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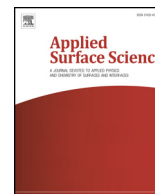
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Full Length Article

Chemisorption of polyester coatings on zirconium-based conversion coated multi-metal substrates and their stability in aqueous environment

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ABSTRACT

In this work, in-situ ATR-FTIR in the Kretschmann configuration is proposed as an interfacial sensitive technique able to probe molecular processes at the buried interface of an industrial relevant polyester primer. Zinc, aluminium and magnesium oxide were used to represent oxides present at galvanized steel sheets used in coil coating. Two competing interactions with polyester resin and melamine-based crosslinker were shown to take place at metal hydroxide sites. This highlights the increased complexity of interfacial phenomena at metal-paint interfaces. Furthermore, in-situ ATR-FTIR was performed in deuterated water (D₂O) to study the evolution of interfacial carboxylate bond degradation, without overlap of dominant water signals. For the first time, interfacial bond formation of paints and its degradation in an aqueous environment is studied in-situ. It is shown that the introduction of D₂O at the interface initially increases the amount of interfacial carboxylate bonds, whereas upon longer exposure times bond degradation occurs. Significant delay of interfacial bond degradation on hexafluorozirconic acid treated oxides indicate successful stabilization of the metal-polymer interface by zirconium-based conversion coatings. Consequently, in-situ ATR-FTIR is able to demonstrate improved interfacial stability due to zirconium-based treatment in real-time and on a molecular level.

1. Introduction

Increasing corrosion performance requirements lead to the development of new alloys, such as zinc-aluminium-magnesium coatings for galvanized steel sheets used in coil coating [1–4]. Also in the automotive industry the use of lightweight metals is of increasing interest since emission regulations put increased pressure on fuel efficiency. These developments resulting in heterogeneous and multi-metal substrates poses a number of new challenges. Although different oxides exist at the surface of such multi-metal substrates, all are lead through the very same chemical surface treatment process, prior to paint application, during common industrial manufacturing operations. Traditional surface treatments, such as hexavalent chrome passivation and phosphating were typically robust in their processing window providing sufficient and efficient corrosion protection and favourable interfacial bonding properties towards coating overlayers for the wide variety of heterogeneous substrates and components processed.

However, due to recent international and strict health and safety regulations and the need for increased process energy efficiency, these traditional processes are currently being replaced by a new generation of more ecologically justified surface treatments. One type of a recognized suitable alternative is the use of zirconium- and titanium-based fluoacid treatments [5]. The free fluorides present in the conversion solution activate the metal surface by thinning and removing natural metal (hydr)oxides [6,7]. The anodic dissolution of metal substrate is accompanied with hydrogen evolution and oxygen reduction, which cause alkalization of the metal and solution interface favoring the deposition of the zirconium-based conversion coating [8–11]. Therefore, the formation of a zirconium-based conversion layer can be considered as a pH-based process. In addition, also the electrochemical activity of the metal surface acts as a driving force for the zirconium oxide deposition, since this consistently starts in the vicinity of cathodic particles [7,9,12–14]. As a result, the formation mechanism for zirconium-based conversion coatings is similar for different substrates [12].

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However, its kinetics, thickness and elemental distribution (lateral and in-depth) strongly depends on metal (alloy) surface chemistry and morphology [15–17]. This strong correlation between with initial and converted surface chemistry is challenging for gaining fundamental insights in the effect of zirconium-based conversion on the bonding properties of multi-metal substrates (such as zinc-aluminium-magnesium alloys used for galvanizing). Therefore, increased organic coating adhesion by zirconium-based treatments has majorly been demonstrated by macroscopic adhesion and delamination testing [18–20]. Whereas more fundamental interfacial studies of zirconium-based converted metal substrates are rather limited due to the complex surface chemistry, consisting of metal- and zirconium oxides, hydroxides and fluorides, as well as possible inorganic and organic compounds, such as phosphates and acrylates depending on the conversion conditions [5]. Another explanation for the scarcity of fundamental studies on the bonding properties of zirconium-based converted substrates relates to the well-known difficulties of studying buried metal-polymer interfaces. The high absorptive properties of realistic polymer coatings with typical applied thicknesses in the μm -range hinders the use of surface sensitive tools such as XPS and IRRAS. Because of this, chemical interactions at metal-polymer interfaces are mostly studied using model polymer or monomer systems with applied thicknesses in the nm-range. Taheri et al. [15] illustrated enhanced chemisorption of succinic acid on zirconium-treated zinc, which was attributed to an increased surface hydroxide concentration. Also Fockaert et al. [17] observed increased hydroxide concentrations after zirconium-based treatment of zinc, aluminium and magnesium oxide resulting in higher portions of Bronsted interactions with amide-functionalized molecules [17]. The use of simplified organic compounds has thus shown to be useful for revealing chemisorption mechanisms [21]. However, hitherto, these insights have not been validated on industrially relevant paints, which typically consist of crosslinkers, curing agents, matting agents, fillers, binders, corrosion-inhibiting pigments, etc. This complex chemistry and constitution of a multicomponent coating is one reason why molecular studies on metal-paint interfaces are limited. Obviously, the effect of adhesion promoters on interfacial properties cannot be neglected. In particular silanes play an important role in the chemical interaction of paints with metal oxides [22]. Another component that affect the interfacial strength are crosslinkers and more specifically, the degree of crosslinking. Too much crosslinking can make the polymer system too rigid hindering dissipation. On the other hand, less crosslinked polymers are more elastic, so when performing the pull-off test they may deform before the interface breaks [23]. Moreover, in case of a not fully crosslinked polymer system a higher amount of functional groups will be available to interact with the metal substrate [24]. Next to the amount of crosslinkers, also curing is assumed to have an impact on the interfacial properties. Chemical interactions at the metal-polymer interface are expected to take place already before curing [25]. However, curing can change the interface significantly. For instance, it has been reported that curing can relieve polymeric constraints leading to a lower steric hindrance and a stronger metal-polymer bonding [26]. Conformational variations as well as improved hydrolysis and metal-bond formation due to curing at elevated temperatures have also been reported for silane primer films on aluminium [22]. It becomes increasingly clear that adhesion properties are not only a result of resin chemistry. In addition, also disbondment phenomena of painted metal substrates result from an interplay of multiple compounds present in the complex paint formulation [21,27,28]. Öhman et al. [29] integrated attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR) with an electrochemical cell (EC), allowing simultaneous electrochemical and molecular characterization of the metal-polymer hybrid system during exposure to electrolyte. Using the integrated ATR-FTIR – EC-setup, it was demonstrated that the character of water in epoxy films differ from the water within the siloxane network [30]. Moreover, in-situ ATR-FTIR studies lead to insights in water transport and polymer swelling phenomena, as well as corrosion processes at the

buried interfaces [27,29–32]. Later, Taheri et al. adopted the in-situ ATR-FTIR approach to study buried metal-polymer interfaces, demonstrating increased polymer stability due to curing, which not only increased barrier properties but also the interfacial stability of carboxylic polymer – zinc oxide interface [28]. The growth of water bands in the ATR-FTIR spectra were correlated to the polymer stability against water. A correlation between water uptake of the coating and initial surface hydroxide density and thus interfacial bonding density was demonstrated [28]. The importance of surface hydroxides for interfacial bond formation with carboxylic polymers was also evidenced by Ple-tincx et al. [33], who showed initial increase of carboxylate bonds between PMMA and aluminium oxide when water was introduced at the interface. However, in-situ real-time monitoring of interfacial carboxylate bond degradation by means of ATR-FTIR is experimentally hindered by the strong OH-bending modes of water which occur at similar IR-frequencies as the carboxylate bonds of interest. Moreover, the role of zirconium-based conversion treatments on interfacial bond formation and degradation with industrially relevant paints has not yet been described. The main reason for this is the high complexity of commercial conversion systems containing inorganic and organic additives which increases the surface chemistry complexity on one hand and the multicomponent paint formulations resulting in information IR-spectra on the other hand. The high share of variables at realistic metal-polymer hybrid systems hindered straightforward interpretation of bonding properties at these hybrid interfaces.

Due to the well-known difficulties of studying buried metal-polymer interfaces, most interface studies are based on simplification of polymer formulation. Nevertheless, from industrial perspective, there is still a need to obtain reliable molecular information of true metal-paint interfaces. This work attempts to validate the chemisorption mechanisms previously described for ester-functionalized compounds [26,27] to industrially relevant multicomponent polyester primer formulations using ATR-FTIR in Kretschmann configuration. For ATR-FTIR studies IR-transparent metal substrates are evaporated on internal reflection elements (IRE) on which subsequently a realistic polyester primer is applied (with a thickness within μm -scale). The incident IR-light passes the IRE generating an evanescent wave which penetrates through the thin metal film (20–50 nm). As a consequence, the attenuated reflected IR beam contains molecular information from the metal-polyester interface. A comparative study between native and zirconium-treated zinc, aluminium and magnesium substrates is conducted. These metal substrates have been chosen because of their presence at zinc alloyed surfaces used in galvanized steel. To gain fundamental insights on the bonding properties associated by the zirconium conversion oxide layer, there has been opted to use a model conversion solution containing H_2ZrF_6 , without organic or inorganic additives. This allows to use study solely the effect of zirconium oxide to the bonding properties and interfacial stability of metal-polymer hybrid systems in aqueous environment. Moreover, the stability of the interfacial bonds in the presence of water will be studied in-situ. However, water is known to give a broad OH-bending band at 1640 cm^{-1} , which is the wavenumber region of interest to monitor carboxylate stretching stretching vibrations [34]. Therefore, the metal-polymer hybrid system was exposed to D_2O , which O-D bend vibration is shifted towards lower wavenumber, i.e. 1200 cm^{-1} , compared to O-H bend vibration [35]. By using model metal substrates and conversion coatings a straightforward mechanistic approach is proposed to study chemisorption mechanisms and interfacial stability at metal-polymer hybrid systems using industrially relevant multicomponent polyester primers. In addition the use of D_2O allowed for the first time in situ studies of interfacial bond formation and degradation at zirconium-treated metal-paint interfaces. This way the contribution of zirconium-based conversion coatings to interfacial phenomena such as bonding properties and interfacial stability can be studied in-situ during exposure to aqueous environments.

Table 1
Polyester primer formulation.

Compound	Quantity (wt. %)	Function	Chemistry + properties
Dynapol LH 820-16 /55%	61.1	Polyester resin	Saturated, medium molecular (MM 5000 g/mol), linear hydroxylated co-polyester resin. $T_G = 60$ °C, (acid value of 2 mg KOH/g and an OH-value of 20 mg KOH /g)
Aerosil 200	0.4	Thickening agent	SiO ₂ , Hydrophilic fumed silica, surface area 200 m ² /g
Kronos 2360	11.1	Pigment white	Rutile TiO ₂
Cymel 303	4.8	Crosslinker	Highly methylated-monomeric melamine-based crosslinker (methoxy methyl functional sites)
Dynapol Catalyst 1203	1.8	Catalyst for crosslinker	Non-ionic blocked sulfonic acid catalyst for aminoplast crosslinking
Deuteron MK	1.1	Matting agent	Methyldiaminomethylether
Resiflow FL2	0.4	Flow control agent	polyacrylate
Solvent Naphta 200	9.6	Solvent	Aromatic solvent
Butyl diglycol	4.0	Solvent	HO-(CH ₂) ₂ -O-(CH ₂) ₂ -(CH ₂) ₃ CH ₃
Butyl glycol	5.8	Solvent	CH ₃ -(CH ₂) ₃ -O-CH ₂ -OH

2. Experimental

Materials and chemicals. 50 nm zinc (Goodfellow, 99.95%), aluminium (Johnson Matthey, 99.99%) and magnesium (Alfa Aesar, 99.9%) were deposited on germanium internal reflection elements (IRE) by means of a high-vacuum evaporation system (VCM 600 Standard Vacuum Thermal Evaporator, Norm Electronics). Zirconium-based conversion was conducted using hexafluorozirconic acid (Sigma-Aldrich Chemistry) diluted to 0.01 M and brought to pH 4 with 0.1 M NaOH. Aluminium and zinc coated IREs were dipped in conversion solution at room temperature for 60 s, whereas the exposure time of magnesium coated IRE to the conversion solution was limited to 10 s, due to the high reactivity of the thermally vaporized magnesium film. Subsequently, the samples were generously rinsed with demineralized water and dried with pressurized air. A polymer coating with polyester-based resin, Dynapol LH 820 (Evonik Industries AG) was applied using a 30 μ m bar coater. The resulting polymer film was cured for 15 min at 130 °C, which is the maximum operating temperature for germanium IRE. The polyester primer formulation can be found in Table 1.

ATR-FTIR in Kretschmann configuration: The FTIR apparatus was a Thermo-Nicolet Nexus equipped with a liquid-nitrogen cooled mercury-cadmium-telluride (MCT) detector and a nitrogen-purged measurement chamber with a Veemax III single reflection ATR accessory. Germanium IRE (PIKE Technologies) with a fixed face angle of 60° were used. IR-light was configured with an incident set angle of 80°. A precision manual polarizer (PIKE) was mounted on the Veemax III and set to 90° for p-polarized and 0° for s-polarized IR-light. For the chemisorption studies infrared backgrounds were obtained from the metallic coated IRE, after zirconium-based treatment when applicable. The established interfacial chemistry was followed in-situ during exposure to D₂O (99.9%, Sigma-Aldrich Chemistry). For these in-situ stability studies, infrared backgrounds were obtained after applying the polymer coating on the respective metal oxides. Consequently, as the interfacial chemistry established after curing was involved in the background, the evolution of interfacial bonds may appear positive, when being increased, or negative when being reduced relative to the initial dry (cured) situation. Infrared spectra were collected every 300 s and averaged from 128 cycles with a resolution of 4 cm⁻¹. The control of the spectra acquisition and incident angles was managed by the OMNIC 8.1 software package (ThermoElectron Corporation, Madison, WI).

3. Results

3.1. Characterization polyester primer

The ATR-FTIR spectrum of bulk polymer, presented in Fig. 1, was collected on a chemically inert germanium internal reflection element at 80° incidence IR angle. A carbonyl stretching vibration (C=O) appears at 1723 cm⁻¹, together with C-O stretching vibration bands in the region 1100–1300 cm⁻¹, with the most intense peak absorption

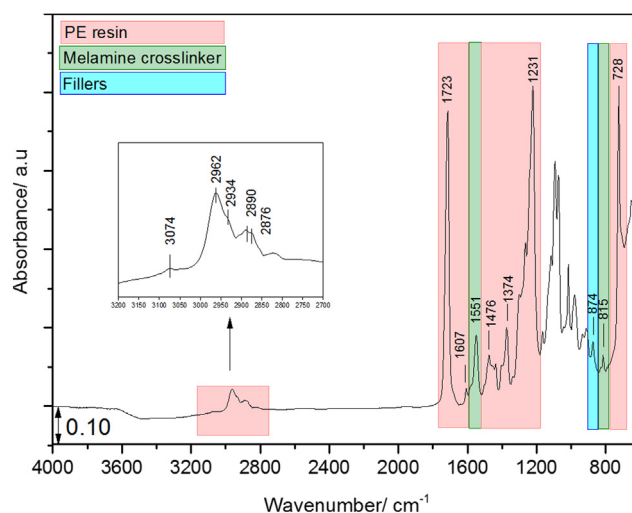


Fig. 1. ATR-FTIR spectrum of cured polyester coating applied on germanium internal reflection element, collected using non-polarized IR-light at an incident angle of 80°.

positioned at 1231 cm⁻¹ (C–O), which is characteristic for a polyester resin [34]. Peaks in the 3000–2800 cm⁻¹ region, enlarged in Fig. 1, indicate the presence of CH₂ and CH₃ bonds. Asymmetric and symmetric C-H stretching vibrations specific to CH₃ groups are observed at 2962 and 2890 cm⁻¹, respectively [34]. Shoulders at 2934 and 2876 cm⁻¹ relate to asymmetric and symmetric C–H stretching vibrations of CH₂ groups [34]. Whereas, the bands at 1476 and 1374 cm⁻¹ are assigned to C–CH₂–C and C–CH₃ bending vibrations, respectively [34]. The occurrence of vibrational bands at 1551 and 815 cm⁻¹ can be ascribed to melamine triazine ring (C–N–C) stretching and side chain (C–N) asymmetric stretching vibrations, respectively, which are specific to the melamine-based crosslinker [34]. The sharp peak observed at 728 cm⁻¹ can be assigned to C–H rocking vibrations of the methyl groups, originating from the highly methylated melamine-based crosslinker. The minor sharp peak at 1607 cm⁻¹ together with the small signal at 3074 cm⁻¹ are indicative for benzene ring vibrations, referring to aromatic structures in the polyester resin [34]. The minor peak at 874 cm⁻¹ can be assigned to CaCO₃ that acts as a filler. The assignment of peaks positioned between 1000 and 1200 cm⁻¹ is more complex, as different vibrations occur in this region. Examples of possible explanations of peaks in this region are skeletal C–H and C–O rocking vibrations related to the resin and matting agent or Si–O stretching vibration specific to the thickening agent SiO₂ [34].

3.2. Bonding mechanism

ATR-FTIR spectra of the cured polyester coats were obtained after

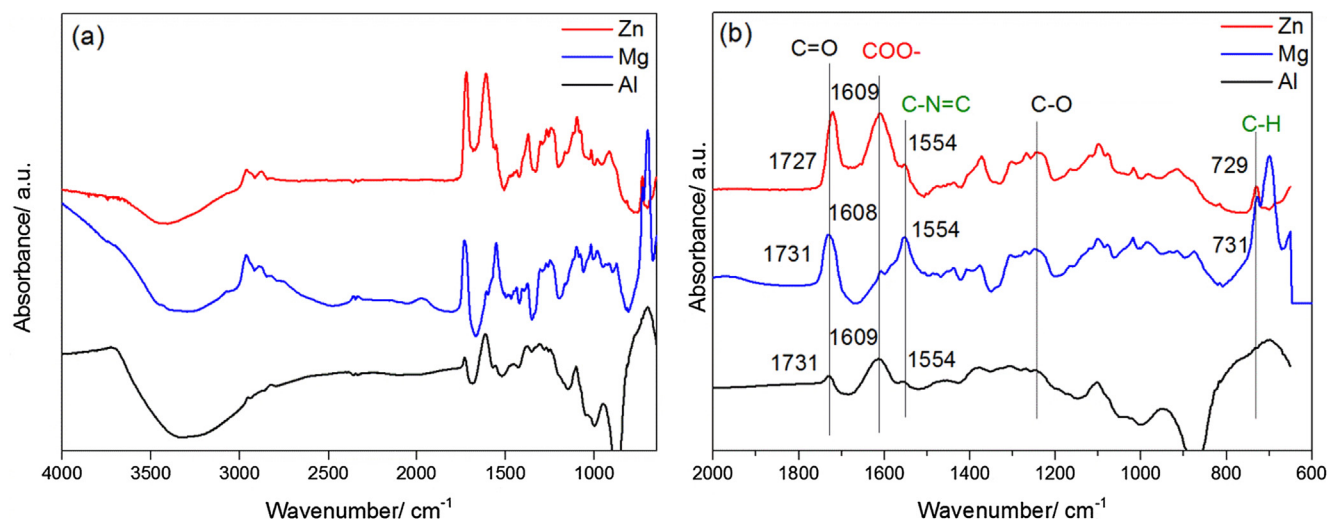


Fig. 2. ATR-FTIR spectra of cured polyester coating applied on native zinc, magnesium and aluminium oxide, collected using p-polarized IR-light with an incident angle of 80° (a) full scale, (b) head group region.

background collection of the metallic coated internal reflection elements. The combination of the high refractive index of germanium with a 80° incident IR angle gives the most interfacial sensitive results. Fig. 2(a) demonstrates a clear reduction of OH-stretch vibrations in the FTIR spectra of cured polyester coats applied on native metal oxides. Since the spectra in Fig. 2 were collected using the native oxides as background, this reduction must be related to the disappearance of OH-groups at the oxide surfaces. For aluminium and magnesium a second negative band characteristic of O–H bending vibrations is observed at ca. 1690 cm^{-1} and 1670 cm^{-1} , respectively. The observed intensity reduction of OH stretch vibrations, can be related to chemisorbed water being removed during curing at elevated temperatures (130°C) and/or the consumption of metal hydroxides in interfacial reactions with the polyester coating. After curing of the polyester primer, an intense peak around 1609 cm^{-1} arises in the ATR-FTIR spectra, presented in Fig. 2. The peak positioned at circa 1609 cm^{-1} is positioned at similar wavenumbers as the aromatic ring vibration observed in the cured polyester coat described in Fig. 1. However, aromatic ring vibrations are rather symmetric and thus their infrared vibrations appear as small sharp peaks [36], whereas the peak shapes in Fig. 2(a) and (b) are broader and more intense. Therefore, the peak is attributed to carboxylate stretching vibrations, which are known to be broad due to interactions with their chemical environment [37]. There are two possible origins for the formed carboxylate species upon interaction with native metal oxides. A first hypothesis relates to the free acid groups present in the polyester resin, as indicated by the acid value in Table 1. The polyester carbonyl peak in absence of metal substrate, presented in Fig. 1, has shown to be positioned at 1723 cm^{-1} . After interaction with metal oxides, the carbonyl peak shifts to higher wavenumbers, being, 1727 cm^{-1} on native zinc oxide, and at 1731 cm^{-1} on native magnesium and aluminium oxide. Since the carbonyl peak appears symmetric without a distinct shoulder, carbonyl bonds specific to acid and ester groups are expected to occur very close to each other. Yet, acid carbonyl stretching vibrations are known to appear at lower wavenumbers ($1700\text{--}1725\text{ cm}^{-1}$) [36] compared to ester carbonyl stretching vibrations ($1725\text{--}1750\text{ cm}^{-1}$) [36]. Therefore, the observed shift of the carbonyl peak towards higher wavenumbers upon interaction with metal oxide is interpreted as a reduced contribution of acid groups at the interface. This implies that acid groups at the interface are being deprotonated and form interfacial carboxylate bonds with the metal oxide explaining the appearance of a new peak at 1609 cm^{-1} assigned to asymmetric carboxylate stretch vibration. A second hypothesis relates to the capability of metal oxides to hydrolyse ester-functionalities

to more reactive acid groups. The formation of interfacial carboxylate bonds between ester-functionalities and metal oxide surfaces has previously been reported for model compounds [38,39]. The high intensity of the asymmetric carboxylate peak with respect to the carbonyl peak, together with the reduced C–O peak intensities, suggest the consumption of ester groups. Therefore, it is expected that zinc, aluminium and magnesium oxide are capable of hydrolysing ester groups of the polyester resin to form interfacial carboxylate bonds. Consequently, chemical interactions with native zinc, aluminium and magnesium oxide is shown to occur with both acid and ester groups present in the polyester resin.

Furthermore, Fig. 2(b) demonstrates variations in C–N–C peak intensities. The crosslinking reaction between polyester resin takes place between terminal CH_3 groups of the highly methylated melamine-based crosslinker and OH-groups of the highly hydroxylated polyester [40], as illustrated in Fig. 3. Yet, similar interactions might take place with metal hydroxides, which are also the bonding site for interaction with ester/acid functional groups of the polyester resin. Consequently, competition between chemisorption of melamine-based crosslinker and polyester resin is expected at the metal oxide surface. The ATR-FTIR spectrum in Fig. 2(b) demonstrates the highest C–N–C peak intensity as well as the lowest $\text{COO}_{(\text{as})}$ peak intensity on native magnesium oxide. Therefore, a higher affinity of magnesium oxide to the melamine-based crosslinker is suggested compared to ester/acid groups specific to the polyester resin.

The ATR-FTIR spectra of cured polyester coating on hexafluorozirconic acid treated (ZrCC) aluminium, zinc and magnesium, obtained using p-polarized IR-light, are shown in Fig. 4. Asymmetric carboxylate stretch vibrations are revealed on all zirconium-treated substrates. Consequently, it can be concluded that the bonding mechanism does not alter upon zirconium-based treatment. Similar to the ATR-FTIR spectra obtained with native oxides, also on hexafluorozirconic acid treated oxides, the carbonyl peak shifts to higher wavenumbers, indicating the consumption of carboxylic acid groups. On the other hand, the intensity of both C–O and C–O bonds remains higher than the asymmetric carboxylate peak characteristic for newly formed carboxylate bonds. Because of this, it is suggested that surface hydroxides at the zirconium-based converted oxides have less tendency to hydrolyse ester groups. Probably, increased surface acidity due to the high valency of zirconium reduces the hydrogen donating properties of surface hydroxides required for ester hydrolysis reactions [17].

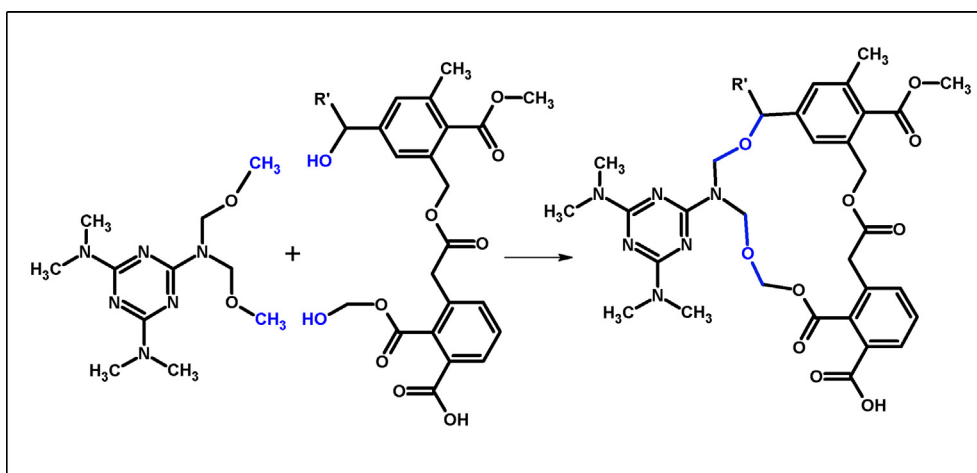


Fig. 3. Crosslinking reaction between CH₃ groups of the melamine-based crosslinker and OH-groups of the polyester resin.

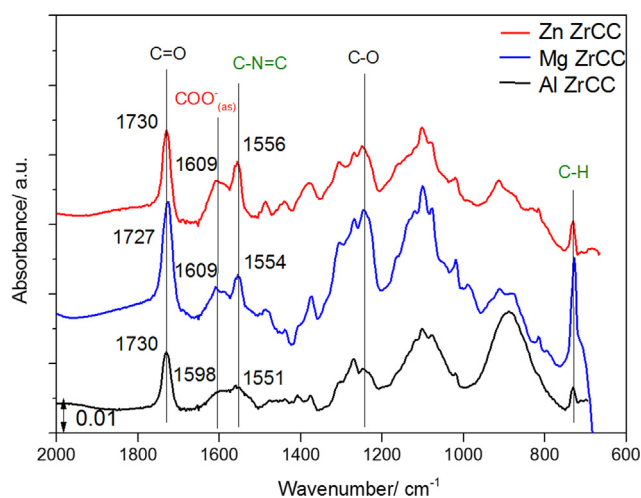


Fig. 4. ATR-FTIR spectra of cured polyester coating applied on hexafluorozirconic acid treated (ZrCC) zinc, magnesium and aluminium, collected using p-polarized IR-light with an incident angle of 80°.

3.3. Effect of curing

It has been demonstrated that the metal oxides interact with the polyester coating by the formation of interfacial carboxylate bonds. The remaining question is whether or not these interfacial interactions are established before curing. Therefore, ATR-FTIR spectra were collected of uncured polyester coat applied on native zinc oxide, illustrated in Fig. 5. The immediate presence of a strong carboxylate peak at 1609 cm⁻¹ verifies that indeed chemical bonds between zinc and polyester are already being formed at room temperature. Three vibrational peaks show a dynamic behaviour during chemisorption of the polyester coat at room temperatures, being the broad OH-band at 3435 cm⁻¹, which slightly reduces during chemisorption, and the growth of peaks at 1609 cm⁻¹ and 1373 cm⁻¹. The reduction of OH stretch vibration can be assigned to hydroxide consumption required for ester hydrolysis. The increase of peak intensities at 1609 cm⁻¹ and 1373 cm⁻¹ are assigned to asymmetric and symmetric carboxylate stretch vibrations, respectively. This means that the asymmetric and symmetric carboxylate stretching peaks are separated by 236 cm⁻¹, which is too high for bridging bidentate coordination ($\Delta\nu$ 120–180) [41] and more in line with monodentate coordinations ($\Delta\nu > 200$) [41]. Comparing the ATR-FTIR spectra of polyester coat before curing, shown in Fig. 6, with those obtained after curing, shown in Fig. 2, significant reduction of peaks at 1373, 1241, 1110 and 728 cm⁻¹ are

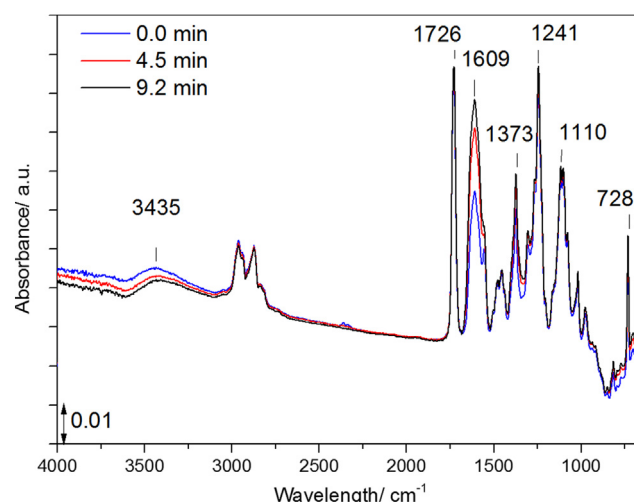


Fig. 5. Chemisorption kinetics of uncured polyester coat applied on native zinc oxide, collected using p-polarized IR-light.

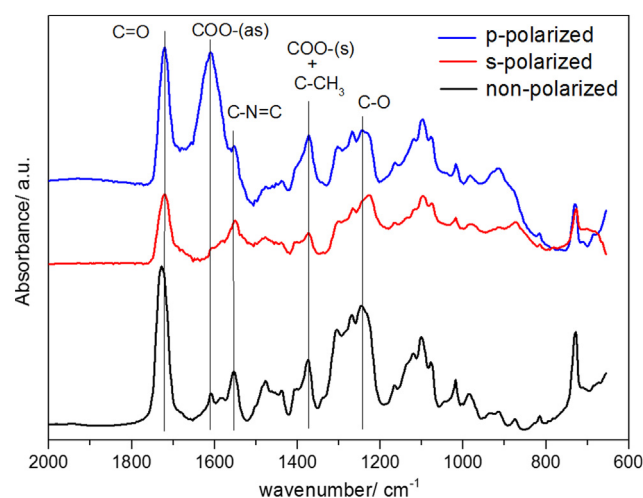


Fig. 6. ATR-FTIR spectra of cured polyester coating applied on zinc coated germanium internal reflection element, collected using p-polarized, s-polarized and non-polarized IR-light with an incident angle of 80°.

being observed after curing. The reduction of the sharp peak at 1373 cm⁻¹ is related to the disappearance of symmetric carboxylate stretch vibrations using p-polarized light. This indicates that upon

curing carboxylate bonds become strongly oriented at the interface. More details on orientation are discussed later in this work. Decreased peak intensities at 1241 cm^{-1} and 1110 cm^{-1} refer to a decrease in C–O bonds as a consequence of the crosslinking reaction illustrated in Fig. 4. Finally, a strong sharp peak at 728 cm^{-1} is assigned to C–H rocking vibrations of terminal CH_3 groups of the melamine crosslinker, which are also being consumed during the curing reaction.

3.4. Orientation analysis

Variations in asymmetric and symmetric carboxylate peak intensities before and after curing indicated strong orientation of interfacial carboxylate bonds upon curing. Fig. 6, compares ATR-FTIR spectra of polyester coated zinc, collected after curing using p-, s- and non-polarized infrared light. It is evidenced that the asymmetric carboxylate stretch vibration becomes most intense when using p-polarized infrared light. The symmetric carboxylate stretch vibration is not directly evidenced, suggesting a strong orientation of interfacial carboxylate bonds upon curing.

The fact that the asymmetric stretch vibration is strongly enhanced using p-polarized light contradicts the expected bridging bidentate coordination, which has previously been observed for carboxylate compounds [42–45]. For bridging bidentate coordination, asymmetric carboxylate stretch vibrations are expected to be most intense using s-polarized IR-light. This is because the dipole moments of asymmetric stretch vibrations are in plane with the substrate in case of bridging bidentate coordinations, as illustrated in Fig. 7. On the other hand, in case of monodentate coordinations, a dipole moment perpendicular to the surface is expected for asymmetric carboxylate stretch vibrations. Thus, based on the enhancement of asymmetric carboxylate bonds using p-polarized IR-light, as well as the large separation between asymmetric and symmetric carboxylate peaks observed before curing, it can be concluded that interfacial carboxylate bonds are oriented at the interface in a monodentate coordination. Likely, the bridging bidentate coordination mode for monomeric ester-functionalized compounds is not favourable for macromolecular structures due to steric effects.

3.5. Stability interfacial bonds polyester coating in aqueous environment

The stability of established interfacial carboxylate bonds has been studied using in-situ ATR-FTIR. Cured polymer coatings applied on nano metallic layers thermally vaporized on germanium IRE have been used as a background. Therefore, positive peaks are interpreted as gained bonds and negative peaks as lost bonds at the interface with respect to the dry state. Consequently, interfacial bonds established

after curing are expected to appear negative at the onset of delamination.

(a) Zinc

D_2O migration through the polyester coat towards zinc oxide is illustrated in Fig. 8(a) and (b). While the O–D stretching peak (2500 cm^{-1}) increases during accumulation of D_2O at the interface, peaks assigned to the polyester backbone appear as negative peaks illustrating the replacement of polyester by D_2O at the metal oxide interface. Contrary, asymmetric carboxylate stretching vibrations appear positive. This can be interpreted as an increase of carboxylate bonds with respect to the dry state. Consequently, it is evidenced that D_2O induces ester hydrolysis, resulting in increased interfacial carboxylate bonds. Yet, after 0.9 h, illustrated by the blue curve in Fig. 8(a) and (b), the asymmetric carboxylate peak reaches its maximum intensity, where after it gradually shifts towards lower wavenumbers when reducing in intensity. Hence, interfacial bond degradation as a result of D_2O penetration is monitored in situ. After 2.1 h, presented as the red curve in Fig. 8, the asymmetric carboxylate peak turns negative. From this point on, a lower amount of interfacial bonds is observed with respect to the dry state.

Fig. 9 presents the quantified peak areas, which have been discussed in Fig. 8. Three stages can be distinguished during exposure of polyester coated zinc to D_2O . First carboxylate peaks increase due to hydrolysis reactions induced by D_2O . Secondly, a maximum of interfacial carboxylate bonds is being established and followed by a gradual decrease of interfacial carboxylate bonds. Finally, the last stage is reached at the moment where positive carboxylate peaks turn negative. Negative carboxylate peak areas are interpreted as a lower amount of interfacial carboxylate bonds with respect to the dry state (background collected before immersion). The exposure time to D_2O required to obtain less interfacial carboxylate bonds than the initial dry state, is expected to depend on the metal oxide properties. Since this moment is a good indication of interfacial stability it will be defined as the onset of disbonding. It needs to be noted though that, strictly speaking, chemical disbonding already starts at the moment that carboxylate peak area starts to decline. This approach used to determine the interfacial stability, based on the COO_{as} peak area is illustrated in Fig. 9.

For hexafluorozirconic acid treated zinc, a maximum of interfacial bonds is observed after 3.6 h, presented as the blue curve in Fig. 10. Interfacial disbondment is observed after 5.5 h, presented as a red curve in Fig. 10. Hence, it can be concluded that hexafluorozirconic acid treatment of zinc increases the interfacial stability in the presence of D_2O .

(b) Magnesium

Fig. 11 demonstrates the interfacial stability of polyester coating applied on native magnesium oxide. An immediate reduction of both carboxylate (COO_{as}) and magnesium oxide peaks, suggest that the interface rapidly dissolves upon interaction with D_2O . The high reactivity of magnesium oxide plays a key-role in the instable magnesium-polymer interface.

The interfacial stability of polyester coated hexafluorozirconic acid treated magnesium is presented in Fig. 12(a) and (b). Peaks at 1595 and 1422 cm^{-1} are assigned to asymmetric and symmetric carboxylate stretching vibrations. Contrary, to native magnesium oxide, carboxylate bonds with zirconium-converted magnesium are shown to increase during initial immersion times in D_2O . The enlarged carboxylate region, given in Fig. 12(b), demonstrates maximum carboxylate peak intensity after 3.1 h where after the asymmetric carboxylate peak gradually reduces. However, disbondment does not occur within the first 19 h of D_2O accumulation. Large variations in actual disbondment time were observed for hexafluorozirconic acid treated magnesium. The high reactivity of magnesium in the conversion solution resulted in ultrathin

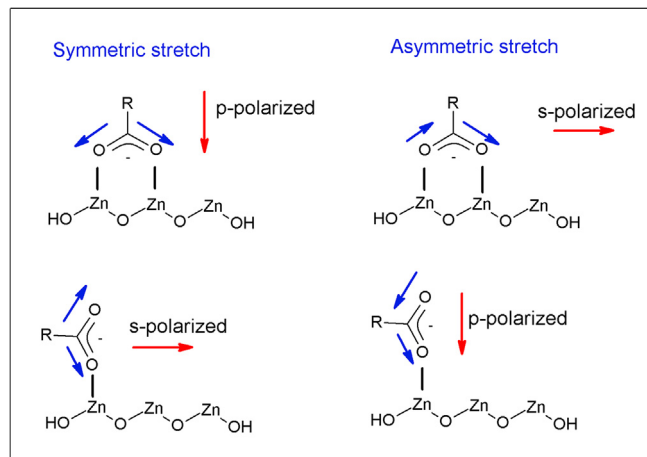


Fig. 7. Transition dipole moments of asymmetric and symmetric carboxylate stretch vibrations in different coordination modes.

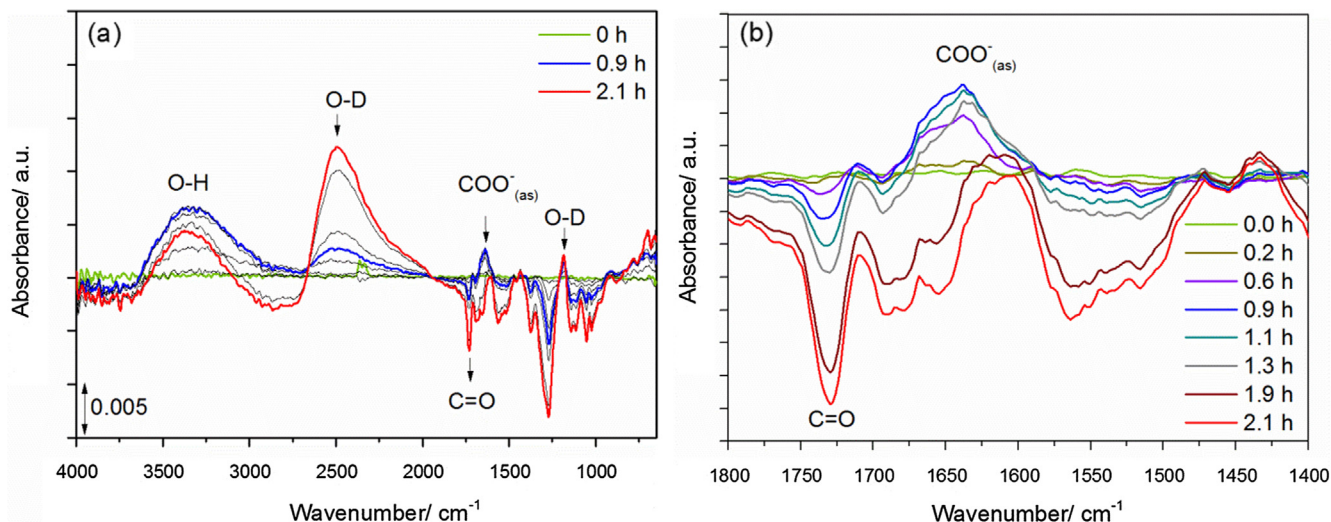


Fig. 8. ATR-FTIR spectra of D₂O permeation through polyester coating applied on native zinc oxide (a) full scale, (b) enlarged carboxylate region.

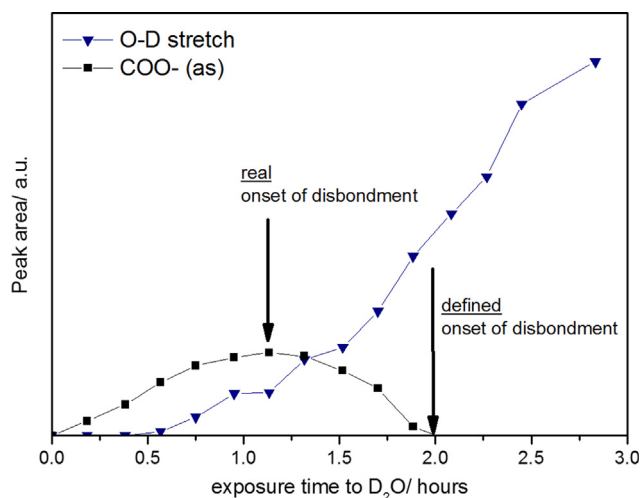


Fig. 9. Peak area dynamics of polyester coated zinc as a function of exposure time to D₂O.

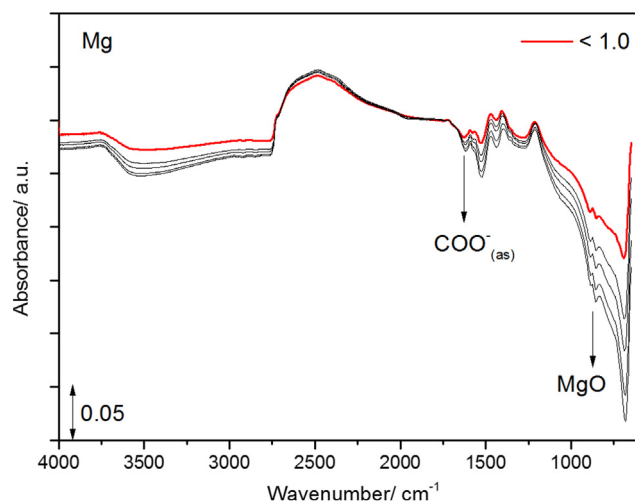


Fig. 11. ATR-FTIR spectra of D₂O permeation through polyester coating applied on native magnesium oxide.

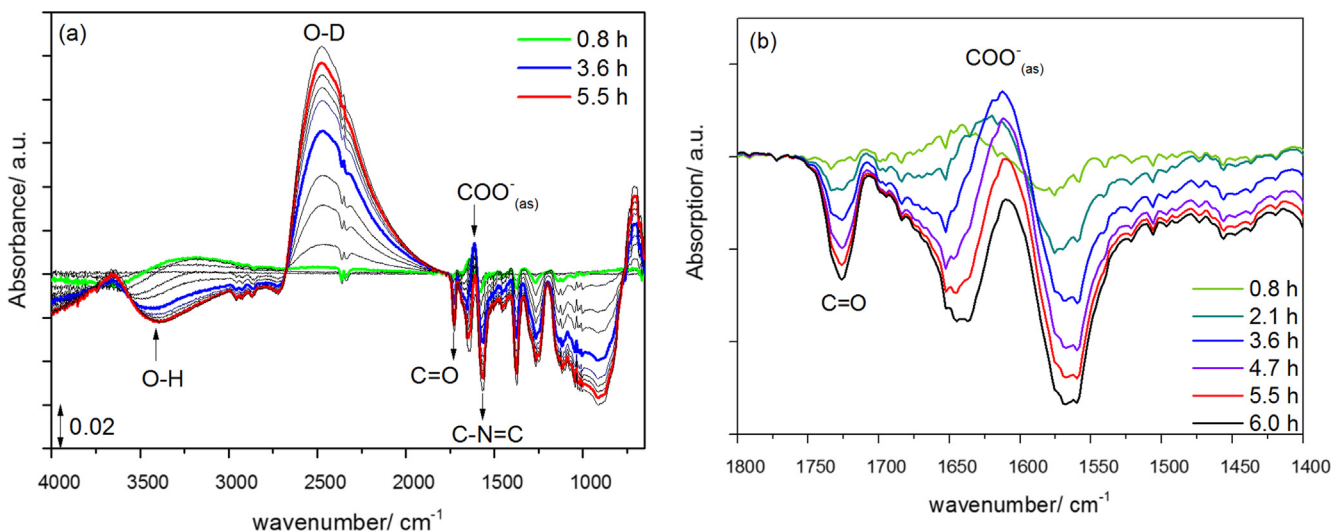


Fig. 10. ATR-FTIR spectra of D₂O permeation through polyester coating applied on hexafluorozirconic acid treated zinc (a) full scale, (b) enlarged carboxylate region.

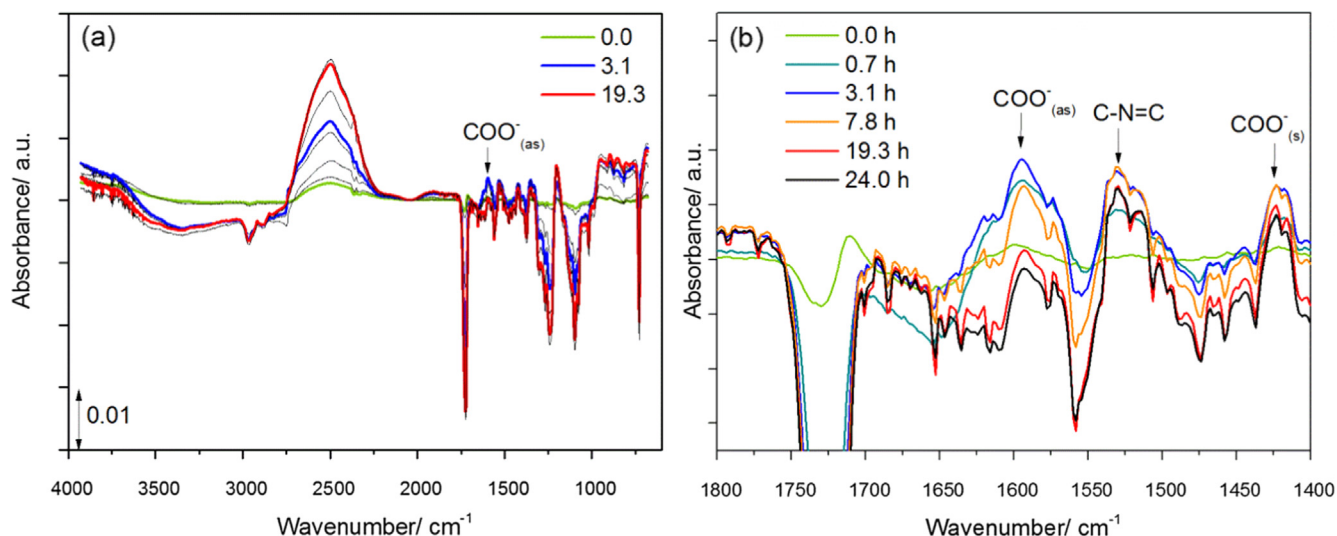


Fig. 12. ATR-FTIR spectra of D_2O permeation through polyester coating applied on hexafluorozirconic acid treated magnesium oxide (a) full scale, (b) enlarged carboxylate region.

converted magnesium films. For this reason, conversion times of 60 s as applied on zinc and aluminium were reduced to 10 s for magnesium substrates. Yet, due to the high reactivity, the conversion process remains hardly controllable and lead to variations in observed interfacial stability. Nevertheless, the interfacial stability significantly improved due to hexafluorozirconic acid treatment, compared to native magnesium oxide. Moreover, next to the growth of asymmetric carboxylate peaks, positioned at 1595 cm^{-1} , also the growth of C–N–C peak, positioned at 1530 cm^{-1} is demonstrated in Fig. 12(a) and (b). The simultaneous increase of both carboxylate and melamine peaks confirm the high affinity of magnesium substrates for the melamine-based crosslinker. Therefore, hydroxylation of the zirconium-based converted magnesium surface by D_2O creates increased binding sites for competing interactions with ester groups related to the polyester resin and uncured methyl groups of the melamine-based crosslinker. From the in-situ data presented in Fig. 12(b), higher interfacial stability is demonstrated for interactions with the melamine, since the asymmetric carboxylate peak reduces more rapidly during immersion in D_2O . However, similar to the stability of carboxylate bonds, also variations in stability of melamine-interactions were observed.

(c) Aluminium

Fig. 13 illustrates the enhancement of interfacial carboxylate bond formation by D_2O on (a) untreated aluminium and (b) hexafluorozirconic acid treated aluminium. The exceptional stability of carboxylate species adsorbed on both native and zirconium-based converted aluminium oxide ($> 24\text{ h}$) is related to the stability of aluminium in the presence of D_2O (theoretical pD of $D_2O = 7$). A broad vibration band at 940 cm^{-1} (Al–O), with a shoulder at 776 cm^{-1} (Al–O–Al) grows at immediate interaction with D_2O . Also remarkable is the presence of carbonyl stretching vibrations during immersion in D_2O . The carbonyl (C–O) peak is positioned at 1723 and 1714 cm^{-1} for untreated and hexafluorozirconic acid treated aluminium, respectively. This means that the carbonyl peak has shifted towards lower wavenumbers with respect to the dry state, indicating its involvement in hydrogen or more correctly deuterium bonds. The higher shift observed in Fig. 13(b) indicates that deuterium bond interactions are stronger on hexafluorozirconic acid treated aluminium. Contrary, to zinc and magnesium, which showed negative carbonyl peaks during immersion, deuterium bonds formed between both native and hexafluorozirconic acid treated aluminium oxide and polyester carbonyl are stable in D_2O .

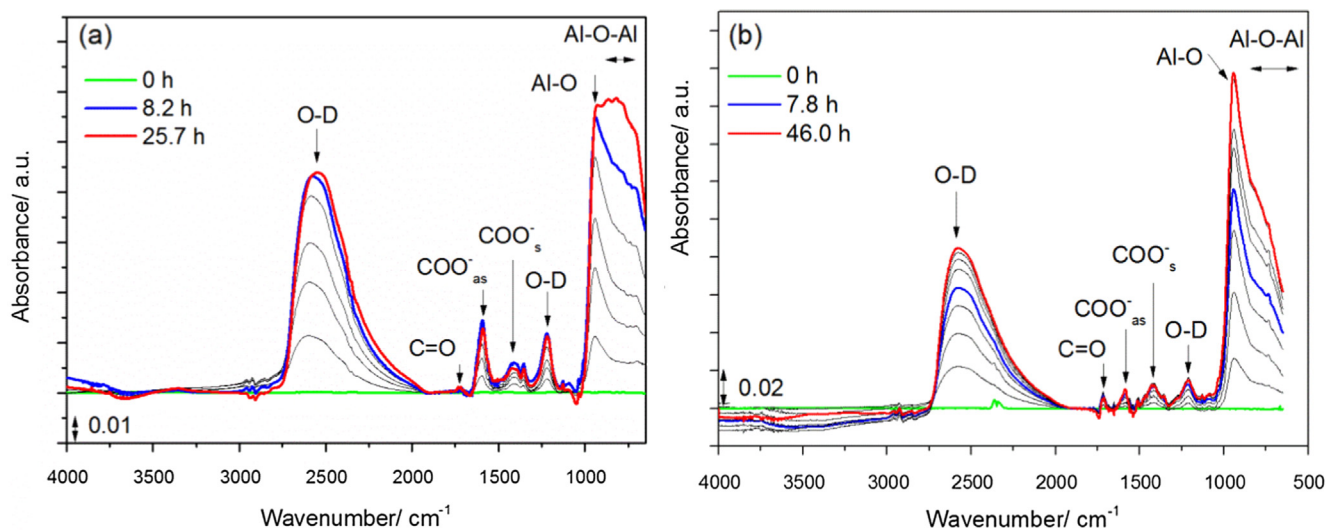


Fig. 13. ATR-FTIR spectra of D_2O permeation through polyester coating applied on (a) untreated and (b) zirconium-based treated aluminium.

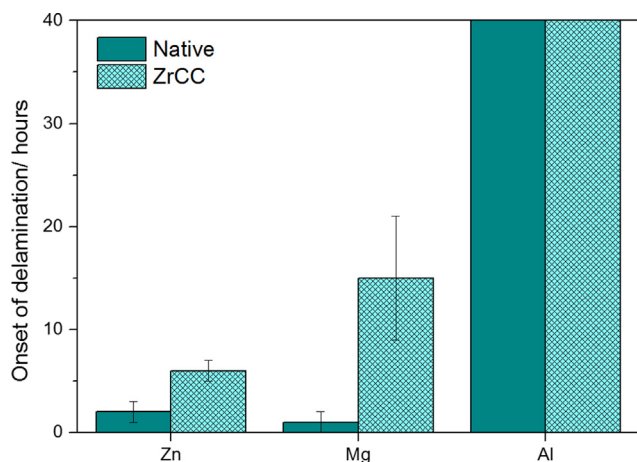


Fig. 14. Onset of delamination based on infrared peak area of asymmetric carboxylate stretching vibration followed in-situ during exposure to D_2O .

Furthermore, peaks attributed to asymmetric carboxylate stretching vibrations appear at 1589 and 1585 cm^{-1} for untreated and hexafluorozirconic acid treated aluminium, respectively. In addition to asymmetric carboxylate peaks also symmetric carboxylate peaks arise upon exposure to deuterated water, positioned at 1408 and 1417 cm^{-1} for untreated and hexafluorozirconic acid treated aluminium, respectively. Consequently, the separation value of the coupled carboxylate peaks reduced to 181 cm^{-1} and 168 cm^{-1} , which indicates altered orientation of interfacial bonds upon exposure to deuterated water.

(d) Summary of interfacial stability

Fig. 14 summarizes the defined onsets of delamination during exposure to D_2O , calculated using the approach presented in Fig. 10. On native zinc and magnesium, chemical disbonding is observed rapidly, within less than 2 h. On the other hand, hexafluorozirconic acid treatment successfully improves the interfacial stability, with 3 and 15 times higher delay time prior to carboxylate disbondment observed on zirconium-treated zinc and magnesium respectively. Furthermore, it is clear that the competitive chemisorption of polyester resin and melamine-based crosslinker, which has been demonstrated to take place on magnesium substrates, should not be considered as detrimental for interfacial stability. The highest interfacial stability is demonstrated for aluminium. Interfacial carboxylate bonds established at both untreated, as well as hexafluorozirconic acid treated aluminium remain stable for more than 40 h. This exceptional durability of the aluminium-polyester interface relates to the stability of aluminium oxide in solutions at neutral pH, or more correct in this case neutral pD values [46]. Whereas, according to the Pourbaix diagrams, zinc and magnesium are known to be unstable at neutral pH values [46]. Hexafluorozirconic acid treatment of zinc and magnesium has shown to passivate successfully, though further improvement should be possible. For example, by adjusting conversion bath concentration and conversion time, as well as by adding organic and/or inorganic additives.

4. Conclusions

Industrially relevant polyester primer has shown to chemisorb on both native and hexafluorozirconic acid treated metal substrates by the formation of monodentate carboxylate bonds. Chemical bonding was shown to take place upon immediate contact at room temperature, before curing at elevated temperatures. Next to carboxylate bond formation, interactions with the melamine-based crosslinker were evidenced. Interfacial chemical bonds established on native zinc and magnesium were shown to disbond rather rapidly, because of their tendency to corrode in neutral aqueous environments. However,

hexafluorozirconic acid treatment improved the stability of established interfacial chemical bonds efficiently by passivating unstable zinc and magnesium oxide, resulting in 300 and 1500% higher delay time prior to interfacial carboxylate disbondment. Aluminium, which has a stable oxide layer in neutral aqueous environments, performed best regarding interfacial durability. ATR-FTIR in the Kretschmann geometry has shown to be a useful technique to evaluate the performance of chemical conversion coatings in-situ on an interfacial level. This provides the opportunity to optimize and create new enhanced metallic/organic coating systems that are better resistant to degradation and can lead to an improved lifetime.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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