

The chemistry and challenges of functional polymers for corrosion protection Joseph Watson,¹ Matthew Unthank¹

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Background

Organic thermoset polymer coatings based on epoxy curing methods have been used extensively to provide excellent physical protection to metal substrates such as aluminium from corrosive environments. However, in the case of automotive protection the complex shapes of alloy wheels lead to uneven coating, with less physical protection on sharp edges making them more susceptible to damage form road debris.

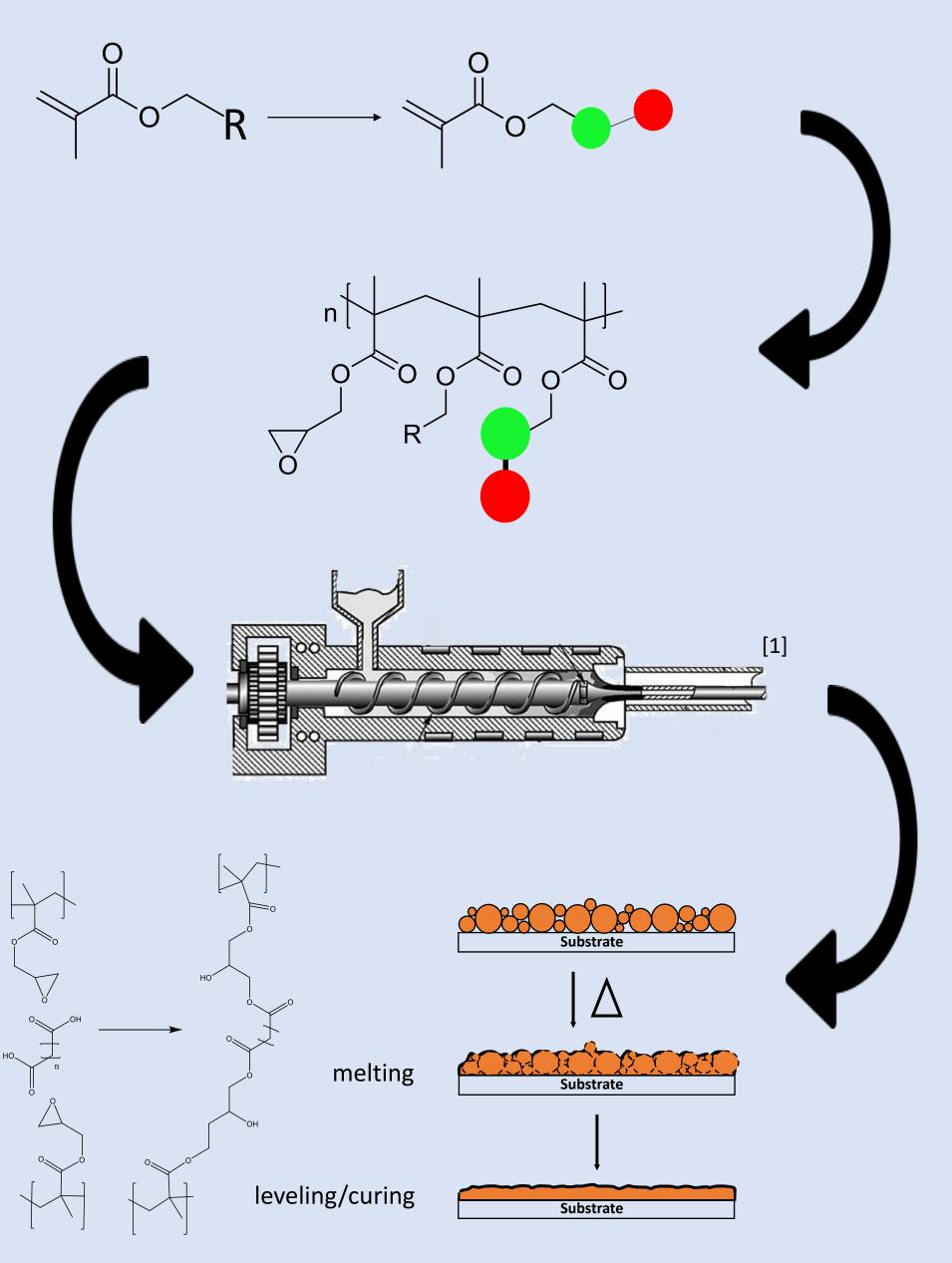
Once exposed to the environment high humidity and corrosive species such as chloride salts can cause filiform corrosion to begin. Filiform corrosion is identified by its unique thread like appearance, which propagates across a metal surface underneath the polymer coating.

To combat this type of corrosion, coatings have been developed to provide active protection. This can be achieved multiple ways, through the addition of microcapsules, fillers, or as part of the polymer systems chemical structure. Here methacrylic monomers have been synthesised with the goal of either

Manufacture of responsive acrylic thermoset powder coatings

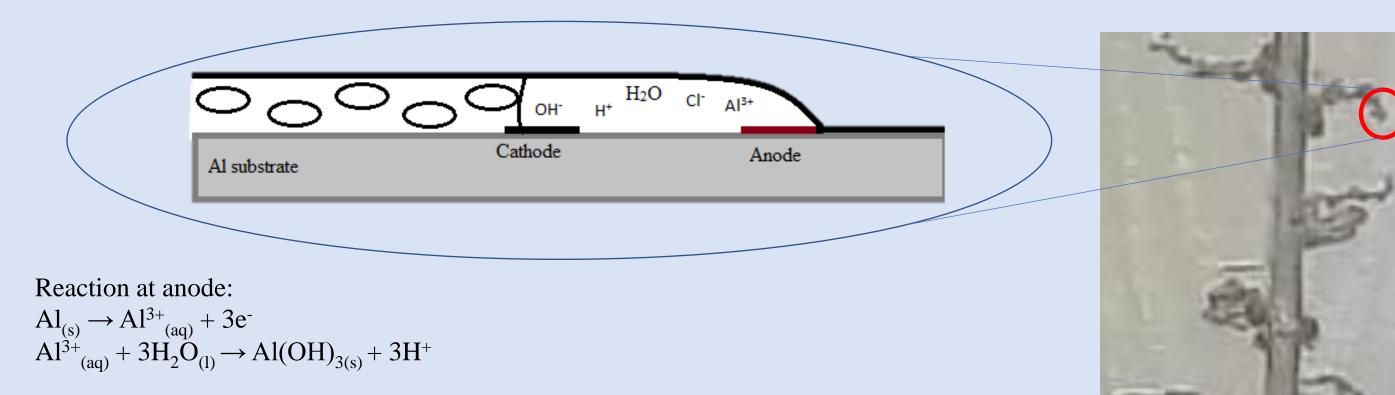
Monomer synthesis, including initial small scale tests leading to larger scale synthesis.

Initial polymerisation, compatibility between functional groups needs to be taken into account to avoid advancement and possible gelation. This is why the groups used in this work are protected.



neutralising the acidic environment of the filiform head or increasing the adhesion between the coating metal interface.

Designing polymer systems for filiform corrosion



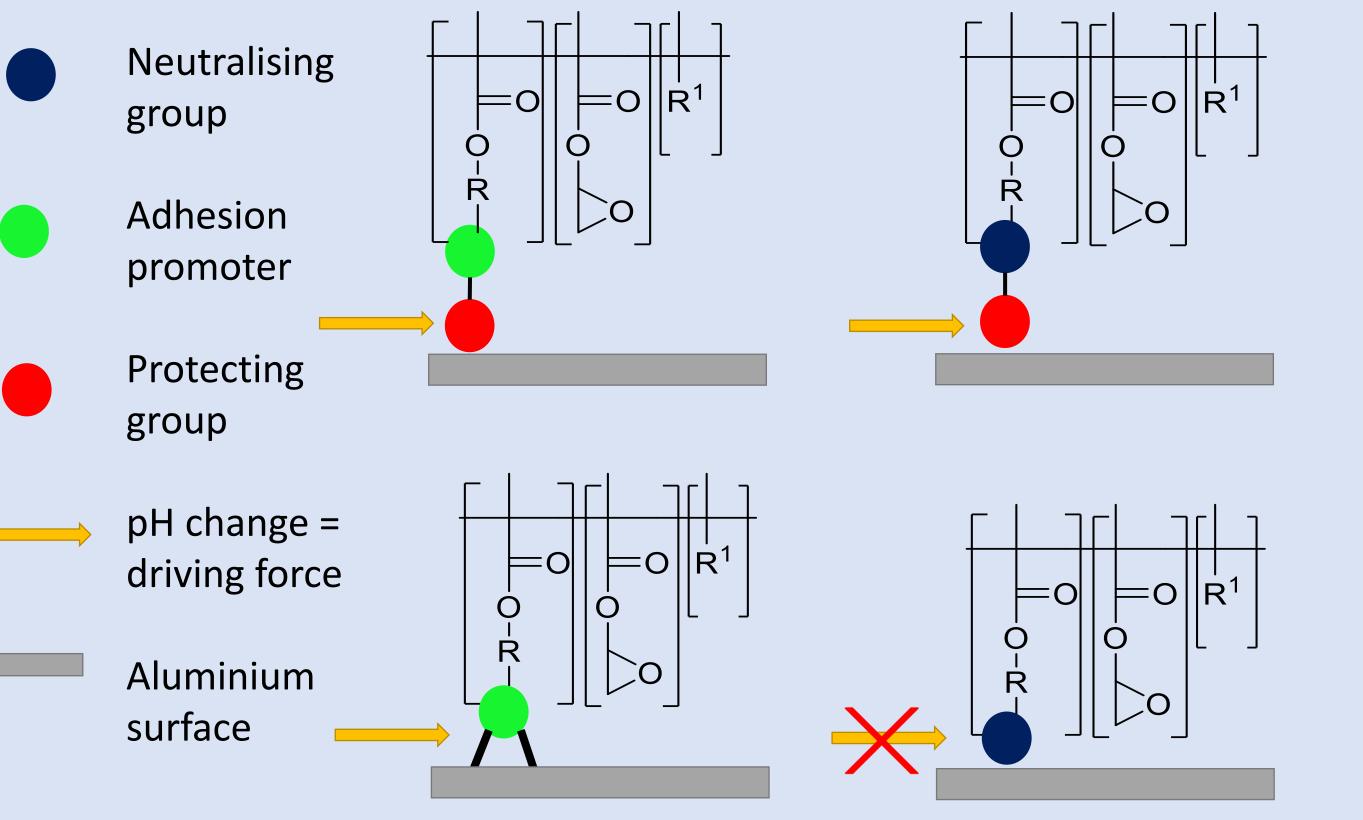
Reaction at cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Overall: $4Al_{(s)} + 3O_{2(g)} + 6H_2O_{(l)} \rightarrow 4Al(OH)_{3(s)}$ [2]

The low pH of the filiform head is maintained via stepwise deprotonation reactions of aluminium hexa aqua-complex cations. The first step is shown below. ^[3]

 $[Al(H_2O)_6]^{3+}$ $(Al(H_2O)_5OH)^{2+}$ + H⁺

Neutralising

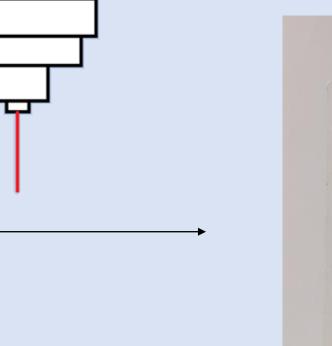


Extrusion and powder formulation, additive such as dicarboxylic crosslinkers are added in this stage.

Final samples are coated and cured for corrosion testing, or end application.

Sample preparation for mechanical testing







- The pH change within the filiform head leads to the cleavage of protecting groups.
- The increase in coating adhesion should inhibit further delamination of the polymer coating.
- For filiform to propagate it needs a low enough pH to dissolve aluminium oxide to form Al^{3+ [4]}, buffering of the environment will interrupt the internal chemistry of the leading edge, stopping further corrosion of the metal form occurring.

- Due to the fragility of samples and the necessity for high levels of accuracy needed to produce defect free samples cutting or pressing the films was not possible.
- A laser cutter was used to create defect free uniform samples for tensile testing.
- Any defect in the form of a fractures or chip, which is common with other cutting techniques, would lead to incorrect measurements do to early mechanical failure.



- The above charts show that up to 10 weight percent of protected functional monomer can be incorporated into the polymer formulation with minimum if any degradation of physical performance.
- While up to 5% inclusion of other less stable protected basic groups caused increased fragility and a loss of tensile strength

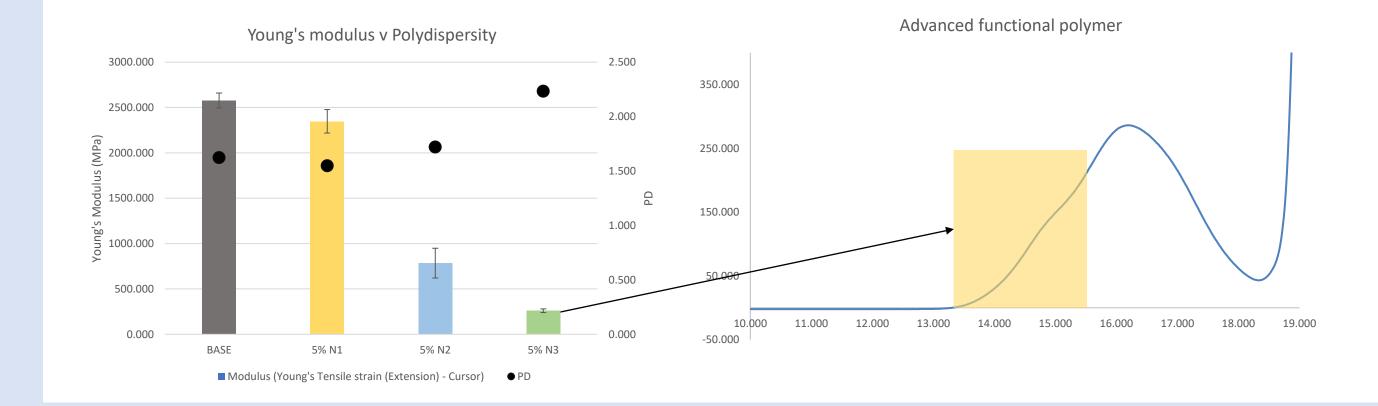


POLYMER COATING

PTFE

ALUMINUM

Samples capable of disassembly post corrosion have allowed for surface analysis of the previously inaccessible polymer metal interface.



Advancement caused by premature crosslinking is detectable by GPC, and is characterised by a shoulder on the left hand side of the peak. Advancement leads to an increase in PD and embrittlement of the coating.

References and thanks

[1] https://www.mechanicatech.com/Plastics/continuousextrusion.html [2] J. V Nardeli et al., "Localised corrosion assessment of crambe-oil-based polyurethane coatings applied on the ASTM 1200 aluminium alloy," Corros. Sci., vol. 111, pp. 422–435, 2016. [3] G. Williams and H. N. McMurray, "Inhibition of filiform corrosion on organic-coated AA2024-T3 by smart-release cation and anion-exchange pigments," Electrochim. Acta, vol. 69, pp. 287–294, May 2012. [4] M. C. Reboul and B. Baroux, "Metallurgical aspects of corrosion resistance of aluminium alloys," Mater. Corros., vol. 62, no. 3, pp. 215–233, Mar. 2011. We would also like to thank AkzoNobel for their continued help and support with this project.