Review

Electrolyte transport in polymer barrier coatings: perspectives from other disciplines

S.G. Croll

Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND, USA

ABSTRACT

Large infrastructure for transportation, energy transmission, water supply etc., must survive for many decades with their carbon steel components protected against corrosion by organic polymer coatings. Modern, environmentally responsible coatings are replaced more frequently than was necessary for some older coating technologies. In order to find useful, additional insights, this review is based on ideas and information from other topics rather than from conventional coatings sources. There is considerable research done on desalination membranes, batteries, and the nervous system that seems useful in understanding better how the composition of polymers affects their barrier properties. Typical crosslinked coatings have characteristics and defects that limit their performance. Very few molecules of water are required to enable corrosion, so improvement of barrier properties requires considerable control over the composition of a coating. There is no common mechanism of how barrier coatings deteriorate, but behavior seems to fall between two patterns. More successful coatings seem to fail slowly due to degradation of the coating upon exposure but less successful coatings fail faster and progressively by mechanisms that have yet to be clarified. Some information and ideas, from non-coating disciplines, are presented delete comma that may be worthy of investigation.

1. Introduction

Installation and repair of large metal infrastructure is extremely costly, time consuming and done as infrequently as possible. Such infrastructure is protected from corrosion failure by a combination of coatings and cathodic protection where the coatings must last for a significant fraction of the service life of the infrastructure. If temperature and humidity fluctuations are limited, thick coal tar enamel coatings seem to be capable of protection for 80 years or more [1] but they are toxic and not easy to apply. Vinyl coatings have also been very successful and long lived [2], but their application requires large amounts of solvent. Thick layers of oil paints containing red lead were very successful. These coatings have serious health and environmental problems and so polyurethane or epoxy coatings are used most often now, but with much less confidence that their service will exceed even 20 years in moderate conditions [3]. Despite all the efforts of the last few decades, modern coating longevity has not improved substantially. Discussions with suppliers, engineers, designers and owners of infrastructure often produce queries about why modern coatings cannot be substantially improved. Questions about longevity of corrosion protection sound simple, but they are very difficult to answer to the satisfaction of the questioner.

A polymer coating may be used as a barrier to prevent the transport of corrosive species to a substrate or as a primer coating which can be used as a reservoir of corrosion inhibitor or as a conductive layer that provides galvanic protection or by using doped conducting polymers [4]. There is a vast body of work on corrosion prevention by coatings, which deserves detailed review, but the primary intention here was to examine information from other disciplines for insights that are not current in coatings literature. The scope here is to look for information outside conventional coatings literature, and focus only on coatings as barriers. Coating adhesion, inhibitor action, blistering, metal treatment etc. are all important topics but they are also very large and deserve separate attention.

Most coatings absorb a certain amount of water and oxygen quite quickly, depending on the external environment, without allowing corrosion immediately. Electrolyte ions and their penetration rates, particularly chloride or other acidic ions, often seem to control the extent and kinetics of the corrosion [5,6]. An effective barrier coating should not only limit the concentration of oxygen and water but also be a barrier to ionic species.

It seems unclear, even now, in the coating literature, what the connection is between coating composition and its ability to limit the flow of water and aggressive ions to the substrate [7–9]. One view is that aggressive species percolate through a network of pores and other imperfections that incorporate both penetrating channels and other

E-mail address: Stuart.Croll@ndsu.edu.

flaws and "regional" generalized absorption at the microscale [10] but without any definitive conclusions about possible composition variations that might account for these features.

Although the topic might be organized differently, it is placed in three sections here:

(i) Possible links between composition and performance as a barrier,
(ii) Potential mechanisms that cause barrier properties to deteriorate
(iii) The amount of water and electrolyte sufficient to initiate corrosion on the metal surface, i.e. what must the coating prevent?

2. Composition and barrier properties

2.1. Polymer-ion compatibility

For corrosion to proceed, ions, water and oxygen must first enter the protective coating, or be able to pass between the coating and its substrate. Since this review does not include adhesion, the latter pathway is ignored here. In addition, although swelling by water deserves more attention than the little it has received in the coatings literature [11], it will not be included here.

For any change to proceed the (Gibbs) free energy of the system should less after the process than it was before, so the change, ΔG, should be negative,

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

Where ΔH = change in the enthalpy; ΔS = change in the entropy; T = temperature

This simple thermodynamics is the basis of solubility parameters as well as many other models. Here we focus on barrier properties, not adhesion, so the discussion here will concern the bulk coating. For water and ionic species to enter a protective coating, the coating must be both compatible enough (via ΔH) and offer spaces within its matrix where the water and ions can reside or move (permit an increase in entropy). One cannot design a protective coating solely by choosing a high level of crosslink density, nor can design be solely concerned with compatibility, but both factors must be addressed. An external solution of salt provides the means of corrosion; the change of enthalpy and entropy in the Gibbs free energy provide the motive and opportunity respectively.

The Born model [12] for the energy barrier, ΔW, to solvation of an ion (going from the external solution to a polymer) is used to describe the ion-selectivity of polymer membranes [13]:

$$\Delta W_{ion} = \frac{z_{ion}^2 e^2}{8\pi\varepsilon_0 a_s}\left(\frac{1}{\varepsilon_{polymer}} - \frac{1}{\varepsilon_{external\,solution}}\right) \tag{2}$$

a_s = radius of cavity formed by the ion
z_i = number of charges on an ion
e = electronic charge
ε_0 = permittivity of vacuum
ε = relative permittivity of either a polymer (~5) or an aqueous solution (80)

As an example, a chloride ion creates a cavity with a radius of 0.2 nm [14], thus the enthalpy of solvation necessary for the ion to leave an aqueous solution and enter a polymer is 26 $k_B T$ (k_B = Boltzmann's constant, T = temperature) which is very much larger than thermal energy available at room temperature which would be ~ $k_B T$.

The Born model uses the overall, bulk permittivity and calculates that it is impossible for a bare Cl^- ion, or similar, e.g. Na^+, to be in a typical organic coating. Ions must need water to accompany them. Even if the ion retained one layer of water molecules, thus forming a cavity of radius 0.332 nm [15] the energy requirement would be > 15 $k_B T$ for solvation in a polymer of typical relative permittivity. It would be impossible for a coating polymer to strip the water from an already hydrated ion. In contrast, we know from the huge literature on corrosion

that ions do pass into coating polymers, so ion transport must require compatibility at the molecular scale rather than the bulk, implying that local, molecular polarizability is important [16].

Na^+ or Cl^- ions, or any other corrosive ions, cannot enter a medium where there are no charged moieties to neutralize them. Water is very polarizable and thus its molecules become distorted near ions and partially screen an ion's charge so it can reside near other species. Hydration of ions is commonly discussed in terms of three shells of water molecules around the ion. Depending on concentration, and other circumstances, sodium ions coordinate with approximately 5 water molecules in their innermost hydration shell and chloride ions with approximately 6 molecules of water [17,18]. The outer, third shell of water molecules are less strongly bound and are close in structure to bulk water with the intermediate layer having some organization in between that of the innermost and the outermost [19]. In all, each ion associates with 20–30 molecules of water. Very similar findings and quantities occur if one examines other ions that are likely to threaten a coating.

2.2. Ion transport

Ion transport is intensely studied in desalination membranes, sensors and other technologies [20–22]. Ion transport through coating films is caused by a salt concentration gradient, rather than an applied pressure gradient as in desalination operations. Any search for insights into the links between the composition of polymer films and ionic transport immediately produces many results from the ion-selective membrane [15] as well as biophysics literatures, not from articles about conventional coatings. It seems to be accepted that ion transport occurs via intra- and intermolecular hopping involving formation and breaking of ion-associations [23,24]. Interestingly, review articles on membrane science completely ignore coatings and corrosion applications.

The Bjerrum length, λ_B, of a medium [25], quantifies the range over which internal, molecular-scale electrostatic forces act on ions.

$$\lambda_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \tag{3}$$

If an ion is located near a local charged side group on a polymer, it is less likely to move if the next nearest charged group is more distant than the Bjerrum length. If the concentration of polar groups is very low, then even if an aggressive ion is present somewhere, only thermal energy ($k_B T$) is available to move it. The Bjerrum length is 11 nm when calculated with the same parameters used earlier for the Born solvation energy. For comparison, λ_B for water under the same conditions is 0.7 nm. Modern crosslinked coatings have polar groups that are much closer together than this Bjerrum length and thus permit ionic hopping. This supports reducing the polarity in coating polymers in order to limit ionic transport and favoring systems in which there is a hydrophobic barrier.

In artificial membranes, selectivity is governed by the charge on the membrane so that oppositely charged ions may pass but like charged ions are excluded, unless the channel is wide enough so the electrical field in its center is weak [20–22]. There are many experimental studies of semi-permeable membrane technology but studies using computational simulations are usually more instructive. In all cases, if a pore is very small, nothing passes. If the diameter of the pore is approximately 1–2 nm it discriminates between ions due to the charge on the channel wall, but as the diameter increases much more water can pass and all ions make their way through [26]. The size of the ion that must be accommodated seems to include the first hydration shell [27], or its equivalent, and thus will have a radius ~0.5 nm, not the much smaller size of a bare ion. Hydration reduces the charge density on ions and makes them more compatible with surrounding channel walls. If there is not enough space for water molecules to surround the ion, then the ion may not pass. An uncharged channel with hydrophobic walls will not allow water through if it is smaller than 1 nm approximately, but it