Waterborne refinishing coatings are therefore much tougher to formulate as faster-drying coatings and therefore lower boiling point solvents are more desirable.<sup>142</sup> With that in mind, automotive refinishing shops are aware of the benefits to worker health in using waterborne coatings over solventborne, and have been seen to voluntarily switch to waterborne as they have been made more readily available.<sup>144</sup> As painting currently consumes 30–50% of the total energy input to the automotive manufacturing process, development of waterborne coatings which can be cured at lower temperatures would result in enormous energy savings, compounding their environmental returns.<sup>72,103</sup>

**2.2.2. Coil coatings.** Coil coatings have the primary purpose of imparting corrosion protection to metal, particularly aluminum and steel.<sup>42</sup> The metal comes uncoated as coils, is unrolled and coated, then rerolled or immediately formed into the final product.<sup>42,68</sup> Since the coating is applied to flat metal sheets and then formed, the coating must be highly flexible such that tight bends can be achieved without cracking or delamination.<sup>68</sup> As well, as mentioned, the coating must be highly corrosion resistant, have weatherability resistance for outdoor applications, and be durable.<sup>68</sup>

Unlike architectural coatings where waterborne coatings are the majority, for coil coatings waterborne adoption is still extremely limited (<1% of market) due to relatively poor performance and higher costs, as well as operational difficulties.<sup>42,68,145,146</sup> The few industrial systems which do exist employ



acrylic or acrylate–epoxy hybrid dispersions.<sup>42,147</sup> Solventborne coil coatings are conventionally polyesters (frequently siliconized), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), and polyurethanes.<sup>42,68,146</sup> Each of these polymers with the exception of PVC has seen successful waterborne formulations for coil coating at lab-scale.<sup>42,145,146</sup> It is important to note as well that the coating performed while the sheet is flattened involves multiple stages and coatings, along with pretreatment. There is frequently a primer/basecoat as well as the topcoat, so ideally the entire system must be changed to be waterborne, increasing complexity.<sup>42</sup> The waterborne coatings are applied in the same manner as solventborne coil coatings, primarily *via* continuous rollers.<sup>42,68</sup> However, solventborne coil coatings are also occasionally coated using electrostatic high-speed discs.<sup>68</sup>

**2.2.3. Architectural.** Architectural coatings are by far the largest coatings market segment, by both revenue and product volume.<sup>23,37</sup> Architectural coatings encompass both indoor and outdoor coatings (especially paints) which improve the appearance of our buildings, while also providing environmental protection to the underlying substrate.<sup>65,148,149</sup> Waterborne coatings make up over 70% of the global architectural coatings market, driven by being the standard for interiors (the largest subsegment).<sup>42</sup> Current interior architectural coatings have very low or zero VOC content.<sup>34</sup> While waterborne interior coatings have been available for over 60 years,<sup>42</sup> waterborne products meeting the more strenuous performance demands of exterior environments has only been met in the past few decades.<sup>150</sup> The higher demands for exterior coatings include resistance to chalking, water absorbance, yellowing, acidity, abrasion, extreme temperatures, and more.<sup>54,148–150</sup>

Currently, waterborne architectural coatings most commonly employ acrylic, styrene–acrylic, alkyd (hybridized, often with styrene/acrylic), polyvinyl acetate, or polyurethane polymer dispersions, with silicones occasionally added.<sup>54,150–154</sup> 5–35% of the waterborne paint is the resin by volume.<sup>65</sup> Pigment, extenders, surfactants, and rheology modifiers are also nearly always present in the formulation while UV

absorbers, dispersants, biocides, defoamers, adhesion promoters, slip agents, and more are added as desired for the specific application.<sup>65,148</sup> Rheological behavior of architectural coatings is critical, as they are generally applied relatively thickly (brush/roller as opposed to spray *etc.*) to vertical surfaces and then dried at ambient conditions.<sup>42,65</sup> A general guide to the desired magnitude of shear thinning is provided in Fig. 5.<sup>65</sup> As waterborne formulations are typically known for having low viscosity, without addition of a thickener the paint will be prone to issues, such as runs, drips, and sags.<sup>65</sup> Associative and cellulosic thickeners are the most common thickeners for waterborne architectural coatings.<sup>42</sup> Due to the number of components in the formulation, the rheological characteristics are quite complex and thus formulations cannot be made *via* modelling alone.<sup>65</sup> Alongside the rheological modifier additive, the polymer particle size (smaller = more viscous),<sup>28</sup> the surfactant, and polymer volumetric concentrations majorly influence the resultant behavior, while factors such as the pigment have a much smaller effect.<sup>65</sup>

Continued innovation in waterborne architectural coatings includes complementation of a broader range of substrates (wood, stone, *etc.*),<sup>148,149</sup> better waterproofing lifespan for high demand applications such as roof sealing,<sup>151</sup> and nanoparticle additives for improved properties, such as dirt resistance and antibacterial activity.<sup>155–157</sup> As the architectural coating market continues to expand and with waterborne architectural coatings continuing to be the dominant option, further research and sustainability regulations may allow further advances, such as bio-renewable and biodegradable resins to become economically viable.<sup>34,70</sup> In the meantime, the very low VOC content of current architectural coatings acts as a goal for other industries still primarily using solventborne coatings.<sup>70</sup>

**2.2.4. Marine.** For marine coatings, the most important aspects are corrosion resistance and anti-biofouling properties.<sup>42,158</sup> Biofouling of large ships can lead to fuel cost increases of over 40%, as well as other issues such as introduction of invasive species.<sup>159,160</sup> For anti-biofouling, there are two classes

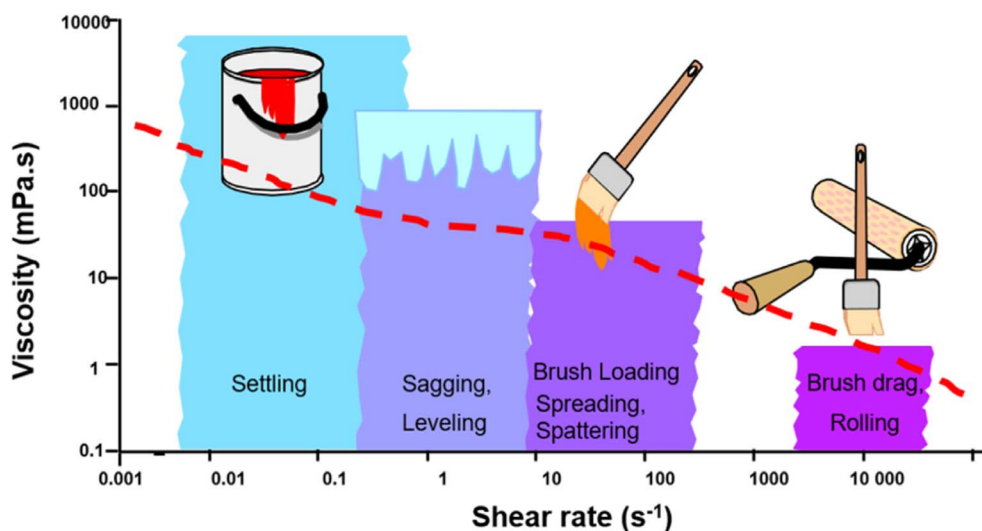


Fig. 5 Desired relationship between viscosity, shear rate, and paint properties. Reproduced from ref. 65 with permission of Elsevier © 2022.



of coating in this space: self-polishing antifouling coatings and foul-release coatings.<sup>42,159</sup> Self-polishing marine coatings employ a biocide which is soluble or reactive with the water, and thus is gradually stripped off over time maintaining a relatively smooth surface.<sup>42,159</sup> The vast majority of these paints were acrylics incorporating tributyltin (TBT) until TBT was banned worldwide in 2008 due to its harmful environmental effects.<sup>159,160</sup> Now, other organometal biocides, primarily copper pyrithione (CuPT), are used, despite persisting environmental concerns.<sup>159</sup>

Foul-release coatings are the primary alternative, using an ultra-smooth surface to stop adhesion of microorganisms to the surface.<sup>42</sup> Fluoropolymers and siloxanes, such as polydimethylsiloxane (PDMS), are incorporated into polymeric materials including waterborne polyurethane (WPU).<sup>42,161</sup> While the PDMS provides the smooth surface, the WPU promotes substrate adhesion, has low cost, and during drying allows for migration of siloxane groups to the surface.<sup>42</sup> Ideally, foul-release coatings would be so smooth that initial adhesion to the surface is halted. However, there is still some adhesion to foul-release coatings in practice.<sup>161</sup> Nevertheless, these adhered fouling organisms can be removed easily during cleaning.<sup>161</sup> As a result, this has not been a significant barrier to adoption, and adoption of foul release coatings increased from less than 1% of the market in 2009 to over 10% in 2014.<sup>159</sup> The largest barrier to further increase is the high cost and requirement for frequent re-application, which can be over 100 USD/L for material alone. While such cost can be justifiable for large commercial boats spending millions on fuel per year, it is exorbitant for the recreational vessels constituting 20% of the market.<sup>159</sup> The other key issue with foul-release coatings is that they usually require a high amount of ship movement to effectively prevent adhesion; as a result, they are ineffective for many vessels and temporary underwater structures which remain stationary for extended periods of time.<sup>159,161</sup> In fact, some shipping companies that committed to adopting foul-release coatings after the 2008 ban on TBT later switched back to biocidal copper paints, such as Maersk in 2012, due to poor foul-release coating performance.<sup>159</sup>

Some coatings newer to the market look to combine the benefits of both antifouling and foul release coatings, or otherwise improve upon the performance of siloxane-based foul release coatings. Sol-gel coatings are available which allow for extremely smooth surface finishes further hindering initial adhesion of fouling agents, allowing effective fouling prevention even for vessels at rest.<sup>159</sup> Other coatings employ micro-encapsulated biocides, which are slow-released leading to over 95% lower biocide emitted than with the traditionally water-soluble biocides.<sup>162</sup>

Beyond the antifouling topcoat for components directly submerged in water, the primer and various fillers provide critical corrosion resistance to all marine components. The intensity of required resistance varies greatly depending on multiple factors, such as location on the interior or exterior of the vessel, fresh or salt water, or presence of the marine component in the water splash zone.<sup>163,164</sup> Waterborne primers and top coats based on acrylics, epoxy, and urethanes are

employed, mostly for low-corrosion stress applications.<sup>163</sup> High-stress applications, such as ocean-submerged pipelines do not use waterborne coatings as they cannot compete in terms of resistance, durability, or cost.<sup>163</sup> Waterborne styrene-acrylic copolymers are also widely used commercially as metallic substrate primers, and additives such as zinc phosphate are used to promote anticorrosive properties.<sup>42,164</sup> In addition to ship hulls, other immersed metal components, such as pipelines and offshore platforms, require coating for anti-corrosion and biofouling resistance.<sup>161,164</sup> Anti-corrosion coatings are further required for any components exposed atmospherically or periodically to the marine environment, such as shipyards, metallic bridge structures, holds, and other interior areas.<sup>158,163,164</sup>

The application and drying process of waterborne marine coatings also causes difficulties. Most shipyard components are coated and dried in the open-air to the detriment of waterborne coatings, which are highly moisture and temperature sensitive for drying.<sup>158</sup> This issue is compounded by the fact that shipyards are by nature generally located in areas of high atmospheric moisture, leading to slow and inconsistent drying.<sup>158</sup> Marine coatings are generally applied *via* spray, rollers, or brushes.<sup>159</sup>

### 2.3. Packaging

Rather than just protecting the substrate, packaging coatings must additionally protect the package contents.<sup>165,166</sup> For food packaging, barrier property performance is critical, protecting contents from moisture and oxygen to preserve freshness.<sup>167</sup> Other products, such as disposable drinking cups, must add a coating to overcome the weak wet strength of paper, which would otherwise tear and fall apart.<sup>168</sup> Packages are frequently comprised of multiple distinct layers and/or use petrochemical-based polymers, making them destined for the landfill, even despite the otherwise biodegradable substrate in the case of paper.<sup>3,167</sup> While extrusion coating and lamination are most common, waterborne dispersion coatings allow for other methods, such as curtain, dip, bar, and roll coatings which have lower film thickness and thus lower dry material usage.<sup>3,169</sup> Packaging comprises a very high percentage of our overall plastic usage, as well as our solid waste.<sup>3,170</sup> As a result, biobased and biodegradable packaging options are heavily researched and factor into consumer decisions and sustainability initiatives.<sup>70,171-173</sup>

Unfortunately, existing commercial paper packaging coatings do not extensively employ waterborne technology.<sup>169</sup> There are however a few in limited use, such as acrylic dispersions from BASF (*e.g.* Joncryl®) and Aquaspersions.<sup>174,175</sup> The implementation of waterborne dispersion coatings for paper packaging is a very promising area of research and is discussed in Section 3.3. For now, commercial waterborne packaging coatings are largely confined to the areas of aluminum coatings.

Metal drink can coatings must also protect the drink from obtaining a metallic flavour or losing its carbonation (if applicable), while also protecting the can from corroding due to the drink acidity.<sup>69</sup> These coatings have been predominantly



waterborne now for decades, with epoxy–acrylic copolymers with phenolic or amino crosslinkers being the common basis.<sup>69,176</sup> Originally, toxic bisphenol A (BPA) was used, but is now largely replaced by other bisphenols with lower or unproven toxicity.<sup>69,177</sup> Polyester-based, as well as a bio-based phenol coating derived from cashew shell waste have also been investigated, although the cashew option is not currently waterborne.<sup>177,178</sup> Waterborne varnishes for exterior coating of the metal drink cans has a much lower rate of adoption, but has grown substantially in recent years.<sup>179</sup>

#### 2.4. Other commercialized coating systems

There remain numerous other commercialized waterborne coatings, which represent smaller markets and may often be considered subsets of the discussed systems due to similarity of the technology.<sup>70</sup> For example, other transportation coatings such as for buses and trains have similar substrate protection and environmental exposure resistance requirements, but with differing cosmetic requirements.<sup>180</sup> As a result, the overall coating system is quite similar, but simplified in terms of layers and additives.<sup>180</sup> Aircraft and automotive refinish paints are also similar to the automotive paints discussed, with different environmental exposure requirements for aircraft and economic considerations for refinish paints.<sup>181–183</sup>

Similarly, as touched on earlier there are countless applications for waterborne paints. Toys, agricultural equipment, appliances, helmets, cookware, gym equipment, and road markings are a few examples which employ waterborne paints in some capacity.<sup>23,67,184,185</sup> Waterborne printing ink has also begun to see market uptake, mainly with waterborne polyurethanes for currently commercialized systems but with some interest in acrylic systems.<sup>55,186–189</sup> Waterborne polyurethanes are also used in adhesives,<sup>50,170</sup> soft-touch materials such as synthetic leather,<sup>5</sup> nail enamel,<sup>190</sup> textile coatings,<sup>191</sup> and more.<sup>192</sup> Waterborne polyurethane/acrylic hybrid systems are often used in these and similar applications where the less expensive acrylic cannot meet performance requirements on its own.<sup>55,193</sup>

Other commercialized waterborne coating systems using a variety of polymeric systems include seed coatings,<sup>194</sup> drug pellet coatings,<sup>195</sup> and anti-smudge coatings.<sup>196</sup> Paper coatings for non-packaging purposes comprises applications, such as paperback books,<sup>67</sup> playing cards,<sup>197</sup> and thermal paper.<sup>198</sup> Emulsified asphalt, especially for the waterproofing layer of pavement structure, commonly employs styrene–butadiene latex but has also been shown to perform well using polyvinyl acetate and waterborne epoxy resin.<sup>199,200</sup> Lastly, polytetrafluoroethylene (PTFE) is used for a myriad of non-stick and non-reactive surfaces and is commonly coated as a waterborne dispersion.<sup>201–203</sup> As stated, this section is not meant to comprise an exhaustive list. Other commercial waterborne coatings exist, and as time passes and new systems are developed or become economically viable this list will continue to grow. The shift to waterborne coatings is already in full swing as solventborne coatings are continually phased out for their more environmentally friendly counterparts.<sup>43,70,204</sup>

#### 2.5. Overview of commercialized systems

A summary of currently commercialized waterborne polymers is given in Table 1, below. Note that this table is not exhaustive, and only considers the main polymer resins rather than polymeric additives such as bactericides and associative thickeners.<sup>205</sup>

While waterborne polymer coatings overall are on the rise,<sup>43,70</sup> they are not without drawbacks hindering their full adoption. Suitable waterborne systems are not currently commercially available for all coating applications, such as paper packaging<sup>169</sup> and some wood products.<sup>30,210</sup> Also, their performance, high drying temperatures, and pot stability makes them inadequate for some applications in their current technological state.<sup>26,32</sup> Lastly, most of the systems do not fully address sustainability concerns. High drying temperatures means high energy usage, there is often still a small amount of organic solvent, and the polymers are often not biobased nor biodegradable.<sup>6,23,26,72</sup> Despite all of this, waterborne systems have demonstrated success for many applications, while improving safety and environmental characteristics.<sup>23,24,192</sup> As the shortcomings continue to be addressed through advancing research (as discussed in Section 3), waterborne polymeric coatings will continue to see increased commercial adoption and success in the foreseeable future.

### 3. The future for waterborne polymer systems

In this section, new developments and trends in waterborne systems are highlighted. A focus is given on progress towards new commercialized systems and improvements to existing systems. New methods of waterborne system formation, materials and additives, and applications are discussed.

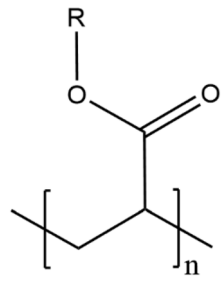
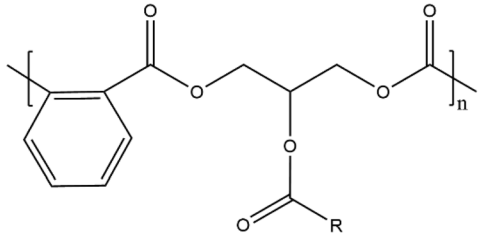
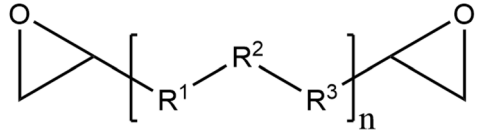
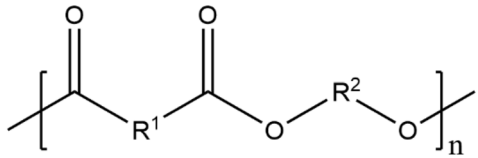
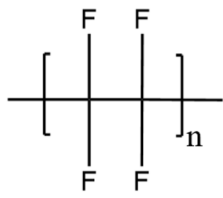
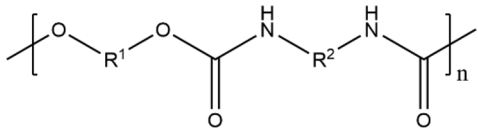
#### 3.1. New methods of formation and stabilization

As a precursor to new materials being made into stable waterborne dispersions, new methods of formation are necessary to overcome innate hydrophobicity and instability.<sup>31,32</sup> For existing waterborne systems the pot life remains a challenge to overcome, often retaining some level of VOC presence to provide stability and expected functionality.<sup>32,42,211</sup>

Perhaps the most exciting trend for formation and stabilization is Pickering emulsions. Aqueous Pickering emulsions use small solid amphiphilic particles bound irreversibly to the interface between the water and immiscible phases in order to provide stability.<sup>212</sup> Compared to systems stabilized using conventional surfactants, Pickering emulsions can boast reduced toxicity and cost, while greatly increasing stability.<sup>212</sup> Pickering emulsions have seen an immense increase in research interest over the past 20 years. In 2000, less than 10 papers on the topic were published, in 2010 more than 100, to now over 800 papers published in 2021.<sup>213,214</sup> Some successful oil-in-water Pickering systems researched for coatings include beeswax stabilized using cellulose nanoparticles for fruit coating,<sup>41,215</sup> paraffin stabilized using cellulose nanoparticles for textile thermal regulation,<sup>216</sup> and glycidyl methacrylate



Table 1 Commercialized waterborne polymer resins for dispersion coatings

Waterborne polymer	General unit structure	Commercialized applications	References
Acrylic Polyacrylate		Wood coating, paint, adhesive, marine	31, 38, 54, 60, 84, 163 and 206
Alkyd		Wood coating, paint	38, 152 and 207
Epoxy Polyepoxide		Anticorrosion (automotive, marine, aluminum can)	83, 89, 163 and 176
Polyester		Paint	84 and 208
PTFE Polytetrafluoroethylene		Non-stick	201 and 206
PU Polyurethane		Wood coating, paint, synthetic leather, adhesives, marine, ink, nail enamel, textile	5, 38, 42, 50, 60, 84, 129, 151, 189–191 and 209

stabilized with graphene oxide for a self-healing coating.<sup>217</sup> Kalashnikova *et al.* have produced excellent images showing the Pickering particle coverage of cellulosic nanorods stabilizing the oil/water interface, as shown in Fig. 6 below.<sup>218</sup>

New methods of formation are continually investigated for reasons. Aims of this research include reduced energy requirements, improved product, allowing new materials, and solvent quantity reduction.<sup>31,50,219–221</sup> For waterborne polyurethanes, hot-melt processing and solvent-free condensation polymerization are promising methods of formation, which emit no organic solvent.<sup>50,219</sup> Other methods, such as radical ring-opening polymerization methods are expanding the ability to synthesize degradable polymers.<sup>222</sup> Emulsion polymerization-

induced self-assembly mediated by reversible addition-fragmentation chain transfer was recently performed using dibenzo [*c,e*]oxepane-5-thione to obtain block copolymer nanoparticles directly in water.<sup>222</sup> Lastly, other stabilization methods seeing interest are thickeners<sup>65,223</sup> and the use of copolymers.<sup>224</sup>

### 3.2. New trends in waterborne materials and additives

Of particular interest for improving current systems are the utilization of hybrid dispersions and the addition of nanoparticles to bring waterborne dispersion performance closer to that of solventborne.<sup>46,50,153</sup> As well, for new systems, development of waterborne dispersions of biobased and biodegradable



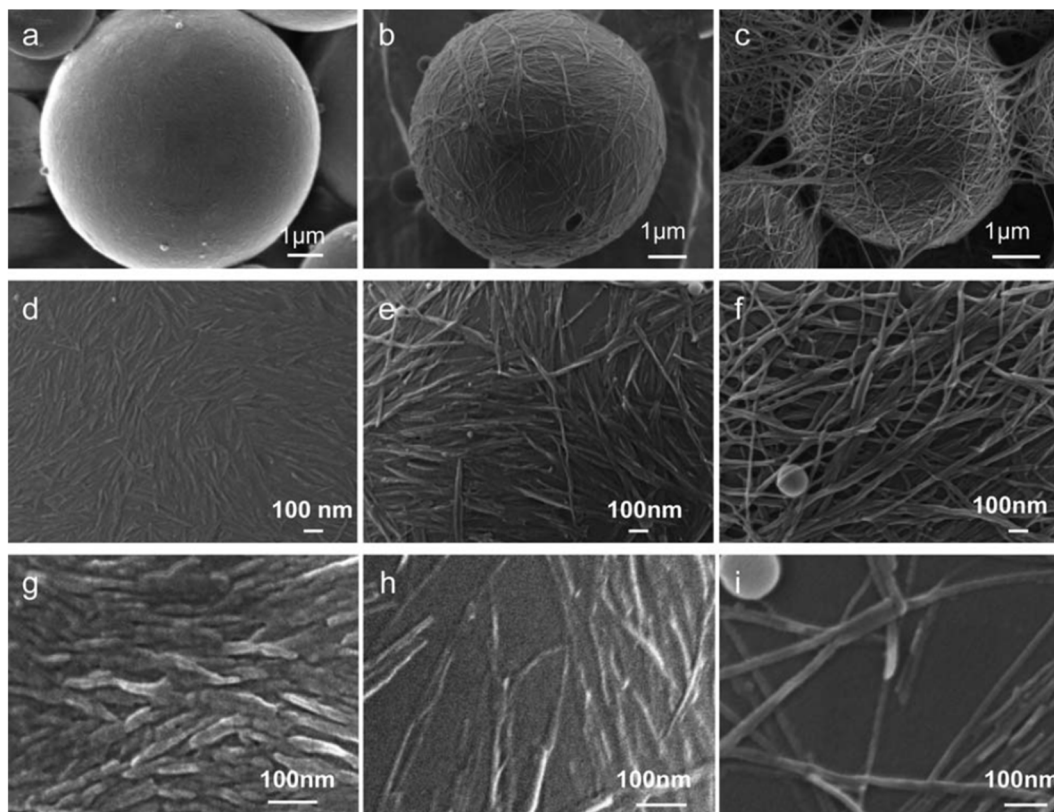


Fig. 6 Scanning electron microscopy (SEM) images of polymerised styrene–water Pickering emulsions stabilized by cotton cellulose nanorods (a, d and g), bacterial cellulose nanorods (b, e and h), and *Cladophora* cellulose nanorods (c, f and i) at two different nanocrystal concentrations:  $5 \text{ g L}^{-1}$  (d–f), and  $1 \text{ g L}^{-1}$  (g and h) – revealing the coverage variation as a function of nanocrystal concentration and length. Reproduced from ref. 218 with permission of The Royal Society of Chemistry © 2013.

polymers is greatly appealing to further reduce the environmental impact of polymer coatings.<sup>21</sup>

Hybrid dispersions combine two or more polymers chemically bound together to form an improved product.<sup>152,153</sup> This synergy can lead to superior performance compared to individual polymers alone,<sup>56,153,225,226</sup> or it can maintain performance levels while decreasing the quantity needed of the costlier polymer.<sup>55</sup> Many hybrid systems already see commercial use, such as the alkyd–acrylic architectural paint and acrylic–polyurethane wood coatings discussed earlier.<sup>60,152,153</sup> New hybridized systems include many new acrylic–polyurethane hybrids due to the flexibility of the underlying polymer formulation.<sup>55,193</sup> Current research on hybrid coatings includes the development of a novel one-package (1 K) waterborne non-isocyanate polyurethane–epoxy hybrid,<sup>227</sup> improvements to the performance of polyacrylate–polyurethane hybrids,<sup>228</sup> and numerous other projects.<sup>229–233</sup>

Nanoparticles and other additives are of great interest to improve existing capabilities and introduce new possibilities.<sup>46,50,149,160,234–236</sup> Nanoparticles offer advantages, such as greater effective surface area, high stability in dispersions, and can impart unique properties not possible with conventional particles.<sup>46,237</sup> The possibilities are immense as both organic and inorganic nanomaterials with varying compositions, different morphologies, and more, lead to

inexhaustible combinations.<sup>4,148,237</sup> Recently, Vijayan *et al.* embedded ceria–zirconia nanoparticles in waterborne epoxy for marine anti-biofouling, with the antibacterial success shown in Fig. 7f.<sup>160</sup> Another interesting finding is by Koyuncu *et al.*, incorporating bismuth oxide nanoparticles into waterborne polyurethane textile coatings to provide protection against ionizing radiation, for example as a lightweight X-ray shielding apron.<sup>238</sup> Incorporation of nanoparticles in waterborne epoxy for a bonded solid lubricating coating<sup>239</sup> and in waterborne polyurethane to improve textile puncture resistance<sup>240</sup> are two additional projects within this immense research space. Novel additives to enhance existing waterborne systems are similarly rife, for example adding engineered polysaccharides to natural rubber latex<sup>241,242</sup> and kaolin to styrene–butadiene latex,<sup>243</sup> both to improve barrier property performance. Other additives can be critical to incorporate, such as those discussed earlier including thickeners, pigments, plasticizers, and more.<sup>39,45,65</sup> Of particular interest to the topics discussed in this publication are additives to reduce the drying energy requirements (directly or indirectly, such as initiators to allow photopolymerization) in order to mitigate that key drawback to waterborne systems.<sup>244–250</sup>

Regarding development of waterborne dispersions using new polymer resins, there is particular focus on biobased and biodegradable materials to further improve the environmental benefits.<sup>6</sup> Pieters and Mekonnen<sup>6</sup> successfully dispersed the



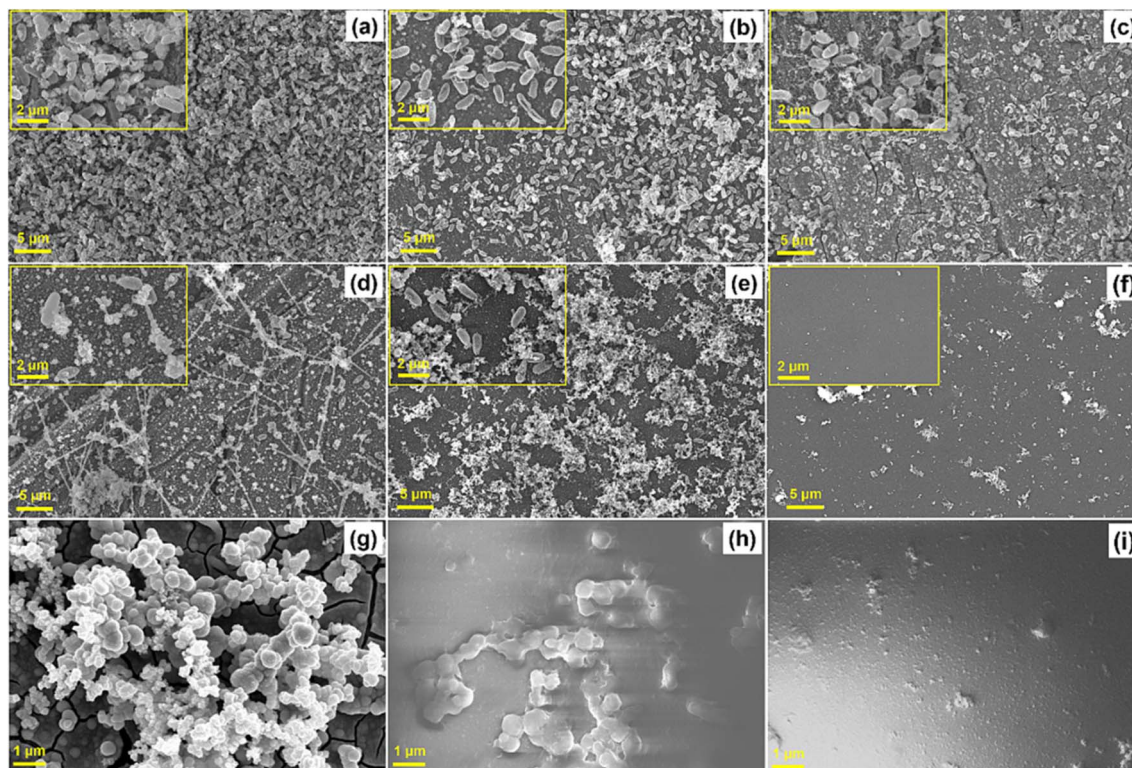


Fig. 7 (a–f) SEM images of uncoated control, epoxy coated, and composites coated mild steel surface after treating with bacteria ((a) control, (b) epoxy, (c) epoxy and ceria, (d) epoxy with 80 : 20 polydopamine (PDA) : ceria, (e) epoxy with 60 : 40 ceria : zirconium and (f) epoxy with 48 : 32 : 20 ceria : zirconium : PDA (EPCZ)). (g–i) SEM images of uncoated control, epoxy coated and EPCZ coated mild steel surface after treating with sea water consortium ((g) control, (h) pure epoxy and (i) EPCZ). Reproduced from ref. 160 with permission of Elsevier © 2024.

biobased and biodegradable polymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) in water. Likewise, Bramhall<sup>35</sup> has dispersed polyhydroxyalkanoates (PHA) in water using a similar approach. Waterborne dispersions of both poly(lactic acid) (PLA)<sup>21</sup> and poly(butylene succinate) (PBS)<sup>251</sup> have also been reported in the literature. The waterborne PLA development may be of particular interest for practical applicability, as PLA is a mature biopolymer, and the extrusion-coated commercial paperboard products are already widely available.<sup>252,253</sup> Each of these works demonstrated the applicability of waterborne polymer systems on paper substrates for barrier coating purposes, a highly desirable application for waterborne biodegradable coatings as discussed further in Section 3.3. Additional newly developed waterborne dispersions include biodegradable polybutylene succinate<sup>251</sup> and biobased carnauba wax.<sup>254</sup> The latter, by Lozhechnikova *et al.*,<sup>254</sup> demonstrated applicability as a wood coating for UV exposure as shown in Fig. 8, as well as other protective properties. Lastly, there has also been substantial work involved in bringing the performance standard of bio-based versions of the existing coatings, for example bio-based waterborne polyurethanes, up to the level of their conventional counterparts.<sup>139,192,255,256</sup>

### 3.3. New applications for waterborne coatings

Research into new applications for waterborne coatings can be categorized into either replacing an existing coating with more

environmentally friendly alternatives or formulating new coating products. For existing applications, packaging is a key target due to the astronomical amount of waste currently produced.<sup>3</sup> For new applications there is a push towards smart and active materials (including within packaging) which can adapt to and alter the surrounding environment, respectively.<sup>12,13</sup> Also, novel waterborne products such as chip-board coatings and hairspray are undergoing significant developments.

Paper is a very common packaging material due to being printable, biodegradable, biobased, recyclable, low cost, light weight, versatility, and more.<sup>3,251,257</sup> In fact, 30% of global packaging material is paper, behind only plastics (40%), and ahead of aluminum (20%).<sup>3</sup> Paper's market share for packaging applications is expected to further grow as bans on single-use plastic are implemented.<sup>251</sup> Unfortunately, paper is porous and hydrophilic, resulting in poor barrier properties (gases, water, grease) and inferior wet strength.<sup>3,251</sup> Surface coatings are used to overcome these challenges.<sup>3,251</sup> Current barrier paper coatings use petrochemical derived coatings, which severely limits recycling and inhibits biodegradation<sup>167</sup> Cost reductions play an essential role for packaging, as they are largely single-use and secondary to the main product contained within.<sup>167,258,259</sup> Dispersion coatings can allow for reduced material usage, reducing cost.<sup>169</sup> Lastly, consumer decisions and government regulations have also promoted shifts to more



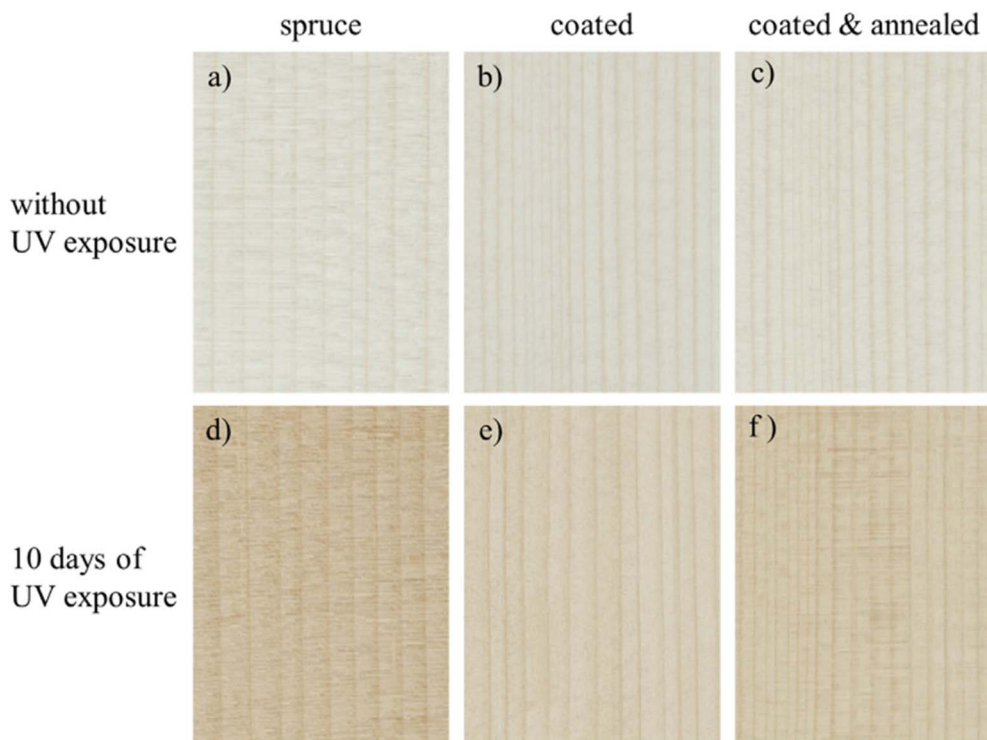


Fig. 8 Photographs of original spruce (a), spruce coated with 8 bilayers ZnO/carnauba wax at  $10 \text{ g L}^{-1}$  without (b) and with annealing at  $110 \text{ }^\circ\text{C}$  (c). Spruce (d), spruce coated (e) as well as spruce coated and annealed (f) after UV exposure for 10 days. All photographs were taken with identical camera settings and illumination. Reproduced from ref. 254 with permission of Elsevier © 2017.

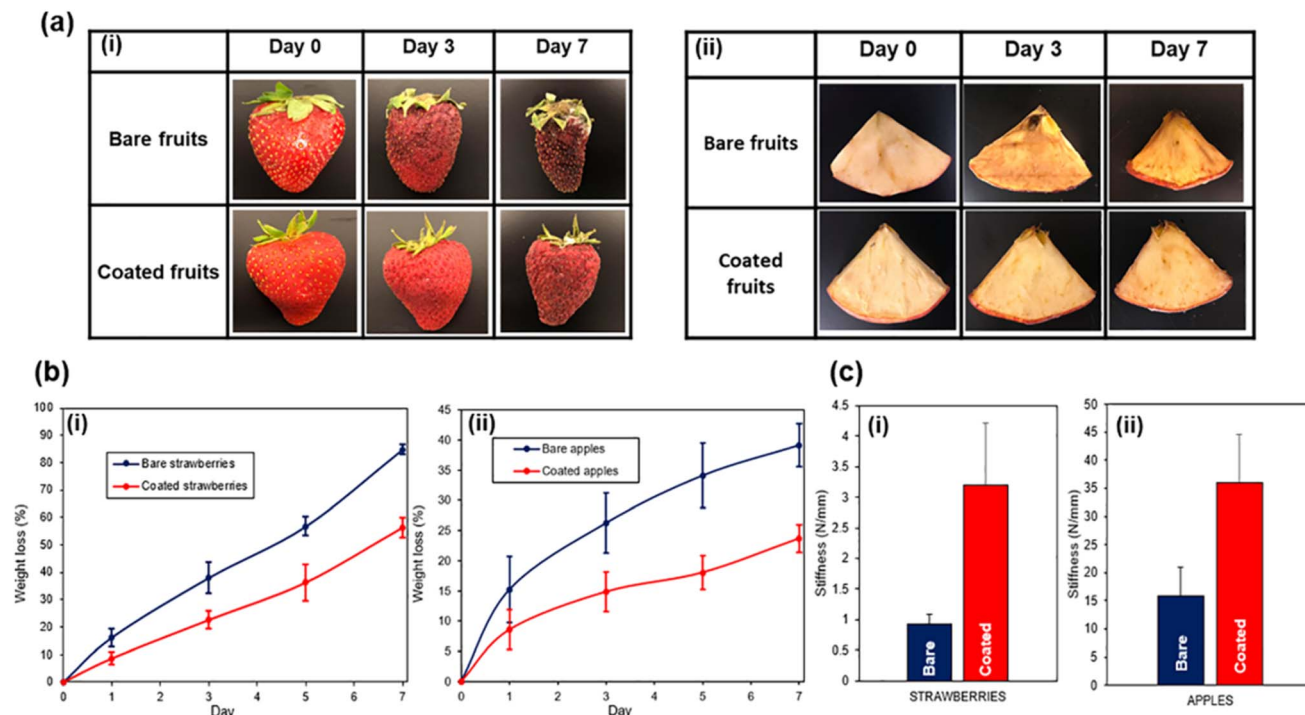


Fig. 9 Effect of edible emulsion coatings on strawberries and apples. (a) Time-lapse photographs of bare and coated (i) strawberries and (ii) flesh-cut apples over 7 days. (b) Water weight loss of (i) strawberries and (ii) flesh-cut apples over 7 days, and (c) comparison between stiffness of bare and coated (i) strawberries and (ii) flesh-cut apples. Reproduced from ref. 41 with permission of Elsevier © 2022.



sustainable packaging options.<sup>70,171–173</sup> As mentioned earlier, there has been experimental success in creating paper packaging with biobased and/or biodegradable waterborne coatings of PLA, PHBV, other PHA's, and PBS, making the introduction of commercialized systems in this area very likely to occur in the near-future.<sup>6,21,35,251</sup>

Other packaging products being developed include direct food coatings, smart packaging, and active packaging. Direct food coatings such as waxes can be biobased and edible, while reducing food spoilage through limiting water and gas transfer.<sup>41</sup> The remarkable effectiveness of these systems can be seen in Fig. 9, in which Trinh *et al.* used an edible Pickering emulsion of beeswax to limit spoilage of strawberries and sliced apples (as shown), as well as bananas.<sup>41</sup> Active packaging employs a multicomponent system, such as encapsulation and embedment in the coating matrix.<sup>260</sup> As an example, Ma *et al.* embedded anti-corrosive agents within a smart pH-responsive capsule in waterborne epoxy for metal coating, with the success shown in Fig. 10.<sup>261</sup> Importantly, smart packaging improves quality through the incorporation of sensors and

indicators.<sup>12</sup> Smart packaging coatings will be similar to active packaging from the perspective of the coating, with the functionality imparted as an addition to or separate component from the primary waterborne coating itself.<sup>12,262</sup> Similarly, functional paints possess additional properties alongside providing protection and improved appearance to the substrate.<sup>263</sup> Self-cleaning, self-healing, antigraffiti, antifouling, and more are possible property additions,<sup>263</sup> as is a specific focus on biocidal behavior.<sup>264–268</sup> Some of these are already commercialized for some applications, such as antifouling marine coatings as discussed earlier in this work. However, as these systems are more complex than simple barrier coatings they are currently not in widespread use and will likely see a longer timeframe for market adoption.<sup>167</sup>

Many innovative waterborne applications are under ongoing investigation across dissimilar industries. For example, a waterborne acrylic photoresist layer for printed circuit boards has recently been produced.<sup>269</sup> With the rapidly rising rate of manufacturing printed circuit boards, waterborne coatings to replace the VOC-intensive processes will be an important step to

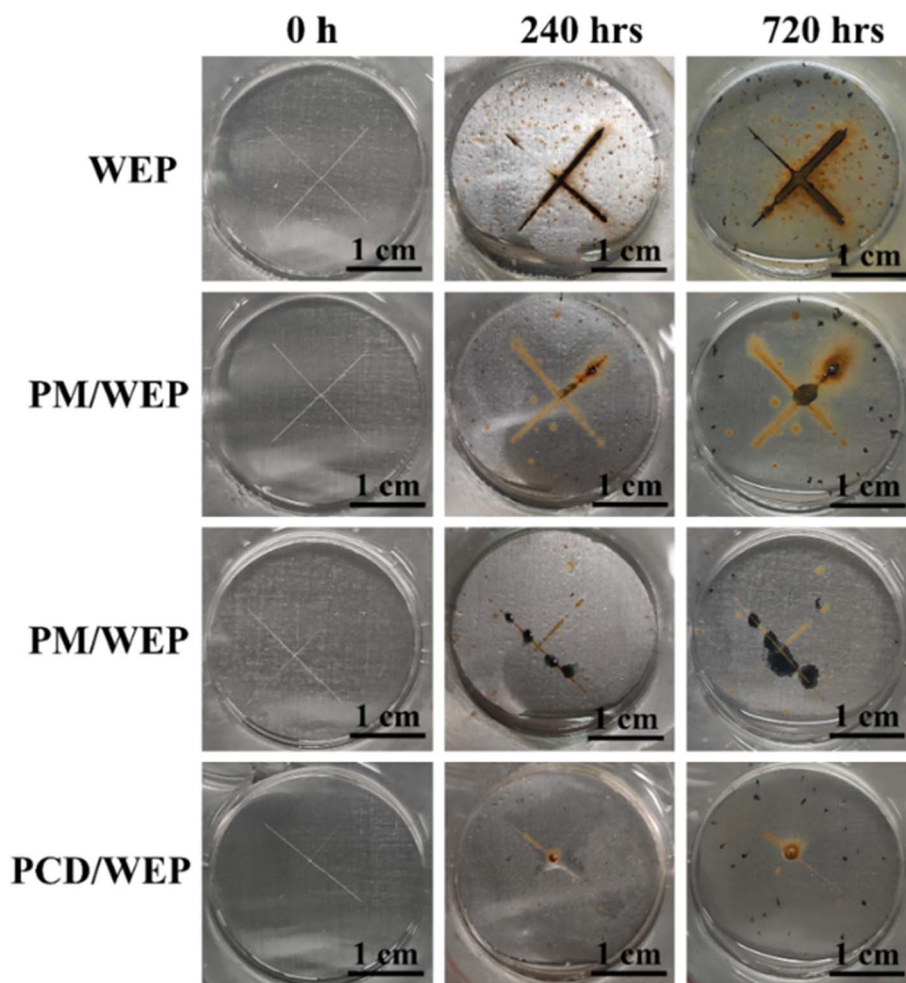


Fig. 10 Visual images of blank waterborne epoxy (WEP), melamine phytate/WEP, melamine phytate with Ce(III)/WEP, and melamine phytate with Ce(III) and polydopamine/WEP of the scratch zone at 0, 240 h, and 720 h immersion stage. The area of the coating exposed to the 3.5 wt% NaCl solution is 7.07 cm<sup>2</sup>. Reproduced from ref. 261 with permission of Elsevier © 2022.



reducing the environmental and safety impacts.<sup>269</sup> Antistatic textile coatings,<sup>270</sup> hair-styling products using bio-based waterborne polyurethanes prepared from castor oil,<sup>271</sup> and slow release fertilizer coatings<sup>272</sup> are just a few more of the various products currently in development.

## 4. Conclusions

The recent adoption of waterborne systems for commercial coatings marks a promising start to the future of sustainable coatings. These systems have demonstrated broad applicability while enhancing environmental and safety characteristics through a reduction in organic solvent emissions. While hybrid systems employing multiple polymers have been used for years, their recent expanded use presents a promising avenue for potential cost-savings and addressing remaining performance issues. Furthermore, the incorporation of nanoparticles and the use of other novel additives are broadening the scope of possibilities regarding the capability and applicability of waterborne coatings.

Despite the various progresses, challenges persist. Certain systems still lack waterborne counterparts that meet acceptable standards for commercialization, notably clearcoats for outdoor applications. Additionally, issues such as pot-life, energy requirements, and the available range of systems still lags behind solventborne alternatives for many applications. Research endeavors aimed at addressing these challenges are ongoing, with emerging stabilization techniques like Pickering emulsions seeing widespread interest. Furthermore, continuous investigation and incorporation of other additives are underway to further enhance waterborne coating performance and applicability.

Lastly, the predominant resins in use are still primarily derived from petrochemical sources. Consequently, the coatings are largely non-biobased and non-biodegradable. Moving beyond the environmental improvements achieved with waterborne systems to achieve fully sustainable coatings will be the next step, and a key challenge in the coming decades. Progress toward this transition is already underway, with the widespread adoption of bio-based waterborne polyurethanes and successful experimental applications of fully biobased and biodegradable polymers in water-dispersive formulations.

Nevertheless, these upcoming endeavors should not overshadow the significant strides made by the coatings industry toward environmental sustainability. Commercialized products must adhere to performance standards, and achieving full sustainability requires considerable time and collective effort. Waterborne systems have emerged as the standard for architectural coatings, the largest commercial coatings sector, as well as automotives, one of the sectors with the highest visibility for coatings innovation. Waterborne coatings will persist in leading environmentally conscious coating options and pioneering new coatings applications.

## Data availability

No raw data was used to prepare this review manuscript.

## Author contributions

Kyle Pieters: conceptualization (equal), methodology (equal), validation, formal analysis, investigation, resources (equal), data curation, writing (lead), visualization, funding acquisition (supporting). Tizazu H. Mekonnen: conceptualization (equal), methodology (equal), resources (equal), writing (supporting), supervision, project administration, funding acquisition (lead).

## Conflicts of interest

The authors declare no competing financial interest.

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