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A Review on the Environmental Durability of Intumescent Coatings for Steels

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Abstract

It is well known that when an unprotected steel structure is exposed to fire, depending on the section factor, the temperature of the steel increases rapidly. This increase affects the mechanical properties of the steel and could result in deformation/failure of the structure depending on the temperature, time, and applied load. Therefore, conventionally, intumescent based coatings are used as protective coatings on steel. However, poor weathering resistance of these coatings is a major problem. Even the slightest changes in chemical composition due to weathering reduces the fire performance of these coatings. This review focuses on elaborating and exploring the protective coatings for steel, the environmental interaction of these polymer-based coatings, sorption kinetics of moisture/water, leaching of flame retardant additives, subsequent changes in chemical composition of the coatings, and the resulting effect on fire performance of coatings. Discussions on UV degradation of polymeric materials, blister formation in weathered coatings and corrosion susceptibility of the substrates are also incorporated in these topics.

Keywords: Intumescent coatings; durability; steel; accelerated weathering; fire protection.

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1. Introduction

When an unprotected steel structure is exposed to fire, the temperature of the steel increases rapidly depending on the section factor and the severity of the fire itself. An illustration of this is given in Fig. 1, which shows temperature contours in an unprotected heavy steel section after exposure to a standard fire curve for 30 min [1, 2]. Fig. 2a shows how the mechanical properties of steel change with an increase in temperature [2]. It should be noted that when permissible stress is used as a basis for design, the maximum stress allowed in a member is about 60% of its ambient temperature strength. Therefore, based on Fig. 2a, 550 °C seems to be the critical temperature above which the structure is bound to deform. Even the ISO 834 fire curves shown in Fig. 2b for unprotected and protected steel beams with a section factor of 200 m^{-1} highlight the problems [2].

Therefore, conventionally, to improve the fire resistance of steel columns, solid concrete protection is provided. Table I provides information on the thickness of concrete needed as a function of time (as per National Building Code of Canada) [3]. This major disadvantage of this methodology of protection is the increase in weight of the structure. Other ways of providing flame resistance to steel substrates include the use of gypsum boards (thermal insulation panels), cementitious coatings, spraying with chopped fibers, coatings comprising of halogen-based compounds for radical quenching, and the use of intumescent coatings [4-9]. Among these, polymer-based intumescent systems, where materials swell and form a porous mass when exposed to fire (or temperature), are widely used due to their efficiency. In fact, by 2024, the market size for intumescent coatings (passive fire protection) is expected to exceed US \$1.25 billion as per Global Market Insights research report [10]. For these systems to intumesce and work effectively, three agents – an acid source, a carbonizing agent, and a

foaming agent, should decompose systematically and in accordance with the matrix polymer. However, loss of cohesion of char structure and poor adhesion to the substrate at high temperatures do not always guarantee the performance of intumescent systems [11]. Even the integrity of the swollen residue is a serious concern.

Fig. 1. Temperature contours in °C (calculated via SAFIR program) in a steel beam upon exposure to fire. Reproduced from [2] with permission from Elsevier, Copyright (2001).

Fig. 2. (a) Changes in yield strength, elastic modulus and proportional limit of steel with temperature; and (b) time-temperature behaviors of unprotected and protected (with mineral

fiber) steel beams when exposed to a standard ISO 834 fire curve. Reproduced from [2] with permission from Elsevier, Copyright (2001).

Table I. Minimum thickness of solid concrete protection provided to steel columns for protection against fire [3].

Time, min	Thickness, mm
30	25
45	25
60	25
90	25
120	39
180	64
240	89

Apart from the above-mentioned issues, environmental interaction of the coatings and durability are extremely important aspects that should be considered [12]. Though there are many studies that discuss the fire performance of intumescent coatings, unfortunately, there is limited information about the topic after their exposure to (in-service) weathering conditions.

There are many questions that require thorough answers like:

- will the fire performance of these polymer-based coatings change after exposure to environmental parameters? If so, to what extent and is there a good indicator for this?
- will there be any leaching of intumescent additives or formation of secondary products due to the interaction of environmental parameters with the coating? If so, can a top coat provide the protection needed, a solution that is commonly employed in the industry?
- If there are chemical compositional changes in the coatings, what happens to their mechanical performance?

It is known that weathering results in chemical structural changes of polymeric materials, affecting their appearance and mechanical properties. Though the interaction of polymeric materials with a combination of environmental elements is complex, it is well reported that the actinic radiation of the sun (wavelength in the range of 280-390 nm) along with oxygen

and humidity are critical in the initiation of the degradation reactions [13-17]. Table II shows the sensitivity of several polymers to UV radiation, which is determined by bond dissociation energies [13, 18]. The photo-oxidation or photo-degradation process includes absorption of light, excitation of the molecules, and deactivation by radiative or radiation-less energy transitions, or by transferring the energy to some acceptors. This ultimately results in the embrittlement of the surface of polymers (caused by localized cross-linking), an increase in surface roughness, changes in aesthetics, yellowing, chalking, etc. [19].

Table II. The wavelength of UV radiation (energy of a photon) causing maximum degradation in polymers or at which polymers have a maximum sensitivity (adapted from [13-15 & 18]).

Polymer	Wavelength, nm	Energy, kcal/mol
Styrene-acrylonitrile copolymer	290, 325	99, 88
Polyvinyl chloride	320	89
Polyethylene	300	96
Polypropylene	370	77
Polyester	325	88
Polystyrene	318	90
Polycarbonate	295, 345	97, 83
Acrylonitrile-butadiene styrene	330, 360	86, 80
Polyamide 6	390	72

The entire auto-oxidative degradation cycle (shown in Fig. 3) can be divided into two stages [20]. In the first stage, the free radicals produced by dissociation of bonds because of absorption of UV light energy react with oxygen and propagate radical chain reactions. This results in the formation of hydroperoxides (ROOH) and peroxides (ROOR), which are strong absorbers of UV radiation. In the second stage, they further dissociate to yield alkoxy (RO•) and hydroxy (HO•) radicals, which are highly reactive towards hydrogen abstraction and yield polymer radicals, resulting in the chain process [21, 22]. This auto-oxidation process results in extensive chain breakage and providing numerous stress concentration sites. Apart from chain breakage, cross-linking is another possibility of photo-oxidative degradation of

polymeric materials. This concept has been widely employed in automotive clearcoats, whereby scratch resistance increases with weathering time [23, 24]. Therefore, photo-stabilizers in the form of additives are incorporated into coatings. These include primary antioxidants such as sterically hindered phenols that scavenge alkoxy and peroxy radicals, secondary antioxidants such as phosphite stabilizers that decompose hydroperoxides into non-reactive products, light stabilizers like benzotriazoles, ZnO and TiO₂ that absorb UV, and hindered amine light stabilizers that quench and scavenge radicals [25-28]. Nevertheless, as many detailed reviews are available on the photo-oxidation mechanisms of different polymers and photo-stabilizers, they will not be discussed here [29-31].

Fig. 3. Schematic of the auto-oxidation cycle for polymers. Reproduced from [20] with permission from Springer Berlin Heidelberg, Copyright (1998).

From the context of ‘performance’ polymer coatings, it is important to understand the interaction of additives/fillers with environmental factors. Also, as the color, thermal conductivity and specific heat capacity of the coatings change with the type and loading of fillers present, temperature differences can be seen between the surface and bulk of these materials. For instance, it was reported that surface temperatures of polymer specimens inside a closed automobile exposed to sunlight can even reach 120 °C [32]. This could easily result in physical stresses between coating and substrate due to a mismatch in their thermal

expansion coefficients. This further results in cracking/surface crazing and loss of adhesion of the coating to the substrate. Thermal fatigue and presence of moisture are other important factors that accelerate or change the performance of coatings over time [33]. As the fire safety regulations require a similar performance throughout the lifetime of the building structure (which may be for many years), hence, ensuring the coating's fire resistive performance even after all those years is important [34]. Therefore, this review focuses on elaborating and exploring the environmental interaction of flame retardant additives in polymer coatings (specifically, intumescent coatings), and subsequent changes in fire performance.

2. Intumescent coatings

In intumescent systems, as mentioned earlier, materials swell when exposed to fire or heat to form a carbonaceous foamed mass that acts as a barrier to heat, oxygen, and other pyrolysis products. Three agents are generally required in this approach: an acid source (e.g., ammonium polyphosphate (APP), boric acid, melamine phosphate), a carbonizing agent (e.g., pentaerythritol (PER), starch, mannitol), and a foaming agent (e.g., melamine, urea, dicyandiamide). The process of intumescence starts with the release of acid (or acidic species) that esterifies the carbon-rich source and later, the ester decomposes *via* dehydration yielding a carbonaceous (or phospho-carbonaceous) residue. The released gases from the decomposition of the blowing (or spumific) agent cause the (phospho-)carbonaceous material to foam [35]. Generally, the closed cells that form during the foaming process have sizes in the range of 20-50 μm with 6-8 μm thick walls [36].

APP-PER-melamine combination, whose chemical structures are given in Fig. 4, is one of the most commonly used intumescent combination of additives in matrices like epoxy, acrylic, and urethane. The intumescent reaction for this system starts with the degradation of APP into polyphosphoric acid and amine at around 250 °C. The polyphosphoric acid then brings about the dehydration of PER by esterification and subsequent charring at 320-400 °C (that is, the elimination of ammonia and water to form cyclic phosphate ester structure, and the repetition of the above-mentioned reactions results in pentaerythritol diphosphate structures). The degradation of melamine, which is the spumific agent, occurs at around the same temperature range of the charring reactions (300-395 °C), releasing ammonia and carbon dioxide, thus causing the char to expand [37, 38]. These reactions are thoroughly discussed in many articles [39-44].

Fig. 4. Chemical structures of (a) APP, (b) PER, and (c) melamine.

As more than one chemical structure is participating in the fire-retardant mechanism, using an optimum ratio between them is critical. There are many efforts on this aspect with suggestions of a weight ratio of 2.7:1:1.1 between APP, PER, and melamine combination [45], 3:1 between APP and PER [46], 2:1 between APP and PER [47], etc. Camino et al. [48] have developed a complete infographic (Fig. 5) that showed the dependence and variation of the limiting oxygen index of polypropylene in the presence of APP-PER-melamine combination (with an overall content of 30%). They have applied a statistical computational

method to explain the oxygen index-composition relationship experimental data. Nevertheless, the optimal ratio will change depending on the matrix, cross-linking density and the type of groups on the chain. Also, the perception will change depending on the type of fire testing standard to be followed. This is particularly important considering the variations between a limiting oxygen index test and an ISO 834 / ASTM E119 or ASTM E84 type of test.

Fig. 5. Limiting oxygen index variation with different compositions of polypropylene, APP, PER and melamine. The concentration of the additives/components (in wt.%) are shown in brackets, and numbers on the curve are oxygen index values. Reproduced from [48] with permission from Elsevier, Copyright (1989).

Though ammonium phosphates (mono- and di-) are water soluble and can easily leach out of the matrix, APPs are relatively less water soluble. The extent of solubility of PER and APP that have been used in some of the studies range from 0.3 g to 16.8 g per 100 g of water [49, 50]. Despite this, their susceptibility and reactivity (that can result in other secondary products) are major issues, particularly under in-service conditions and over a lengthy period. This could ultimately change the optimal ratio between the intumescent system additives. For example, Fig. 6 shows the DTA curves of APP-PER-melamine (in the ratio of 5:1.6:1) based acrylic coating before and after accelerated aging for 500 h. Evidently, differences exist

between the two in terms of the position of the endothermic peaks, their intensities, and enthalpies (particularly the peak in between 300-400 °C which points to the esterification/charring reactions) [38].

Fig. 6. DTA curves of samples before and after 500 h of accelerated aging. Accelerated weathering test procedure involved a wet and dry cycle of spraying water for 18 min per 2 h at a test temperature of 50 $\pm$ 5 °C, relative humidity of 70 $\pm$ 5% and with exposure to UV radiation from Xenon Arc lamp with an intensity of 550 W/m². Reproduced from [38] with permission from Elsevier, Copyright (2006).

3. Fire performance of environmentally exposed intumescent coatings

As evident from the chemical structures of intumescent flame retardant additives, their hydrophilicity is an issue for long-term environmental stability. Many studies have reported a negative impact on flame retardant properties with the weathered coatings [37, 38, 50-54]. Before going into the details of those studies, in Fig. 7, a summary of the relative changes in fire performance of a few intumescent systems is shown that clearly illustrates the poor performance of weathered samples. It is important to note that the purpose of Fig. 7 is not meant to cross-compare between different systems as the weathering conditions and imposed fire curves are different.

Systems	Thickness in mm		Weathering exposure conditions	Chosen critical temperature
	Steel substrate	Coating		
A1 and A2: epoxy based APP-melamine-TiO ₂ intumescent coatings	1.5	1.5	A1: one-month immersion in distilled water A2: one month immersion in 5% NaCl solution at 20 °C	400 °C
B: acrylic resin based APP-PER-melamine coating	5	1	Accelerated aging for 500 h (cyclic application of water spray and drying with exposure to UV radiation)	300 °C
C is an acrylic resin based APP-PER-melamine system (containing some other fillers)	10	1	Distilled water immersion for 500 h at 25 °C	300 °C
D1 to D4 are acrylic resin	5	1	Exposure to cycles of salt	300 °C

based APP-PER-melamine coatings with different loadings of SiO ₂ particles			spray (3.5% NaCl) and drying for 500 h	
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Fig. 7. The plot on the top shows the relative % reduction in fire performance and intumescent factor (extent of swelling) in different systems. The nomenclature and weathering conditions are given below the plot. Fire performance is defined in terms of resistance time to reach a particular critical temperature at the backside of the substrate. As the thickness of coatings and substrates vary from system to system, the plot is not intended to compare among systems. The data for A, B, C and D is extracted from [53], [38], [37] and [55], respectively.

Wang et al. [37] have compared the ISO 834 fire curves of ~1 mm thick acrylic based APP-PER-melamine coatings on 50 x 50 x 10 mm³ steel plates before and after water immersion for 500 h. Fire-resistant time was defined as the time required to reach 300 °C at the back surface of the steel plate. As evident in Fig. 8, fire-resistant time has decreased significantly from 70 min to 46 min, which is a 34.3% reduction, affirming that the exposure to water has had a detrimental effect. The thickness of char layer has decreased from ~20.3 mm before water immersion to ~11.1 mm after immersion. However, in the additional presence of 8.5 wt.% of expandable graphite (EG), evidently, the fire performance before and after water immersion test is similar. This was attributed to the platelet-like structure of graphite layers, which increased the resistance to diffusion of water and other molecules through the coating. This, in fact reduced the leaching of flame retardant additives during water immersion test and helped in retaining the fire performance after the water immersion test. In a similar study on APP-PER-melamine coatings, up to 1.5 wt.% of nano-SiO₂ was used as an additional additive instead of EG [55]. After subjecting the coatings containing the additional 1.5 wt.% SiO₂ to salt spray test for 500 h, a 32% reduction in fire-resistance time was noted as compared to a 43% drop for the coatings without silica. In yet another study by Wang et al. [38], it was shown that the addition of even other particles like layered double hydroxides and

TiO₂ to intumescent coatings can improve the resistance to weathering and subsequently fire performance.

Fig. 8. Effect of 500 h of water immersion on the time-temperature curves of acrylic-based intumescent coatings on a steel substrate subjected to ISO 834 conditions. Adapted from [37].

Jiminez et al. [53] have shown that even a month's time of immersion in salt water is enough to induce a detrimental effect on the fire-resistance of the coating. A 1.5 mm thick epoxy based intumescent coating containing APP, melamine, and TiO₂ was applied on a 10 x 10 cm² steel plate. Fire resistance of the coated samples has been evaluated by subjecting them to a UL1709-like fire curve in a small furnace. The authors have chosen 400 °C as the critical temperature for defining the fire-resistance time. As shown in Fig. 9, bare steel plate (without coating) has reached 400 °C in 250 s, whereas the coated plate has taken 730 s. Fire-resistance time has not changed drastically even after exposing the coated plates to a humid

(80% moisture) and hot (70 °C) atmosphere for 2 months in a climatic chamber. Immersion of coated samples in distilled water for one month at 20 °C has resulted in a drop of fire-resistance time to 600 s. But the most severe effect is seen when immersed in salt water instead of distilled water, where the protection time was only 285 s. The swelling of the char has also decreased by 2-folds after immersion in distilled water for one month; while there was no swelling at all for the sample immersed in salt water for one month.

Fig. 9. Effect of exposure to various conditions on the time-temperature curves of epoxy-based coatings on a steel substrate subjected to UL1709 conditions. Adapted from [53].

As mentioned earlier, char homogeneity is another parameter that can be linked to the drop in fire-resistance times of intumescent coatings after exposing to accelerated environmental conditions. As an example, char morphologies of epoxy based APP-PER-melamine coatings after subjecting to an ISO 834 fire curve before and after 600 h of immersion in water are

shown in Fig. 10 [51]. Presence of larger cells is evident in the char for water immersed samples as opposed to unexposed samples. In fact, swelling ratio has reduced from ~ 10.3 to ~ 6.1 , which is a 40.8% reduction. It has also been reported that while performing the fire-resistance test on the samples immersed in water, the char layer has detached from the steel damaging the fire-resistive properties. In an acrylate based APP-PER-melamine intumescent system [38], the authors have claimed the formation of “a three-dimensional honeycomb-like phospho-carbonaceous char” for the samples that were exposed to 500 h of accelerated weathering instead of a conventional “disordered amorphous carbon structure” (Fig. 11). The accelerated weathering test procedure involved a wet and dry cycle of spraying water for 18 min per 2 h with exposure to UV radiation. Fire-resistance time has dropped from 120 min to 49 min after 500 h of accelerated aging according to the ISO 834 test. Also, the thickness of char has diminished from ~ 32.5 mm to ~ 9.7 mm after accelerated aging attributed to the reduction in the reaction of the acidic phosphate species due to the loss of APP. Further, though not directly relevant, it is important to note that proper conditioning of the weathered samples is required before furnace or combustion testing as the excess moisture could catalyze the ignition behavior of polymeric materials [56-58].

As the critical period during the formation of the char layer is in the semi-liquid phase, this coincides with the formation of gases/volatiles and hence, swelling. The gases released from the degradation of the fire retardants, especially melamine, must be effectively trapped in the highly viscous melt for homogeneous char and for the swelling ratio to be high. If the viscosity of the degrading matrix is too low, gases can diffuse out easily [59]. When this happens, larger pores and less extent of swelling are expected. Nevertheless, in the literature, there is definitely a lack of quantitative and specific details on the resultant char morphologies after exposure to environmental conditions. The following section explores the

fundamentals behind the leaching process to answer some of the questions and identify the missing links.

Fig. 10. SEM micrographs of char layers of epoxy based APP-PER-melamine coating after subjecting to an ISO 834-like fire curve, and (a) before water immersion; (b) after water immersion for 600 h. Reproduced from [51] with permission from Elsevier, Copyright (2011).

Fig. 11. SEM micrographs of char layers of acrylate based APP-PER-melamine intumescent system after subjecting to an ISO 834-like fire curve, and (a) before accelerated aging; (b) after 500 h accelerated aging. Reproduced from [38] with permission from Elsevier, Copyright (2006).

4. Mechanism of leaching process

In general, the magnitude of leaching of additives/compounds is governed by [37, 51, 52, 60, 61]:

- Permeation of water molecules into the coating; and

- Solvation, followed by migration of susceptible compounds to the top surface of the coating

Permeation of water molecules through a polymeric binder/resin is generally explained by the free-volume approximation theory [62, 63]. According to this and as shown in Fig. 12 [64], polymer volume consists of:

- Occupied volume by the polymeric chains;
- Interstitial-free volume that originates from the vibrational energy of polymer bonds, which is generally thought to be inaccessible; and
- Hole free volume due to the volume relaxation and plasticization upon thermal cycling.

The hole free volume is where the diffusion of the water molecules take place and when such diffusion is occurring, the hole free volume is modified resulting in the swelling of the film/coating. This suggests that the glass transition temperature (T_g) of the polymers play a critical role in determining the kinetics of this process. That is, below T_g , there is generally very little free volume. Even at temperatures just slightly above the glass transition, the probability that a local fluctuation in density will produce a hole with enough size to allow the jumping in of a solvent molecule is low. Thus, according to this model, to reduce permeation of water molecules, the polymer that is chosen as the binder should have a high T_g . It should be noted that this is the case for a “perfect” polymer; but degradation of the polymer due to other environmental parameters like UV can result in defects such as cracks and this would accelerate the penetration of water molecules, as these defects act as “free paths” for the diffusion of the water molecules. Further, higher T_g means that the resilience of the coatings would be less. This could impact many properties. An excellent example is the adhesion of ice to the coatings. Irrespective of the material chemistry and the surface nature of coatings, recently, Golovin et al. [65] have shown that it is possible to design coatings with

low ice adhesion values provided that the polymer chains within the coating were sufficiently mobile.

Fig. 12. Schematic of polymer volume as a function of temperature. Reproduced from [64] with permission from the International Union of Pure and Applied Chemistry, Copyright (1979).

As mentioned before, based on weight changes in the coating, it has been reported that APP/PER and/or melamine could crystallize and migrate from the coating to the water during the water immersion testing process [51, 52]. Wang and Yang [51] have carried out Fourier Transform Infrared Spectroscopic (FTIR) analysis to support this argument. In Fig. 13, the presence of characteristic 3312 cm^{-1} and 3160 cm^{-1} peaks corresponding to O–H bond stretch in PER and N–H bond in APP, respectively, was evident. In the crystals, apart from the 3312 cm^{-1} and 3160 cm^{-1} peaks, the 2790 cm^{-1} peak was attributed to saturated C–H stretching, the 1254 cm^{-1} peak to the APP's P=O bond, the 1076 cm^{-1} peak to the C–O stretching, and finally, the 896 cm^{-1} peak to P–O–P bond. Based on the presence of these bands, the authors have concluded that the crystals are mixtures of APP and PER. Generally, due to the intermolecular hydrogen bonding between the APP molecules in the APP clusters in the coating (Fig. 14), there is a greater probability for water molecules to solvate and form hydrogen bonds causing the breakage of the intermolecular hydrogen bonding between APP

chains and hence their separation. The separated APP chains thus have more mobility and can penetrate through the hole free volume of the binder more easily. The concentration difference between the water bath and coating drives the migration of APP chains out of the coating into the water bath. Once the saturation point of APP in the water bath is reached, crystallization/precipitation could occur explaining the formation of APP-based white crystals [51, 52]. However, it is not known how APP and PER can precipitate together as a crystal.

Fig. 13. FTIR spectra comparison of crystals, APP and PER. Reproduced from [51] with permission from Elsevier, Copyright (2014).

Fig. 14. Schematic showing the intermolecular hydrogen bonding between APP chains.

In another similar study [66], APP-PER-melamine based acrylic coatings were subjected to accelerated aging tests (each cycle constituted 8 h at 40 ± 3 °C and 98 ± 2 % RH, and 16 h at 23 ± 3 °C and 75 ± 2 % RH) instead of water immersion tests. As shown in Fig. 15, FTIR spectra from the surface of the coatings was consistent with the expected changes in APP and PER with aging. The intensities of the peaks corresponding to the various chemical bonds in APP and PER have decreased with increasing number of aging cycles. However, the peaks at 1428 cm^{-1} (CH_2 group in acrylic acid and/or PER as well as the absorption of triazine rings in melamine) and 1668 cm^{-1} ($\text{C}=\text{O}$ bonds in acrylic acid resin) have changed in shape and intensity with increasing number of cycles of aging. As compared to the coating before aging, 1428 cm^{-1} peak that has undergone 11 cycles of aging is smaller and wider. The authors have attributed this to polymer degradation causing oxidation of some CH_2 groups into $\text{C}=\text{O}$. This was supported by the increase in 1668 cm^{-1} peak height. After subsequent aging cycles, the 1428 cm^{-1} peak intensity has increased again; since 1428 cm^{-1} peak not only corresponds to the absorption peak of CH_2 but the absorption peak of triazine rings in melamine as well, it was concluded that melamine could also be migrating to the surface.

Fig. 15. FTIR comparison of APP-PER-melamine based acrylic coatings' surface after accelerating aging cycles. Reproduced from [66] with permission from Elsevier, Copyright (2013).

However, simply based on the FTIR data, it is difficult to understand the exact changes in chemical composition and/or elaborate on the reactions involved. It is even difficult to estimate whether the crystals are forming only on the surface or in the core of the coatings as well. In the case of thermosets like epoxies which have been adopted as the binder in various studies [51, 52], since the T_g is usually significantly above the room temperature, there is very little hole free volume. This makes it extremely difficult for the permeation of water molecules and migration or leaching of APP, melamine, etc. As a consequence, it can be thought that only the surface APP, PER, and melamine are influenced by weathering until the diffusion pathways are created.

Further, hydrolysis of the phosphate bonds on the main chain of APP is another possible interaction of APP with water. This results in the conversion of APP into polyphosphoric acid, which subsequently can be hydrolyzed to smaller phosphates, finally yielding orthophosphates. With salt water, this is expected to be more severe. That is, sodium and chloride ions could easily migrate rapidly into the matrix. Na^+ replaces the ammonium

cations in APP and forms sodium polyphosphate. This also explains the absence or reduced swelling of the char in these coatings after exposure to salt water conditions for a period of time. It is also possible that some of the NH_4^+ ions form ion pairs with Cl^- , and the NH_4^+Cl^- will migrate into the water. This in fact is confirmed by Jiminez et al. [53]. They have carried out the solid state ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy and electron probe micro-analysis (EPMA) of epoxy based APP-PER-melamine intumescent coatings before and after immersion for one month in distilled water and salt water. As shown in Fig. 16, before immersion, the coatings have produced two peaks at -21 and -23 ppm, pointing to a crystalline structure with Q2 phosphorous units contained in polyphosphate chains. Even after immersion in water for one month, the coating has shown the original -21 and -23 ppm peaks along with new peaks between -25 and -27 ppm. These additional peaks were attributed to less crystallized Q2 units of polyphosphoric acid (H^+ substituting NH^+). However, the presence of a new peak at 3 ppm after immersion in salt water for a month confirmed the formation of sodium orthophosphates. Also, instead of the two peaks characteristic of the crystalline APP phase at -21 and -23 ppm, a large massif of low-resolution peaks was seen between -15 and -30 ppm attributed to less crystallized sodium polyphosphates. The EPMA mappings of P, Na, and Cl across the cross-section of the coating immersed in salt water for a month is shown in Fig. 17. A low amount of phosphorus representing APP is present in the whole zone where sodium appears, in addition to a high number of chloride ions on the sample surface. Considering the solubility of APP in water as ~0.5 wt.% compared to sodium polyphosphate's 14 wt.%, the authors have concluded that the latter detaches easily from the matrix. This allows for the creation of more pathways for diffusion and solvation.

Fig. 16. ^{31}P -NMR plots for epoxy based APP-PER-melamine coatings before and after immersion in water as well as saltwater for one month. Reproduced from [53] with permission from American Chemical Society, Copyright (2013).

Fig. 17. EPMA cross-sectional images of epoxy based APP-PER-melamine coatings after immersion in salt water for one month for (a) P, (b) Na, and (c) Cl. Reproduced from [53] with permission from American Chemical Society, Copyright (2013).

5. Kinetics of leaching process

As discussed in previous sections, when coatings are exposed to the environment (or immersed in water), the water molecules will start to penetrate into the coating along with possible leaching of the susceptible coating ingredients. The kinetics of this process are dependent on the chemical composition of the coatings and the concentration gradient. If the leaching process continues, the empty voids could form interconnected pores, which will allow for mass transport across the coating resulting in corrosion of the metallic substrate. However, as will be shown below, in most of the literature on this topic, sorption kinetics are only evaluated based on weight change of the coatings with time during the immersion process or accelerated aging [37, 67, 68]. This suggests that only macroscopic behavior is taken into account, and the complete molecular level phenomena and the chemical reactions occurring during the exposure are not captured. This may also result in misleading conclusions. Moreover, in most of the studies, the substrate interactions with the coatings during the immersion/exposure process are not considered.

Wang et al. [37] have noted that with acrylic based APP-PER-melamine coatings, the first 150 h of immersion in distilled water at room temperature was dominated by the permeation process. During this stage, water molecules have penetrated through the coating and resulted in an increase in weight of the coating (Fig. 18). The next 150 h was dominated by solvation and migration processes. In here, as the hydrophilic flame retardants leached out of the coatings, a sharp drop in weight was observed. Finally, the authors have claimed that a physical and chemical equilibrium has been reached between the two processes when the weight change was almost constant with immersion time. A similar trend has been noted in [68] where epoxy based APP-PER-melamine intumescent coated samples were immersed in

water with 5% sodium hydroxide. Dong et al. [67], however, have reported that the dominant process in epoxy based APP-PER-melamine coatings was the migration of the flame retardants, other than a very brief induction period initially during which permeation dominated (Fig. 19). However, accelerated aging conditions are used in this study where the dry periods allowed for evaporation of water affecting the mass change contribution due to the penetrating water molecules.

Fig. 18. Weight change of acrylic intumescent coating with immersion time in distilled water at 25 °C. Coating contains 25 wt.% acrylic, 17 wt.% PER, 26 wt.% APP, 11wt.% melamine & 21 wt.% of other additives including TiO₂, glass fiber, alumina etc. Adapted from [37].

Fig. 19. Weight change in epoxy based intumescent coating (37.9 wt% epoxy with curing agent, 27.1 wt.% of APP, 16.4 wt.% of melamine, 12.6 wt.% of PER and 6 wt.% of TiO₂) with accelerated aging time (aging conditions: temperature – (38 +/- 3 °C), wetting time 18

min every 2 h, relative humidity during dry period (40-60%), and time-averaged intensity of irradiation and wavelength were 60 W/m² and 300-400 nm respectively. Adapted from [67].

From the above studies, it is clear that weight change analysis is not comprehensive enough as the absolute content and kinetics of what has leached out are missing. Hence, it is debatable to claim that a physical and chemical equilibrium (or more precisely pseudo-equilibrium) is reached as many parameters are still unknown. It is also important to consider the depth of penetration of water molecules, driving force for solvation in different systems particularly epoxies, reasons for the lack of swelling of coatings (or even there is lack of information on lowering of T_g of matrix by plasticization), and even roles of polarity and crystallinity/cross-linking density of polymer matrix.

Generally, sorption, where the solute dissolves and diffuses into the coating resulting in a weight-gain, is expressed as [69]:

$$\frac{M_t}{M_\infty} = k_n t^n \text{ --- (1)}$$

where M_t and M_∞ represent the mass uptakes at time t and infinite time, respectively; k is a constant, and n defines the type of diffusion and so, may assume different values. Depending on the n value, the type of diffusion is termed as supercase II, case II sorption, anomalous, Fickian case and pseudo-Fickian for $n > 1$, $n = 1$, $\frac{1}{2} < n < 1$, $n = \frac{1}{2}$ and $n < \frac{1}{2}$, respectively.

Fickian is generally observed if the coating is at a temperature significantly higher than its T_g . The assumption behind Fickian diffusion is that the diffusing molecules are able to diffuse freely without any structural rearrangement of the polymeric chains. Since $T \gg T_g$, the rate of relaxation is much faster than the rate of diffusion and hence the structural rearrangement component can be considered negligible if the diffusing species is small [70, 71]. The corresponding schematic plot is shown in Fig. 20a [70]. For the opposite case when

polymer's relaxation rate is much slower than the rate of diffusion of the molecules, the kinetics are described by case II sorption as shown in Fig. 20b. [70]. This is the case when $T \ll T_g$, and so the diffusion of solute as it enters the polymer is very slow. It has to plasticize the polymer matrix, and thus reduce its T_g , and subsequently increase the diffusion coefficient of that portion of the polymer. This has also been described as a moving front [69].

Fig. 20. Schematic of the mass profiles versus time for (a) Fickian Diffusion, and (b) case II sorption curve. Adapted from [70].

There are many investigations on the above concepts, particularly in the field of food packaging. For example, in a study conducted by Harogoppad et al. [72], sorption and permeation results of the probe molecules were reported through neoprene, styrene-butadiene-rubber (SBR), ethylene-propylene-diene terpolymer (EPDM), and natural rubber (NR) membranes. The probe molecules included 2,2,4-trimethylpentane (TMP), dodecane, tetradecane, and hexadecane (that is, carbon atoms ranging from C_8 to C_{16}). As expected, the overall sorption rates have decreased with increasing molecular weight of the penetrant (see Figs. 21a & 21b for EPDM system as a representative example). Besides, factors like chain segmental mobility and interactions control the sorption magnitude and penetrant molecular mobility within the polymer. However, in most of the cases, the values of n were between 0.50 and 0.60, suggesting a deviation from the Fickian mode to anomalous. Despite this, no significant swelling or even surface corrugation was observed. Hence, Fickian diffusion

model (Eq. 2) was used to calculate the effective diffusivity, D , of the polymer-solvent systems (as an example, EPDM is chosen again, see Fig. 21c). The authors have also shown that for non-interacting penetrant molecules in a polymer, a classical Fickian behavior with a nearly constant diffusion coefficient was observed. An increase in interactions would result in more sorption of the penetrant such that the diffusion process often becomes concentration dependent.

$$D = \pi \left(\frac{h\theta}{4M_{\infty}} \right)^2 \quad (2)$$

where h is the initial thickness of samples, θ is the slope of the linear portion of the plot of M_t vs $t^{1/2}$ before attainment of 50% equilibrium.

Fig. 21. (a) & (b) Sorption of penetrant molecules in EPDM at different temperatures where (o) represents 25 °C, (□) represents 44 °C and (Δ) represents 60 °C; and (c) diffusion coefficients of different penetrant molecules in EPDM as a function of concentration and at a constant temperature of 25 °C. Reproduced from [72] with permission from American Chemical Society, Copyright (1991).

Similar mass transfer experiments have also been conducted to understand the leaching kinetics of certain additives from polyethylene terephthalate (PET) package/bottle into food. These additives included PET cyclic trimer [73], UV-blocking additive Tinuvin 234 [74], and

antimony* [75]. Similar to what has been discussed so far, factors such as storage time and temperature, the concentration of the penetrant/migrant in the polymer, type and nature of the penetrant/migrant, and its solubility in food are some of the major factors affecting the migration. For example, in [75], antimony migration kinetics from PET bottle were investigated by totally immersing PET in 4% acetic acid at various temperatures. Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) was employed to determine the kinetics of migration of antimony (Fig. 22). GFAAS is based on the principle that when a sample is vaporized in a furnace coated with graphite, the free atoms absorb light at wavelengths that are characteristic of the element and based on the amount of absorption, the quantity of that element is determined. As evident, a simple Fickian behavior was observed in all cases.

Fig. 22. Migration kinetics of antimony from PET bottle into acetic acid. Adapted from [75].

* Sb_2O_3 or its reaction product with ethylene glycol is widely used as a polycondensation catalyst in the manufacturing of PET.

In an effort to understand the importance of a mean number of monomeric units of APP on the kinetics of leaching, in [50], epoxy based APP-PER-melamine coatings containing APP with different degrees of polymerization ($DP = 5, 30, 78, 125$ and 184) were subjected to accelerated weathering conditions. After weathering tests, X-ray Photoelectron Spectroscopy (XPS) analysis of the coatings has revealed the importance of DP. Fig. 23 shows that the higher the DP, the smaller the losses. Also, the rate of migration of APP for all DPs has decreased significantly with time pointing to the depleting concentration gradient near the surface. The depleting concentration gradient is typical of the diffusion process, thus suggesting that the kinetics of the whole leaching process from this stage onwards (in here, it can be approximated to 14 days) are dominated by the diffusion/migration of hydrophilic flame retardants rather than the penetration of water molecules into the coating. If the migration of hydrophilic additives is what determines the kinetics of the leaching process, then it can be presumed that the kinetic models that describe the diffusion of molecules out of polymeric films should resemble the kinetics of the leaching process.

Fig. 23. APP mass fraction in epoxy based APP-PER-melamine coatings with different degrees of polymerization of APP subjected to accelerated aging conditions. Reproduced from [50] with permission from Elsevier, Copyright (2014).

6. Effects of leaching on physical properties of the coating

It is important to understand that a simple correlation of physical characteristics with mechanical properties like hardness and strength is not enough. Accompanying chemical and physical changes in the system should also be considered. These include reagglomeration of nanoparticles, if present, due to degradation of the polymer, cross-linking density and flexibility changes of the coating, changes in roughness and surface characteristics, and magnitude of visco-elastic properties of the polymer. Depending on the nature of leached products, they could have a lubricating effect on the surface or increase the friction causing an acceleration of the wearing of the coating. We have recently reviewed the effects of weathering on scratch/wear properties of polymer-based coatings. Interested readers can refer to [76] for more information on this aspect. Another negative effect that the leached components can have is on the aesthetics of the coatings.

Permeation of water molecules into coatings can result in the build-up of high osmotic pressures that may cause blistering or delamination of the film [77]. An example of this is shown in Fig. 24 for a polyurethane coating after exposure to accelerated weathering conditions [78]. In another study on polyurethane coatings, XPS and FTIR analysis of the exposed coating surfaces have indicated an increase in the hydrophilicity on the surface due to the build-up of urea and urethane groups [79]. This, in fact, will facilitate the diffusion of water into the coating and accelerates the blistering process. Leaching of additives or secondary reaction products will also leave behind voids that act as traps for water molecules. This phenomenon has been observed in a study done by Wang et al. [52] after immersion of an epoxy based APP-PER-melamine coating in water for 200 h.

Fig. 24. Atomic force microscope image showing the blisters morphology on a polyurethane coating after accelerated weathering testing. In the weathering chamber, the samples were exposed to UV radiation at 60 °C for 4 h followed by 4 h of water condensation at 50 °C. Reproduced from [78] with permission from Elsevier, Copyright (2002).

It is also well known that locally on the steel substrate, cathodic and anodic sites arise due to variation in the amount of oxygen and water arriving/present at different regions on the substrate beneath the coating [80]. The regions that are rich in oxygen and water act as local cathodic regions, while the remaining regions act as anodic regions. In the anodic regions,

iron is oxidized into Fe^{2+} and subsequently, hydrolysis and oxidation of the Fe^{2+} occur giving rise to metal hydroxides and oxides (Eq. 3-5) [81]:

At the cathodic regions, the following oxygen reduction reaction occurs:

As the rate of oxygen reduction is significant [82], intermediate radicals are formed destructing the bonds at the steel surface-coating interface as well as degrading the polymeric coating in the vicinity [83]. The formation of intermediate radicals is given below (Eq. 7-12) [84]. Their reactions with the polymer are similar to those described earlier (Fig. 3).

If the coating is uniform, blisters form only when the penetrating water molecules or other ions reach the interface between the steel substrate and the coating [85, 86]. This results in local (cathodic) delamination, as osmotic pressure overcomes the bonding between the substrate and coating. In the surrounding regions, the adhesion bond between substrate and coating still dominates resulting in the blistering phenomenon. Upon blister initiation at the cathodic regions, corrosion products from the local anodic regions (Fe^{2+} and Fe^{3+}) diffuse through the electrolytic channel to these H_2O -rich regions and undergo hydrolysis and oxidation reactions forming rust on the underside of the coating. A schematic of this process

is shown in Fig. 25. Subsequently, the initial cathodic region becomes deprived of oxygen and H_2O due to the barrier action of the rust layer making it anodically polarized. Hence, the regions beside it become locally cathodic in nature and cathodic delamination proceeds in these regions causing the lateral growth of the blisters. This causes a reduction in adhesion of the coating to the steel substrate and finally, (chemical) detachment of the coatings [87].

Fig. 25. Anodic polarization of initially cathodic blister regions leading to blister growth laterally. Reproduced from [87] with permission from Elsevier, Copyright (1981).

Furthermore, when the bonding strength between the substrate and the coating decreases, the resistance to stresses developed due to the difference in coefficient of thermal expansion during freeze-thaw cycles also drops. For example, the bonding strength of an acrylic based APP-PER-melamine coating on a steel substrate before and after immersion in water for 500 h has dropped from 0.32 MPa to 0.21 MPa, respectively [37]. Similarly, the resistance to the number of freeze-thaw cycles has decreased from 17 to 11. The same mechanism is expected when the coating is exposed to salt water conditions. For example, in [55], after subjecting

acrylic based APP-PER-melamine intumescent coating to 500 h of salt spray test (continuous cycles of 3.5% NaCl for 15 min per 45 min at 40 +/- 2 °C and pH of 7.2), the interfacial adhesive strength has decreased from 0.29 to 0.19 MPa, and the resistance to freeze-thaw cycles has dropped from 16 to 10.

7. Summary and Outlook

Intumescent coatings have been widely used for fire protection on steel structures due to their good performance and ease of applicability. However, their weathering resistance has become a major issue as the fire performance of these coatings dropped significantly after accelerated or natural weathering tests. Various aspects of this problem were considered and reviewed in this article. These included leaching of intumescent additives (mechanisms and diffusion kinetics), the formation of secondary products in the coating during weathering exposure, osmotic effects, and physical changes in coatings. A major consequence of leaching was the effect on the optimal ratio between the intumescent additives (for instance, APP-PER-melamine), which subsequently impacted the intumescent reaction (extent of swelling), and therefore, fire performance. Besides fire performance, mechanical and optical properties of the coatings were affected by weathering as well. Further, the changes in the resilience of the coatings and in combination with osmosis have affected the interfacial adhesion between the substrate steel and coatings.

To reduce the leaching of hydrophilic flame retardants, many efforts have been diverted towards adding fillers that increased the diffusion path of the penetrating water molecules or the migrating fire-retardant components. In this context, as explained earlier, particles like glass flakes, EG, synthetic and natural clay platelets, silica/titania nanoparticles, etc. were considered [37, 38, 51, 52, 55, 88, 89]. These studies have shown that the presence of these

particles increased the coatings' resistance to weathering (either under accelerated or natural conditions) and attributed this to the minimal changes in chemical composition of the coatings even after weathering. In other words, the increase in diffusion path length due to the presence of these particles increases the resistance to leaching of intumescent additives and the penetration of water into the coatings. However, it is difficult to appreciate this conclusion without the actual permeability data for these systems after the addition of fillers or the changes in the cross-linking density and resilience of the coatings. Other approaches that have been adopted to improve resistance to water diffusion included enhancing the cross-linking density of the matrix [68], surface modification of APP and substituting PER with macromolecular charring agents [90, 91, 92]. For the surface modification of APP, typically silane-based agents were used along with melamine formaldehyde resin [93, 94, 95]. Again, many properties of the coatings will be affected by these approaches, which should be considered as well. Practicality and economic feasibility are other aspects that act against these approaches. Usage of a sacrificial layer (generally, a hydrophobic/weathering resistant topcoat) was another simple approach that has been employed [22, 54]. For instance, Wang [54] has utilized a polyurethane topcoat on the traditional polyurethane based APP-PER-melamine coating. After exposure to natural weathering conditions for 12 months, the fire resistance time (as per ISO 834) dropped by only ~22% as compared to ~63% without any topcoat. In here, fire resistance time was defined as the time taken for the backside of 1.2 mm thick steel plate to reach 538 °C. Similar results were observed by Jiminez et al. [34] wherein a topcoat was added to improve durability to environmental conditions.

To sum-up, in addition to the complexity of the factors associated with weathering like diffusion kinetics of moisture/water, leaching of additives, and UV degradation of the matrix, the relative qualitative nature of many studies reported even on the mechanisms of (poor) fire

performance of weathering exposed coatings has made it difficult to correlate and extract the specific parameters that are critical for improvement. Even in most of the studies that deal with weathering and fire performance, coating interaction with the substrate is not considered. The effect of temperature, UV and moisture cycling on mechanical stresses in the coating is not clear as well. Therefore, further research is required to answer these unknowns and overcome the obstacles with the wide usage of intumescent coatings for external structures.

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