PHENOLATED METHYLOLEATE-BASED POLY(BENZOXAZINE) FILMS AS CORROSION PROTECTION LAYERS ON Zn/Mg/Al-ALLOY COATED STEEL

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Three phenolated methyloleate-based benzoxazine derivatives were spincoated on or spraycoated on Zn-Mg-Al alloy coated steel surfaces. Upon heat-curing under formation of the corresponding poly(benzoxazine) films, their corrosion protection properties were investigated using longterm open-circuit potential (OCP) measurements, SEM imaging and EDX elemental analysis, before and after the OCP measurement in chloride-containing electrolyte. The influence of the poly(benzoxazine) film thickness on the corrosion protection of Zn-Mg-Al alloy coated steel was investigated using an automatic scanning droplet cell and sequential potentiodynamic polarization curves.

Keywords: phenolated methyloleate; benzoxazine derivatives; poly(benzoxazine); corrosion protection; Zn-Mg-Al alloy coated steel; scanning droplet cell

1. Introduction

Coating of metal surfaces with polymer films is a commonly applied strategy for passive corrosion protection [1]. The polymer layers are considered to prevent the access of water and ions to the metal surface by creating a physical barrier, thus substantially decreasing the anodic reaction, and hence, the overall corrosion currents [2]. Poly(benzoxazines) are a class of polymers which exhibits a number of interesting properties such as low water absorption and almost no shrinkage upon curing [3]. These properties make poly(benzoxazines) good candidates for anticorrosion coatings. Despite these extraordinary properties, only little attention was devoted to the application of poly(benzoxazine) films as anticorrosion coatings [4-8]. Moreover, recent reports demonstrated that benzoxazine monomers can be derived from bio-based resources, starting e.g. from euge-

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nol, cardanol, vaniline, etc., as the phenol component in benzoxazine synthesis [9-11].

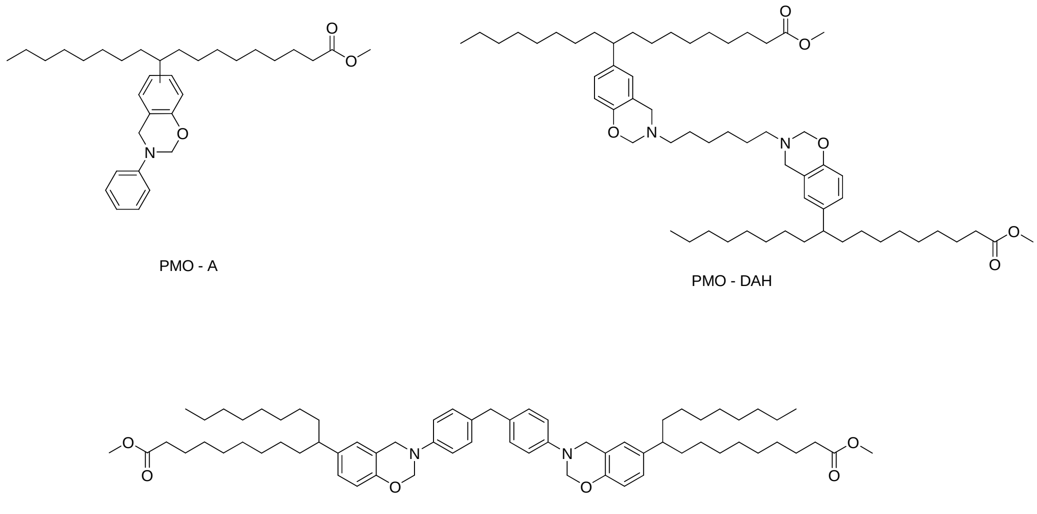
A new synthesis strategy for benzoxazine monomers using bio-based resources has been recently presented by our research group [12, 13]. Methyl oleate was used as model compound for the synthesis of three new benzoxazine monomers. The corrosion protection properties of the resulting poly(benzoxazine) films on Zn-Mg-Al-alloy coated steel (ZM-steel) were evaluated using open-circuit potential (OCP) determination, as well as linear sweep voltammetry (LSV) measurements. The poly(benzoxazine) coatings induced an anodic shift of the break-through potential, and a substantial decrease in the cathodic current densities in the Tafel representation of the LSV experiments.

In this work, an in-depth investigation of the corrosion protection properties of phenolated methyl oleate-based poly(benzoxazine) films on ZM-steel was performed, controlling on the one hand, the polymer-film thickness, and on the other hand, the curing conditions for the formation of the poly(benzoxazine) coating. An automatic scanning droplet cell system which allows for the sequential investigation of small areas of a coated sample was employed, in order to attain comparable results. Air-brush type spraying using a specifically developed spray coater enabled us to create defined polymer film thickness gradients, which encountered the same heat curing steps. Together with longterm OCP measurements and SEM/EDX images obtained before and after OCP measurements, a deeper insight into corrosion protection by poly(benzoxazine)-based polymer films was obtained.

2. Experimental

2.1. Chemicals and materials

The Zn-Al-Mg alloy coated (ZM) steel sheets were from ThyssenKruppSteel Europe AG. The Zn-Al-Mg alloy coating contains 90.25% Zn, 3.97% Al, and 5.78% Mg by weight. The benzoxazine monomers named PMO-A, PMO-DAH and PMO-DDM were synthesized from phenolated methyl oleate and different amines, as previously shown [12]. The chemical structures of the benzoxazine monomers are shown in Scheme 1. Toluene, acetone, isopropanol and ethanol were from Sigma-Aldrich.


PMO - A

PMO - DAH

PMO - DDM

Scheme 1: Chemical formulas of the benzoxazine monomers

2.2. Poly(benzoxazine)-coatings on ZM steel sheets

Before benzoxazine deposition, the ZM substrates were cleaned in an ultrasonic bath using acetone, isopropanol (two times), and ethanol for 10 min each. In the final cleaning step, the samples were immersed in 1.5 wt. % Ridoline solution at 60 °C. For longterm open circuit potential (OCP) measurements and SEM/EDX imaging, the benzoxazine was coated on ZM steel sheets (1.5 x 1.5 cm^2) by spin-coating of 50 μL of a 0.25 mg/mL solution of each benzoxazine monomer in toluene for 2 min at 1000 rpm. This step is followed by successive heat treatment of the benzoxazine-coated ZM steel substrate for 2 h at 180 °C, 2 h at 200 °C, and 1 h at 250 °C, in air, in order to obtain the corresponding poly(benzoxazine)-coated ZM steel samples. The resulting poly(benzoxazines) are named in accordance with the phenol component phenolated methyloleate (PMO) and the amino component used for the synthesis of the poly(benzoxazine) derivative: using aniline as amino component leads to **pPMO-A**, using diaminohexane leads to **pPMO-DAH** and using 4,4'-diaminodiphenylmethane leads to **pPMO-DDM**.

For the evaluation of the anticorrosion properties in dependence on the polymer film thickness, other 1.5 x 10 cm^2 ZM steel sheets were spray coated with solutions of the benzoxazine monomers (35 mg benzoxazine/50 mL toluene). For spray deposition, a home-built air-brush type spray coater was used. During deposition, the metal plates on which the ZM-steel samples are located were heated at 70 °C to immediately evaporate the solvent. The specifically developed software has controlled the x-,y-,z-position of the spray nozzle, in order to obtain a linear thickness gradient ranging from < 1 μm to about 10 μm film thickness. Heat curing was performed in Ar atmosphere.

2.3. Characterization of the poly(benzoxazine)-coated ZM steel sheets

Longterm OCP measurements were performed in a specifically designed electrochemical cell with an opening of 5 mm diameter, using a PalmSens potentiostat in a Faraday cage, in order to avoid electromagnetic noise. The electrochemical cell contained the coated ZM steel as working electrode, a Pt gauze as counter electrode, and Ag/AgCl/KCl (3M) as reference electrode. The OCP was measured in NaCl (3.5 wt. %) solution.

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were performed using a Quanta 3D FEG scanning electron microscope (FEI), operated at 20.0 kV for SEM imaging, and at 4.4 kV for EDX analysis. SEM and EDX images of the poly(benzoxazine)-coated ZM steel sheets were recorded before and after longterm OCP measurements.

An in-house built scanning droplet cell (SDC) previously described [14,15] was used for automatic LSV along the polymer thickness gradient of the spray-coated ZM steel samples. The SDC contains a Teflon orifice with a 1 mm opening diameter, which is pressed on the sample surface with a constant force, to assure a well-defined surface area to be wetted by the electrolyte solution. The polymer-coated ZM steel sheet is connected as working electrode, a Pt wire as counter electrode and a Ag/AgCl/3 M KCl as reference electrode. 3.5 wt.% NaCl was used as electrolyte. The electrode potentials were referred to saturated hydrogen electrode (SHE). The sample was initially polarized to -1.25 V vs. SHE and the current was recorded until a stable background current was obtained. The potential was scanned positively to -0.75 V vs. SHE with a scan rate of 1 mV/s while the current was recorded. Three dimensional false-color images were obtained by plotting log ***i*** *vs.* ***d*** *vs.* ***U***, where ***i*** is the current, ***d*** the estimated layer thickness and ***U*,** the applied potential value *vs.* SHE. The breakthrough potentials correspond to the minimum of log ***i*** value (violet/black areas).

3. Results and discussions

The electrochemical properties of the poly(benzoxazine)-coated ZM-steel samples were investigated by means of longterm OCP measurements, in chloride-containing electrolyte for about 70 h (Fig. 1). It is assumed that the polymer coating prevents access of ions and/or oxygen from the electrolyte to the underlying ZM surface, which is obviously depending on the properties of the poly(benzoxazine) coatings including the film porosity and the film thickness. As a matter of fact, if the polymer film is completely non-permeable for the electrolyte solution or too thick, electrochemical investigations are not possible.

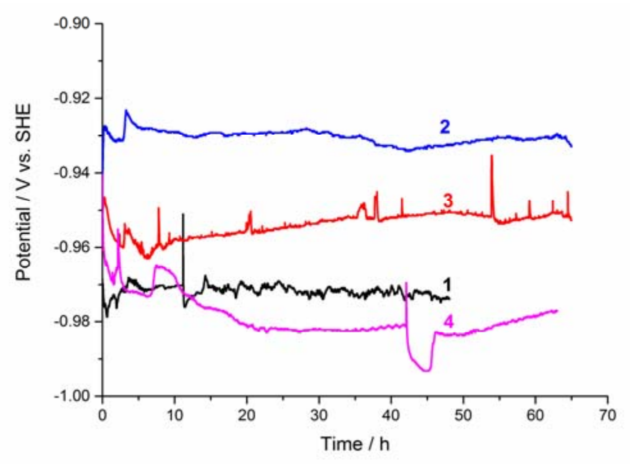


Fig. 1: Longterm OCP – time curves for **1** - uncoated ZM steel, **2 - pPMO-A**, **3 - pPMO-DAH** and **4 - pPMO-DDM** coated ZM steel

The OCP of the only ZM-coated steel was initially -0.975 V *vs.* SHE and stayed constant after an initial small shift to -0.97 V *vs.* SHE (curve 1). An OCP value of 0.97 V *vs.* SHE is typical for uncoated ZM steel sheets, and is due to the formation of a passive Mg/Zn-oxide layer upon initial corrosion. The OCP value of **pPMO-A** (curve 2) is considerably more positive (about -0.93 V *vs.* SHE) and stays constant during the course of the experiment. The OCP of the **pPMO-DAH** (curve 3) coated ZM-steel sheet shows an initial OCP of -0.95 V *vs.* SHE, which is shifted during the first 10 h to -0.96 V *vs.* SHE, and afterwards it moves again to -0.955 V *vs.* SHE during the longterm OCP measurement. The **pPMO-DDM** (curve 4) coated ZM steel shows a substantially different behavior. The OCP value is initially -0.96 V *vs.* SHE and is shifted to -0.98 V *vs.* SHE during the course of the measurement. This value is substantially more negative than that of the uncoated ZM steel sheet. We may consider that the **pPMO-A** and **pPMO-DAH** coated ZM sheets showed no significant changes in the OCP during the longterm OCP measurement in the chosen highly corrosive electrolyte. Hence, it can be assumed that the Zn-Al-Mg alloy of the underlying passivation layer is remaining intact, due to the protection through the poly(benzoxazine) film. A quite substantial shift is seen for the OCP of the **pPMO-DAH**-coated ZM steel, which is initially -0.96 V *vs.* SHE and moves to -0.98 V *vs.* SHE during 70 h. The more positive OCP values of **pPMO-A-** and **pPMO-DAH**- coatings are likely due to a slowing down of the anodic partial reaction due to the decreased access of ions (e.g. chloride) to the steel surface, through the dense and hydrophobic poly(benzoxazine) coating. It can be expected that the degree of crosslinking in the poly(benzoxazine) films is highest for **pPMO-DAH**; however, the most negative OCP in the case of the **pPMO-DDM** coating cannot be explained from the molecular structure of the parent benzoxazine compound.

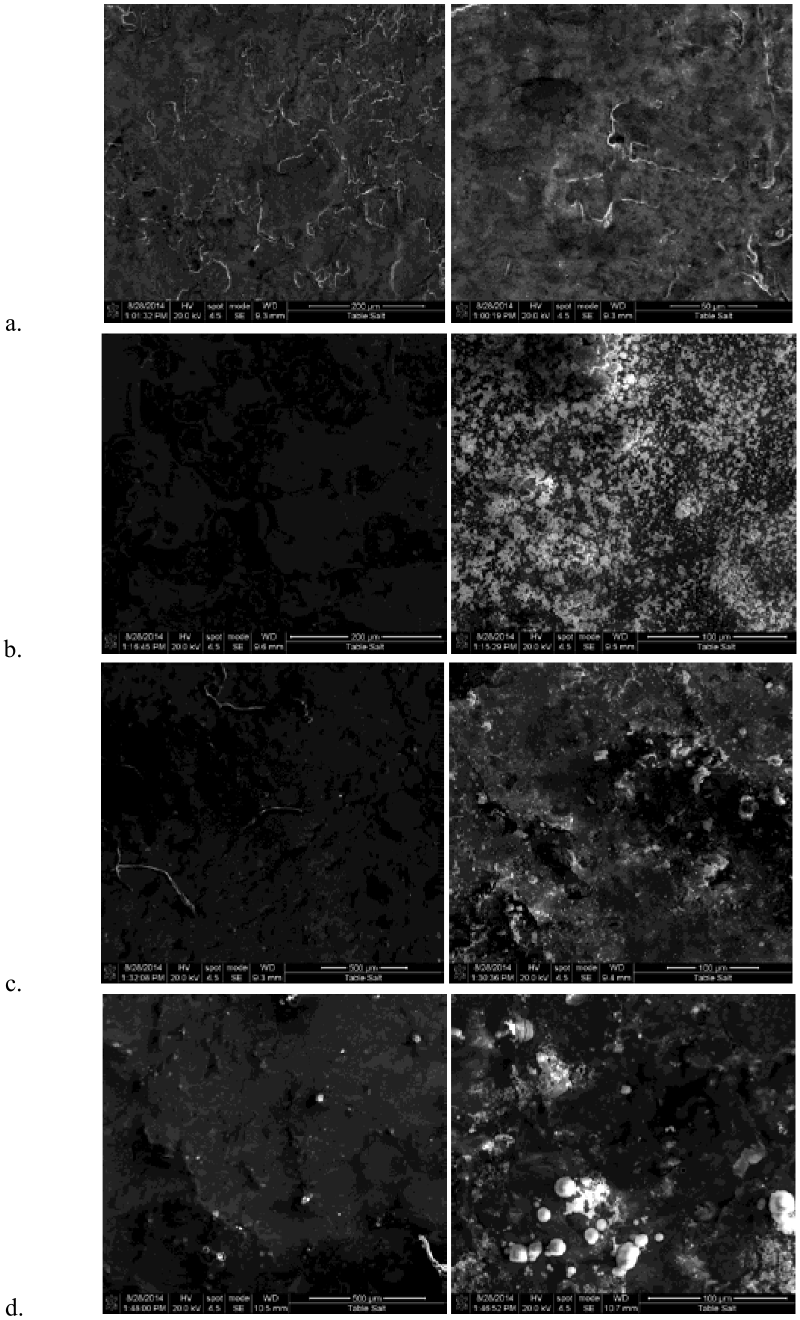


Fig. 2: SEM images for the (a) uncoated ZM steel and ZM steel coated with: (b) **pPMO-A**, (c) **pPMO-DAH** and (d) **pPMO-DDM,** before (left) and after (right) the longterm OCP measurement

Fig. 2 shows SEM images obtained before and after the longterm OCP measurements. A significant difference between the surfaces of the uncoated ZM steel and the poly(benzoxazine)-coated ZM samples is obvious. After the longterm OCP measurement, there is no visible change in the morphology of the uncoated ZM steel. Certainly, the formation of the Zn/Mg passivation layer leads to a similarly smooth surface as that of the initial specimen. For the poly(benzoxazine)-coated samples, a substantial roughening is observed, which may be attributed to a swelling of the polymer film, blistering and depositing of oxide layers within the pores of the polymer films.

The longterm OCP measurement was performed in a specifically designed electrochemical cell, in which a defined surface area of 5 mm diameter is exposed to the electrolyte, while the rest of the sample surface is never in contact with the electrolyte, due to sealing with an O-ring. Thus, after the longterm OCP measurement, two adjacent areas are found on each sample: the electrolyte-exposed area and the pristine unchanged area. The elemental composition in both areas was investigated using EDX analysis, as shown in Fig. 3.

The left column in Fig. 3 shows the SEM images of the zone between the exposed and pristine surface area with the border marked with a white line. The center column shows the distribution of Mg and the right column that of Al. The uncoated ZM steel exhibits a slightly increased Mg concentration, concomitant with a very small decrease of Al content on the exposed surface. The Mg distribution is less homogeneous compared to the pristine ZM steel surface. For the **pPMO-A** (b) and **pPMO-DAH** (c) samples, the SEM images show a similar substantial roughening as already discussed for Fig. 2. Moreover, the electrolyte-exposed area shows a significant increase of a homogeneous Mg distribution. In the case of the **pPMO-A**-coated sample, the Al distribution is significantly decreased, while it is less decreased for the **pPMO-DAH**-coated sample. The **pPMO-DDM**-coated sample shows a similar elemental distribution for Mg and Al as the uncoated ZM steel, suggesting that the permeability of the film is higher, leading to the formation of the Mg/Zn-oxide passivation layer. This is in accordance with the most negative OCP during the longterm OCP measurement. As pointed out above, it is supposed that the thickness of the poly(benzoxazine) film has an impact on the corrosion protection properties of the polymer films.

In order to evaluate the film-thickness dependence, some stripes of ZM steel were coated with the benzoxazine precursors, using an automatic airbrush-type spray-coating system mounted on a x-,y-positioning frame. Coating thickness gradients from about 1 to 10 µm were obtained. The corrosion protection properties were evaluated from LSV measurements, using an automatic scanning droplet cell setup previously described [13, 14].

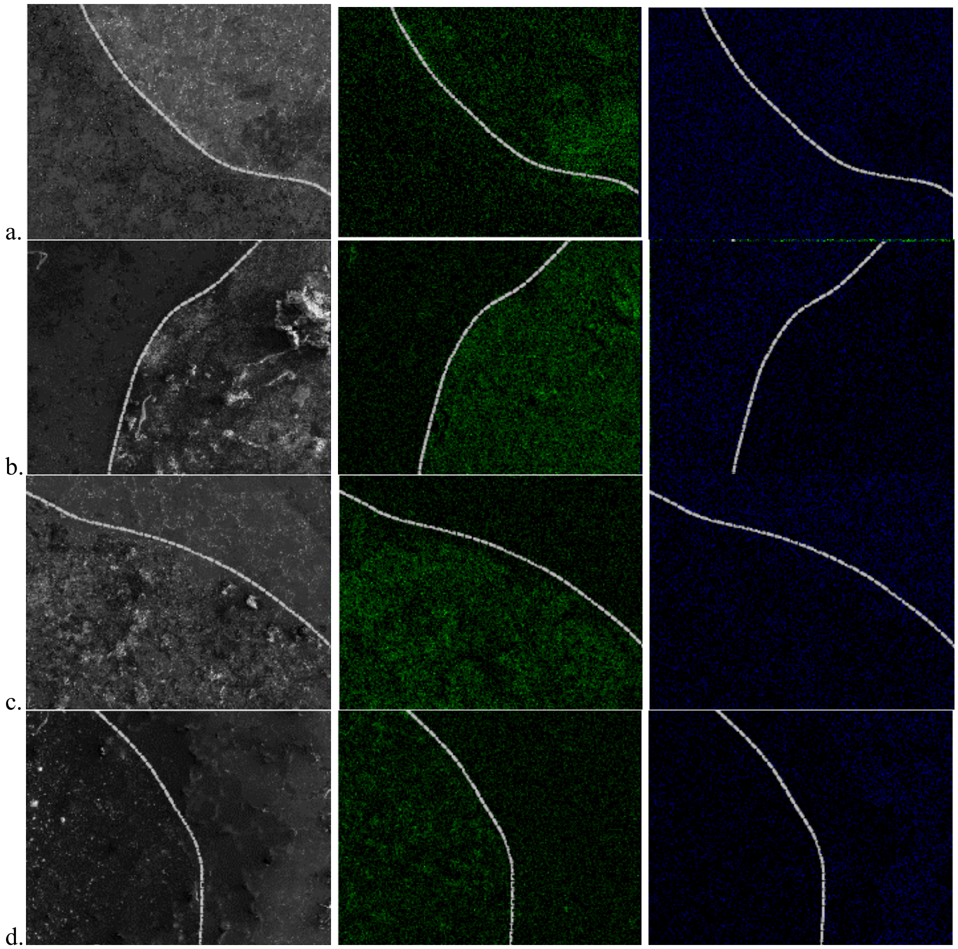


Fig. 3: SEM images (left), EDX for Mg (center) EDX for Al (right) for (a) uncoated ZM steel and ZM steel coated with: (b) **pPMO-A**, (c) **pPMO-DAH** and (d) **pPMO-DDM** (area outside ring – sample before OCP, area inside ring – sample after OCP)

The scanning droplet cell selects a highly reproducible area of about 1 mm diameter of the sample surface, by pressing a Teflon orifice with a controlled force onto the sample surface. It performs predefined electrochemical measurements using the selected sample surface area as working electrode. The droplet cell is completed with a double-junction Ag/AgCl/3 M KCl reference electrode, and a Pt wire counter electrode. Fig. 4 shows the false-color representation of LSV recorded from an initial potential of -1.25 V to -0.6 V *vs.* SHE. The Tafel representation of the LSV shows the absolute value of the logarithm of the current density versus the applied potential. Each poly(benzoxazine) modified sample was cured in Ar to evaluate the difference in terms of formation of volatile Mg species and the formation of oxides at elevated temperature in air.

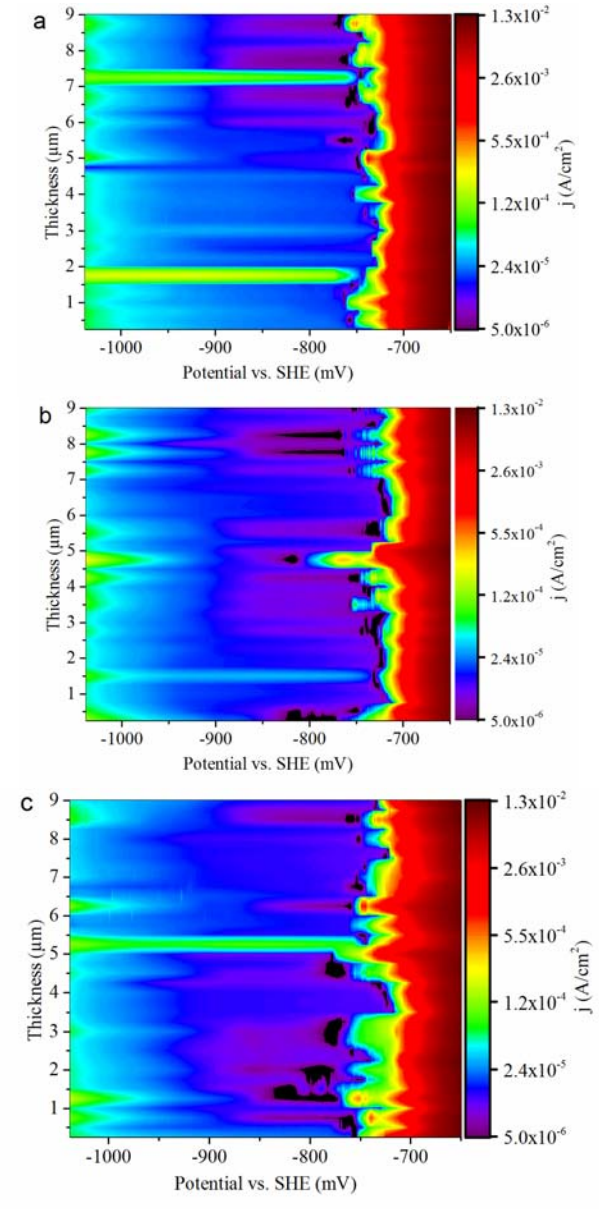


Fig. 4: Three-dimensional false-color representation of a series of LSV obtained using SDC for (a) **PMO-A** coated ZM steel cured in Ar, (b) **PMO-DAH** coated ZM steel cured in Ar, (c) **PMO-DDM** coated ZM steel cured in Ar.

The **pPMO-A**-coated ZM steel exhibits a shift to higher break-through potentials upon curing in Ar atmosphere. The breakthrough potential after curing in Ar is largely independent from the film thickness, being of about -0.72 to -0.73 V *vs*. SHE. For film thicknesses between 6 and 9 µm, the cathodic current densities at potentials slightly cathodic than the breakthrough potential are significantly lower. In the case of **pPMO-DAH**-coated ZM steel the breakthrough potential is more positive (-0.7 V *vs*. SHE) and independent from the polymer film thickness. Finally, at low values of poly(benzoxazine) film thickness, very low cathodic currents were obtained at potentials slightly cathodic of the breakthrough potential. In the case of the **pPMO-DDM**-coated sample, the situation is very similar to the **pPMO-DAH**-coated ZM steel. Low cathodic currents were already reached at small polymer-film thicknesses, and the breakthrough potential stayed constant for all film thicknesses.

4. Conclusions

Phenolated methyloleate-based benzoxazine derivatives were synthesized using aniline, 1,6-diaminohexane or 4,4'-diaminodiphenylmethane as amine component. The corresponding poly(benzoxazine) films were obtained after spin coating or spray coating of ZM steel sheets with the monomer solutions and subsequent heat-curing. Longterm OCP measurements in combination with SEM/EDX imaging revealed a significant impact on the corrosion protection of ZM-coated steel. Polybenzoxazine-coated steel samples based on phenolated methyl oleate and 1,6-diaminohexan showed a substantially increased OCP value. The corrosion protection properties were not substantially influenced by the poly(benzoxazine)-film thickness, as it was observed from the three-dimensional false-color LSV representation obtained for the spraycoated samples using an automatic scanning droplet cell.

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REFERENCES

[1] *E. Sharmin*, *F. Zafar*, *D. Akram*, *M. Alam, S. Ahmad*, "Recent advances in vegetable oils based environment friendly coatings: A review" in Ind. Crops Products, **vol**. **76**, 2015, pp. 215 - 229

[2] *U. Riaz*, *C. Nwaoha*, *S. M. Ashraf*, "Recent advances in corrosion protective composite coatings based on conducting polymers and natural resources derived polymers" in Prog. Org. Coat., **vol. 77**, 2014, pp. 743 – 756

[3] *N. N. Ghosh*, *B. Kiskan*, *Y. Yagci*, "Polybenzoxazines - New high performance thermosetting resins: Synthesis and properties" in Prog. Polym. Sci., **vol. 32**, 2007, pp. 1344-1391

[4] *C. Zhou*, *X. Lu*, *Z. Xin*, *J. Liu*, "Corrosion resistance of novel silane-functional polybenzoxazine coating on steel" in Corros. Sci., **vol. 70**, 2013, pp. 145-151

[5] *C. Zhou*, *X. Lu*, *Z. Xin*, *J. Liu*, *Y. Zhang*, "Polybenzoxazine/SIO_2 nanocomposite coatings for corrosion protection of mild steel" in Corros. Sci., **vol. 80**, 2014, pp. 269-275

[6] *C. Zhou*, *X. Liu*, *Z. Xin*, *J. Liu*, *Y. Zhang*, "Hydrophobic benzoxazine-cured epoxy coatings for corrosion protection" in Prog. Org. Coat., **vol. 76**, 2013, pp. 1178-1183

[7] *S.-C. Lin*, *C.-S. Wu*, *J.-M. Yeh*, *Y.-L. Liu*, "Reaction mechanism and synergistic anticorrosion property of reactive blends of maleimide-containing benzoxazine and amine-capped aniline trimer" in Polym. Chem., **vol. 5**, 2014, pp. 4235-4244

[8] *J. Escobar*, *M. Poorteman*, *L. Dumas*, *L. Bonnaud*, *P. Dubois*, *M.-G. Olivier*, "Thermal curing study of bisphenol A benzoxazine for barrier coating applications on 1050 aluminium alloy" in Prog. Org. Coat., **vol. 79**, 2015, pp. 53-61

[9] *B. S. Rao*, *A. Palanisamy*, "Synthesis of bio based low temperature curable liquid epoxy, benzoxazine monomer system from cardanol: Thermal and viscoelastic properties" in Eur. Polym. J., **vol. 49**, 2013, pp. 2365-2376

[10] *P. Thirukumaran*, *A. S. Parveen*, *M. Sarojadevi*, "Synthesis of eugenol-based polybenzoxazine – POSS nanocomposites for low dielectric applications" in Polym. Compos. 2014, DOI: 10.1002/pc.23107

[11] *A. Van*, *K. Chiou*, *H. Ishida*, "Use of renewable resource vanillin for the preparation of benzoxazine resin and reactive monomeric surfactant containing oxazine ring" in Polymer, **vol. 55***,* 2014, pp. 1443-1451

[12] *B. Balanuca*, *M. Raicopol*, *A. Maljusch*, *S.A. Garea*, *A. Hanganu*, *W. Schuhmann*, *C. Andronescu*, "Phenolated oleic acid based polybenzoxazine derivatives as corrosion protection layers" in ChemPlusChem, **vol. 80**, 2015, pp. 1170–1177

[13] *M. Raicopol*, *B. Balanuca*, *K. Sliozberg*, *B. Schluter*, *S.A. Garea*, *N. Chira*, *W. Schuhmann*, *C. Andronescu*, "Vegetable oil-based polybenzoxazine derivatives coatings on Zn-Mg-Al alloy coated steel" in Corros. Sci., 2015, Doi:10.1016/j.corsci.2015.08.018

[14] *D. Schäfer*, *C. Mardare*, *A. Savan*, *M. D. Sanchez*, *B. Mei*, *W. Xia*, *M. Muhler*, *A. Ludwig*, *W. Schuhmann*, "High-throughput characterization of Pt supported on this film oxide material libraries applied in the oxygen reduction reaction" in Anal. Chem., **vol. 83**, 2011, pp. 1916-1923

[15] *K. Sliozberg*, *D. Schäfer*, *T. Erichsen*, *C. Khare*, *R. Meyer*, *A. Ludwig*, *W. Schuhmann*, "High-throughput screening of thin-film semiconductor material libraries I: System development and case study for Ti-W-O" in ChemSusChem, **vol. 8**, 2015, pp. 1270-1278