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Aminic epoxy resin hardeners as reactive solvents for conjugated polymers: polyaniline base/epoxy composites for anticorrosion coatings

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Abstract

Polyaniline (PANI) has much been studied in the context of corrosion prevention, particularly on steel and aluminium. To prepare epoxy coatings consisting of PANI has turned to be nontrivial, due to its relatively rigid conformation and poor solubility. Therefore, as the aim has typically been first to dissolve PANI in the epoxy component before curing, auxiliary solvents have been required, and less attractive Lewis-type hardeners have been required if the conducting salt form has been used. In this work, we describe a particularly simple concept where emeraldine base (EB) form of PANI is first dissolved in specific aminic hardeners which are observed to be solvents for EB at low concentrations, and the mixtures are unconventionally cross-linked upon adding epoxy resin, diglycidyl ether of bisphenol-A (DGEBA). Suitable hardeners are *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine (DAB-AM-4) and trimethylhexanediamine (TMDA). Even if the subsequent cross-linking promotes phase separation, the forming cross-link sites may also control the phase separation. As a result, sufficiently homogeneous coatings are identified which contain only 1 wt% EB in the cured EB/DGEBA/TMDA composites where in aqueous 3.5% NaCl solution the corrosion front propagation is suppressed, and electrochemical impedance studies indicate the formation of a charged interface or reaction product layer between EB and steel. For reference, similar net EB/DGEBA/TMDA-compositions were prepared, where EB was first mixed in DGEBA without any solubility and which were cured by added TMDA, and they gave essentially no anticorrosion effect. We expect that the present concept opens new ways to prepare cured epoxy composites also with other conjugated or nonconjugated polymers for anticorrosion and other functional purposes.

Keywords: Polyaniline; Epoxy composite; Anticorrosion

1. Introduction

Conjugated polymers have extensively been pursued for functional materials as they can have feasible optical, electrical, redox and other properties [1,2]. However, due to their semi-rigid or rod-like conformations and strong aggregation tendency, they are usually poorly soluble in common solvents. To reduce aggregation and to impart solubility, side-chains have covalently or physically been bonded to the backbones which leads to comb-like architecture and self-assembly [3–16]. While such concepts are remarkably useful in applications which typically require only small sample volumes, such as in electronic and photonic devices, in large scale applications such tailored polymers may not always be acceptable due to cost and production reasons. Therefore, it becomes important to identify new facile concepts for conjugated polymers using commodity starting materials, e.g. to render multicomponent materials and coatings where the different components simultaneously can tune the different properties.

In this context it becomes interesting that Meijer et al. have introduced techniques to process semi-rigid nonconjugated polymers, e.g. poly(2,6-dimethyl phenyl ether) (PPE), using reactive solvents [17–21]. They first mix PPE in oligomeric epoxy resins, such as diglycidyl ether of bisphenol-A (DGEBA) which is observed to be a solvent for PPE, and subsequently cure the mixture by adding aminic hardeners. Also additional polymer components and fiber reinforcements can be added in the composite. Such

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concepts allow a feasible and facile construction of cross-linked multicomponent materials with synergistic properties.

Inspired by the possible potential of such methods also for conjugated polymers, we investigate here cured conjugated polyaniline (PANI)/epoxy composite coatings, aiming at anodically passivating anticorrosion function. Electrically conducting polyaniline salts with sulphonic or phosphoric acids have much been studied in the context of corrosion resistant coatings of steel and aluminium [22–31]. As the conducting PANI salts have not turned to be soluble in the epoxy resin, additional solvents such as *m*-cresol have been needed to render their mutual solubility before curing [32]. This complicates the curing process, as the solvent has to be removed in a controlled manner. In addition, the conventional basic (aminic) hardeners of epoxy resins cannot be used in the context of conjugated PANI-salts, as they induce dedoping of the latter. Therefore BF_3-based Lewis acids have been used which is less attractive for commodity applications [25,32,33]. Now it becomes relevant that also the unprotonated i.e. nonconducting emeraldine base (EB) form of PANI is feasible in anticorrosion coatings, especially under mild conditions [34–42]. In this case, the conventional aminic hardeners can be used, but there still exists the problem that EB is not soluble in epoxy resins. This forbids directly using the Meijer-type [17–21] reactive solvent approach using the oligomeric epoxy DGEBA as a solvent. Note that EB is soluble in selected bases such as *N*-methyl pyrrolidone (NMP) [43].

In this work, aminic oligomers *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine (DAB-AM-4) and trimethylhexanediamine (TMDA) are observed to dissolve EB at low concentrations, and act also as hardeners of epoxy. Therefore they allow reactive solvent approach to prepare cross-linked EB/epoxy composites upon adding the DGEBA component, see Fig. 1(a). For comparison, exactly similar net compositions are studied where EB is first dispersed in DGEBA, where no trace of solubility is observed, and subsequently cured by adding TMDA, see Fig. 1(b). The feasibility in corrosion prevention applications is assessed by investigating corrosion front propagation and electrochemical impedance spectroscopy in aqueous saline solutions.

2. Experimental section

2.1. Materials and blend preparation

Generation 1 polypropyleneimine tetraamine dendrimer *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine (DAB-AM-4), see Fig. 2(a), and generation 2 polypropyleneimine octaamine dendrimer 4,17-bis(3-aminopropyl)-8,13-bis[3-[bis(3-aminopropyl)-amino]propyl]-4,8,13,17-tetraazaeicosane-1,20-diamine] (DAB-AM-8) were provided by Aldrich. Also ethylenediamine ($H_2N–C_2H_4–NH_2$), diethylenetriamine ($H_2N–C_2H_4–NH–C_2H_4–NH_2$), triethylenetetramine ($H_2N–(C_2H_4–NH)_2–C_2H_4–NH_2$), tetraethylenepentamine ($H_2N–(C_2H_4–NH)_3–C_2H_4–NH_2$), and pentaethylenehexamine ($H_2N–(C_2H_4–NH)_4–C_2H_4–NH_2$) were provided by Aldrich. Commercial trimethylhexanediamine (TMDA), see Fig. 2(b), and standard liquid-like diglycidyl ether of bisphenol-A epoxy resin (DGEBA) ($M_w = 380$ g/mol) were also used. Reagent grade sodium chloride was obtained from Baker.

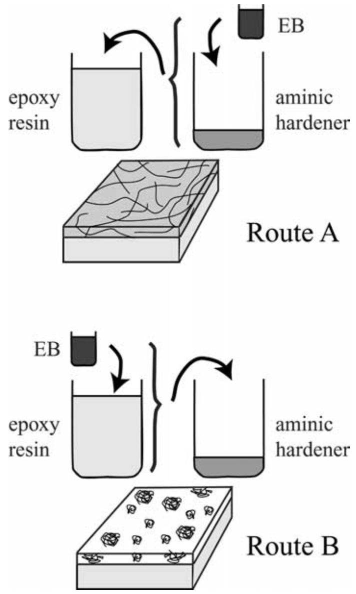

Fig. 1. Schematic illustration of the used concepts. (a) *Route A:* Aminic hardeners are identified which dissolve EB at low concentrations and which, therefore, efficiently disperse EB at higher concentrations. The EB/hardener mixture is subsequently cross-linked by adding the epoxy resin. (b) *Route B:* Mixing EB first in epoxy resin leads to macroscopic phase separation unless an additional solvent is used. The macroscopically phase separated morphology remains after adding the basic hardener to EB/epoxy mixture and cross-linking.

The emeraldine base polyaniline, see Fig. 2(c), was provided Panipol Oy: Polyaniline Batch EB122 ($M_w = 50{,}000$ g/mol) was used in the compositions containing

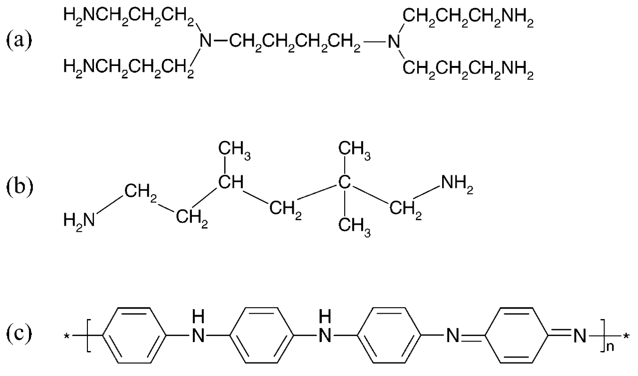

Fig. 2. (a) *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine (DAB-AM-4). (b) Trimethylhexanediamine (TMDA). (c) Emeraldine base (EB) form of PANI.

DAB-AM-4 and DAB-AM-8 whereas Batch R01 ($M_n = 25{,}400$, $M_w = 140{,}000$ g/mol) was used for other compositions. The molecular weights for R01 were given information from supplier and for EB122 determined using GPC using NMP and PS standards, as in Ref. [44].

The solubility of EB in DAB-AM-4, DAB-AM-8, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and trimethylhexanediamine was studied by adding EB slowly until a net concentration of 0.5 wt% was reached, followed by mixing 7 days using a magnetic stirrer. The solubility was qualitatively inspected using optical microscope.

As suggested by the results of the above solubility tests, DAB-AM-4 and TMDA were selected for closer investigation to prepare cured EB/DGEBA/DAB-AM-4 and EB/DGEBA/TMDA composites. For the first one, the above-mentioned 0.5 wt% EB/DAB-AM-4 solution was cross-linked by adding DGEBA using the weight fraction DGEBA/DAB-AM-4 190/40 w/w. This leads to net EB concentration of 0.1 wt% in the cured EB/DGEBA/DAB-AM-4 composite. DGEBA was added in the following way: 2 min of mixing with a glass rod, 5 min of waiting, 2 min of mixing with a glass rod, 1 min of waiting and the paint was applied on a steel panel (Q-Panel Lab Products, Inc, size 0.8 mm × 102 mm × 152 mm) using a paint applicator with a 200 μm gap. The coatings were cured at 60 °C for 24 h. EB/DGEBA/TMDA compositions were prepared in principle similarly but in this case EB concentrations 0, 0.5 and 1.0 wt% in the cured composite were used. For curing, the weight ratio of TMDA and epoxy was fixed to be 40:190 in all compositions. To obtain 1 wt% of EB in the final EB/DGEBA/TMDA composite, a relatively high EB concentration of 5.8 wt% had to be used in the EB/TMDA mixtures. Obtaining homogeneous mixtures at such high concentrations was challenging due to the intractability of EB using simple magnetic stirring device and flask. In further studies more efficient mixers and process optimization is required. Correspondingly, 2.9 wt% of EB was first dissolved/dispersed in TMDA to render the concentration 0.5 wt% in the final cured composite. Also in these cases, EB was slowly added in TMDA and mixed using a magnetic stirrer for 7 days. DGEBA was added as described before with a glass rod and the paint was applied on a steel panel. Paint applicator with a 200 μm gap was used for the corrosion front propagation tests and with 60 μm for electrochemical impedance spectroscopy. The paint coatings were cured at 60 °C for 24 h. In this work, the above concept where EB is first dissolved in the aminic hardener and subsequently cured by added DGEBA is denoted as *Route A*.

Reference compositions with similar net compositions (0, 0.5, and 1.0 wt% of EB in the cured EB/DGEBA/TMDA compositions) were prepared by first dispersing EB in DGEBA using magnetic stirrer during 7 days and subsequently curing the compositions using TMDA. This concept is denoted here as *Route B*.

2.2. Characterization

The feasibility of the coatings was first qualitatitively studied by preparing controlled scratches on the cured EB/DGEBA/TMDA-coated steel panels and subsequently investigating propagation of the corrosion front upon immersing in an aqueous 3.5% NaCl solution. The back side and edges of the test panels were protected with a solvent-free commercial transparent epoxy lacquer from Teknos Oy. Controlled scratches of width of 1.0 mm and length of 5 cm were prepared using a multifunction scratching machine from Braive Instruments on the front sides of the panels and imaged using a digital camera. Separate plates were removed from the immersion tests after 1, 3, 7 or 17 days and pictures of the scratches were taken with a digital camera. The average width of the scratch was determined using digital image analysis with a custom Matlab based program. The averaged difference between the original width of the scratch and the width as a function of time was called the propagation of the corrosion front.

Electrochemical impedance spectroscopy (EIS) was performed as a function of time in aqueous 3.5% NaCl solution at open circuit potential (OCP). Film thickness was 60 μm. Both pure epoxy coating and coating containing 1.0 wt% EB prepared using *Route A* were studied. Three parallel samples were studied of each type. The coatings were not scribed before the test. The frequency range was from 100 kHz to 10 mHz and the amplitude was ±70 mV. Working electrode area was 20 cm^2, a platinum plate was used as counter electrode and saturated calomel electrode (SCE) as a reference electrode. All potentials are referenced to SCE.

3. Results and discussion

Aminic hardeners of DGEBA were searched that dissolve EB. To first set the background, EB at rather low concentration 0.5 wt% was mixed in *N*-methyl pyrrolidone using magnetic stirring and after 7 days an almost particle-free mixture was observed in an optical microscope. This agrees with the well-known observation that EB is soluble in NMP [43]. Next we selected amines that potentially could dissolve EB and also cure epoxy resins, i.e. ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, trimethylhexanediamine, and dendrimeric DAB-AM-4 and DAB-AM-8. In each case, 0.5 wt% of EB was slowly added and mixed for 7 days using a magnetic stirrer in a flask. It, however, turned out that EB was not soluble in most of the above amines, as revealed by optical microscopy where hard walled large aggregates within only mildly colored background were observed. However, three amines seemed more promising, i.e. the dendrimeric DAB-AM-4, tetraethylenepentamine and trimethylhexanediamine (TMDA) (see Fig. 3(a) and (c)). All of them showed in optical

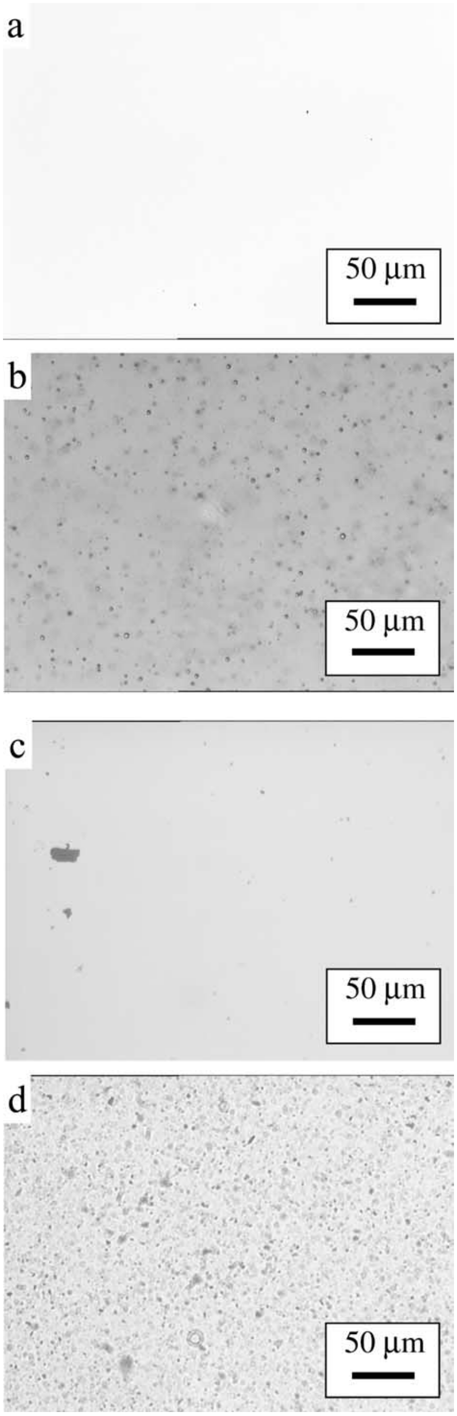

Fig. 3. Optical micrographs (a) 0.5 wt% EB in DAB-AM-4 stirred for 7 days. (b) The corresponding cured epoxy composite which contains 0.1 wt% of EB upon adding DGEBA. Note that closer inspection shows that most of the dark spots are in fact air bubbles and not phase separated EB. (c) 0.5 wt% EB in TMDA stirred for 7 days. (d) The corresponding cured epoxy composite which contains 0.1 wt% of EB upon adding DGEBA.

microscopy only few individual undissolved particles in uniformly blue background, suggesting relatively good solubility. However, during extended mixing, tetraethylenepentamine had a tendency for increased aggregation and therefore only DAB-AM-4 and TMDA were selected for closer inspection.

To preliminarily investigate the effect of curing on the morphology, DGEBA was added in the above 0.5 wt% solutions of EB/DAB-AM-4 and EB/TMDA and cured at 60 °C for 24 h. The relation between the hardener and DGEBA was fixed as 190/40 w/w. Also the cured composites were under visual inspection homogeneously blue, even if in optical microscopy the cross-linking had induced slight phase separation, see Fig. 3(b) and (d). Note that it can be expected that phase separation of PANI does take place during the curing process because the molecular weight of the solvent medium increases towards infinity. On the other hand, the extent of phase separation can be 'topologically' limited due to formation of the cross-link sites. In this case, the actual morphology would depend on the details of the processing conditions. Even if the cured compositions, see Fig. 3(b) and (d), cannot be claimed completely homogeneous, they were encouraging, in particular as no process optimization was needed. Further investigations showed that cured EB/DGEBA/DAB-AM-4 rendered hard and brittle coatings that were susceptible to delamination in the immersion tests, and therefore only TMDA was considered as potential candidate for more detailed corrosion tests.

Next, feasibility to construct composites with considerably higher EB concentration in the final cured composition was inspected after first mixing higher concentrations of EB in TMDA. Even if 0.5 wt% EB/TMDA mixtures were essentially particle-free, 2.9 wt% mixtures showed clear undissolved but soft-walled particles and 5.8 wt% mixtures were in microscopy rather unhomogeneous (see Fig. 4(a)), although under visual inspection the mixture still appeared homogeneous. Also the cured composites appear rather homogeneous and bright blue to the naked eye. In optical microscopy, however, some phase separation can be seen in the cured composition (Fig. 4(b)).

Cured EB/DGEBA/TMDA-coated steel plates having controlled scratches were immersed in aqueous 3.5% NaCl solutions to investigate propagation of the corrosion fronts that start from the scratches.

The scratches were made with a 1.0 mm wide tool but due to the brittleness of the coating the scratches were actually slightly wider (see Fig. 5(a)). After 1, 3 or 7 days selected plates were removed from the solution for inspection whereas the other plates remained in the solution, until the last plates were removed from the solution after 17 days. The average widths of the scratches before and after stopping the tests after different immersion times (see e.g. Fig. 5(b)) were analyzed using digital image processing for each test plate. It must be emphasized that the actual corrosion front is the thick dark line in the middle in Fig. 5(b) surrounded by an area where reaction products have been accumulated. After one and three days immersion the initial scratch was not fully corroded in some of the samples. In addition, dark reaction products near the

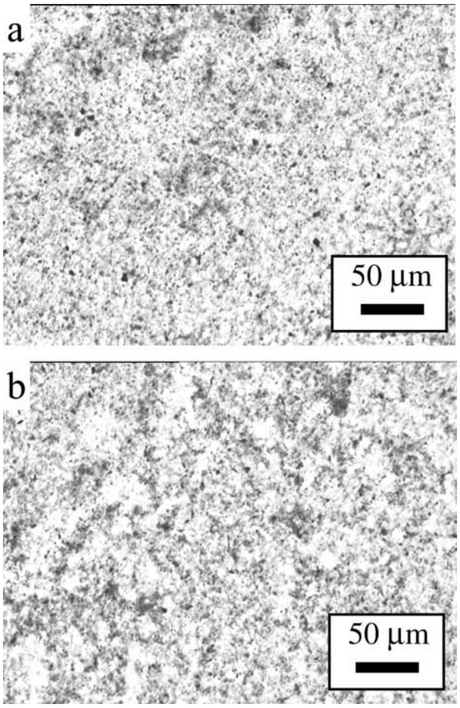

Fig. 4. Optical micrographs for (a) 5.8 wt% EB in mixed TMDA and stirred for 7 days and (b) the corresponding cured EB/DGEBA/TMDA composite which contains 1.0 wt% of EB.

corrosion front hindered the evaluation of scratch width for short immersion times, and thus data for one and three-day immersion cannot be reliably presented. The propagation of corrosion front is presented in Fig. 6(a). It shows that in the cured DGEBA/TMDA composite with no EB, considerable progression of corrosion front took place during 17 days, as the average width of the scratches was doubled. Adding 0.5% EB using *Route A* caused slightly reduced propagation whereas 1.0% EB showed drastically reduced propagation.

For comparison, the similar final net compositions of the cured composites were made using different order where EB was first dispersed in DGEBA in which case no solubility was observed and thereafter cured upon adding TMDA, i.e. *Route B*. In this case, the propagation of the corrosion front was in all cases equally rapid as in the cured DGEBA/TMDA composite with no EB, see Fig. 6(b). This could be expected because in this case PANI is in large aggregated particles that are far apart from each other and there is no active material between them.

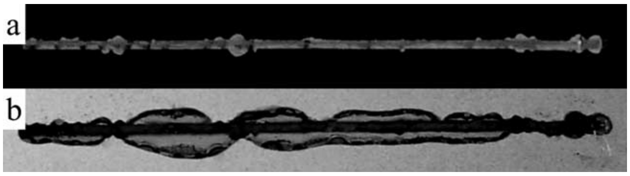

Fig. 5. Photographs of scratches on the cured 1 wt% EB/DGEBA/TMDA samples made using *Route A*. (a) Before the immersion test. The coating is dark. (b) After immersing 17 days in 3.5% NaCl the coating has been removed and the average width of the scratch is wider than in the beginning.

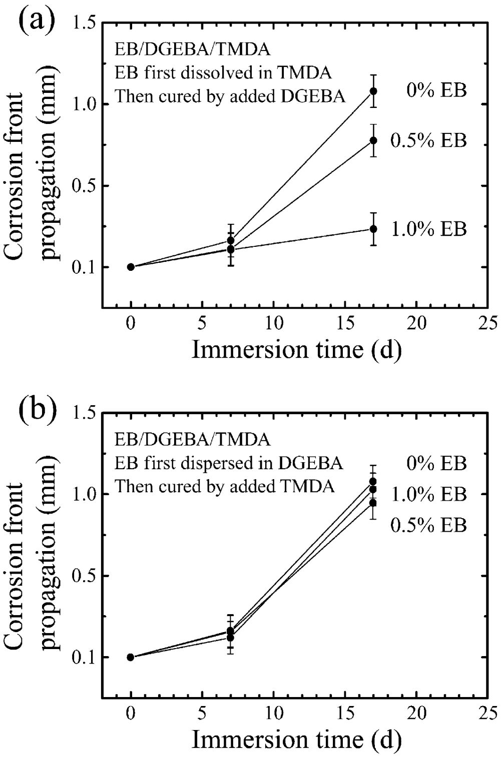

Fig. 6. Propagation of corrosion front in immersion test in 3.5% NaCl solution. (a) *Route A* where EB is first dissolved/dispersed in TMDA and subsequently cured by added DGEBA. (b) *Route B* where EB is first dispersed in DGEBA without any solubility and subsequently cured by added TMDA. The net compositions in the final cured blends are exactly the same.

Another qualitative observation was made in connection with electrochemical impedance spectroscopy from longer immersion tests in aqueous 3.5% NaCl solution where cured DGEBA/TMDA and cured 1.0% EB/DGEBA/TMDA coatings by *Route A* were prepared on steel panels (Q-Panel). In the beginning, there were no clear detectable defects or imperfections. After a few months immersed in 3.5% NaCl, the reference coating consisting cured DGEBA/TMDA reference without EB began to fail and corroded areas were observable. Within the same time period, the corresponding cured 1% EB/DGEBA/TMDA coatings did not have any visible damage.

In summary, this qualitative observation and the systematic investigations of the corrosion front propagation in aqueous 3.5% NaCl solutions indicate that the propagation of corrosion is considerably suppressed in samples made using *Route A*.

Pure DGEBA/TMDA and 1.0% EB/DGEBA/TMDA cured coatings as prepared by *Route A* on steel panels (Q-Panel) were studied using electrochemical impedance spectroscopy in aqueous 3.5% NaCl solution. A perfect coating without any imperfections is an electrical insulator, and electrochemical impedance studies cannot therefore be performed within a reasonable period of time. In this case, a few minor imperfections were observed in some of the coatings at the preparation stage, which turned useful as they enabled direct electrochemical contact between the steel surface and solution, and thus allowed electrochemical impedance studies. As an indication of such solution contact, the open circuit potentials (OCP) of these coatings were clearly in the active range.

The first colour change in the pure epoxy coating was seen already after two weeks. Despite the fact that both the OCP and impedance of this coating started rising as a function of immersion time, see Fig. 7(a) and (b), growing rust spots on the metal surface and partial delamination of the coating were observed as the immersion continued. Finally, the pure epoxy coating was completely delaminated after about 100 days immersion time and the metal surface was covered with rust.

The OCP of 1% EB/DGEBA/TMDA was around −700 mV in the beginning of the immersion test. Impedance was also quite low. During about three months immersion time the total impedance increased to the level of 10^4 MΩ* cm, see Fig. 7(b). After that the OCP rose to about −200 mV, see Fig. 7(a). Both impedance and OCP remained stable for a long time thereafter. Importantly, the imperfections in the coating did not grow bigger and no rust was observed as can be expected from the high impedance and OCP values. A more detailed analysis of the impedance spectra will be presented elsewhere [45].

The impedance of 1% EB/DGEBA/TMDA increased substantially during immersion. Normally this kind of increase in impedance is attributed to the formation of a protecting layer on the metal surface [46]. The increase of the potential to passive range is another indication of electrical interaction between EB and steel. In this kind of environment, the addition of EB to the epoxy matrix is clearly favorable. This effect can be reached with a very small amount of EB when polyaniline is sufficiently homogeneously distributed, as seems to be the case using the *Route A*. The results confirm that EB is not just a barrier material but it is actively preventing corrosion of steel. The mechanism of protection is probably mainly due to electron transfer resulting in the formation of a charged interface or reaction product layer between EB and steel.

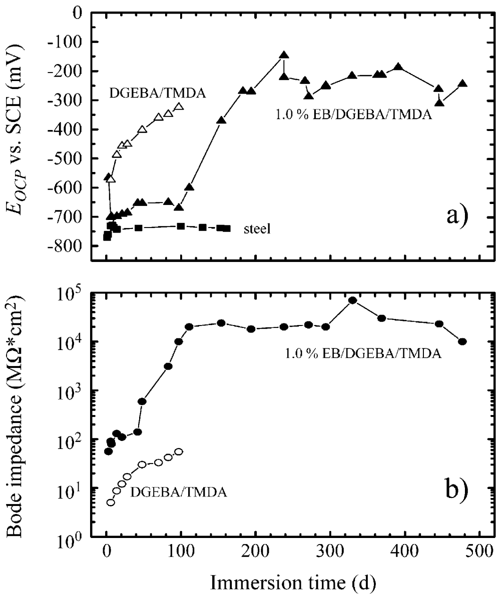

Fig. 7. (a) Open circuit potential for pure DGEBA/TMDA and 1.0% EB/DGEBA/TMDA as prepared using *Route A* on steel in 3.5% NaCl. Open circuit potential for steel is also presented. (b) Total impedance at low frequency region for DGEBA/TMDA and 1.0% EB/DGEBA/TMDA.

We finally point out that after these qualitative findings, it becomes important to develop the process conditions, such as to study more powerful mixing techniques to dissolve/disperse EB in TMDA more homogeneously and to achieve higher concentrations. In addition, the phase separation kinetics could be monitored using light scattering, even if the strongly absorptive nature of PANI may provide considerable difficulties. The final comment is that after completing this work [47] we learned on a related study, where tetraethylenepentamine was used in the corresponding manner [29]. In our studies, TMDA seemed more encouraging, however.

4. Conclusions

We identified aminic solvents of the emeraldine base (EB) form of PANI that are at the same time hardeners for DGEBA epoxy resin. Suitable compounds are *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine and trimethylhexanediamine. Reverting the conventional order of preparation, the EB/TMDA-mixture can be cured by adding DGEBA. As little as 1% EB in such compositions suppresses the propagation of corrosion front considerably in mild aqueous conditions in comparison to similar samples where EB is in poorly dissolved aggregates. In electrochemical impedance studies, the increase of both the potential and impedance values showed the positive effect of EB.

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References

[1] Skotheim TA, Elsenbaumer RL, Reynolds JR. Handbook of conducting polymers. New York: Marcel Dekker, Inc; 1998.

[2] Wallace GG, Spinks GM, Teasdale PR. Conductive electroactive polymers; Intelligent materials systems. Lancaster: Technomic Publishing, Co; 1997.
[3] Yoshino K, Nakajima S, Sugimoto R-I. Jpn J Appl Phys 1987;26(6): L1038–9.
[4] Wenzel M, Ballauff M, Wegner G. Makromol Chem 1987;188(12): 2865–73.
[5] Helmer-Metzmann F, Ballauff M, Schulz RC, Wegner G. Makromol Chem 1989;190(5):985–94.
[6] Winokur MJ, Spiegel D, Kim YH, Hotta S, Heeger AJ. Synth Met 1989;28(1-2):C419–26.
[7] Leclerc M, Martinez Diaz F, Wegner G. Makromol Chem 1989; 190(12):3105–16.
[8] Vahlenkamp T, Wegner G. Makromol Chem Phys 1994;195(6): 1933–52.
[9] Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, et al. Nature 1999;401(6754):685–8.
[10] Pron A, Rannou P. Prog Polym Sci 2002;27(1):135–90.
[11] Wernet W, Monkenbusch M, Wegner G. Makromol Chem, Rapid Commun 1984;5(3):157–64.
[12] Cao Y, Smith P, Heeger AJ. Synth Met 1992;48(1):91–7.
[13] Zheng W-Y, Wang R-H, Levon K, Rong ZY, Taka T, Pan W. Makromol Chem Phys 1995;196(8):2443–62.
[14] Kosonen H, Ruokolainen J, Knaapila M, Torkkeli M, Jokela K, Serimaa R, et al. Macromolecules 2000;33(23):8671–5.
[15] Ikkala O, ten Brinke G. Science 2002;295(5564):2407–9.
[16] Dufour B, Rannou P, Djurado D, Janeczek H, Zagorska M, de Geyer A, et al. Chem Mater 2003;15(8):1587–92.
[17] Venderbosch RW, Meijer HEH, Lemstra PJ. Polymer 1994;35(20): 4349–57.
[18] Venderbosch RW, Meijer HEH, Lemstra PJ. Polymer 1995;36(15): 2903–13.
[19] Venderbosch RW, Meijer HEH, Lemstra PJ. Polymer 1995;36(6): 1167–78.
[20] Goossens JGP, Rastogi S, Meijer HEH, Lemstra PJ. Polymer 1998; 39(25):6577–88.
[21] Jansen BJP, Meijer HEH, Lemstra PJ. Polymer 1999;40(11):2917–27.
[22] DeBerry DW. J Electrochem Soc 1985;132(5):1022–6.
[23] Kinlen PJ, Silverman DC, Jeffreys CR. Synth Met 1997;85:1327–32.
[24] McAndrew TP. Trends Polym 1997;5(1):7–12.
[25] Talo A, Passiniemi P, Forsén O, Yläsaari S. Synth Met 1997;85: 1333–4.
[26] Sitaram SP, Stoffer JO, O'Keefe TJ. J Coat Technol 1997;69(866): 65–9.
[27] Lu W-K, Basak S, Elsenbaumer RL. In: Skotheim T, Elsenbaumer RL, Reynolds JR, editors. Corrosion inhibition of metals by conductive polymers. Handbook of conducting polymers. New York: Marcel Dekker, Inc; 1998. p. 881–920.
[28] Wessling B. J Corrosion Sci Eng 1999;1. http://www2.umist.ac.uk/corrosion/JCSE/Volume1/paper15/v1p15.html.
[29] Wang X-H, Li J, Zhang J-Y, Sun Z-C, Yu L, Jing X-B, et al. Synth Met 1999;102:1377–80.
[30] Talo A, Forsén O, Yläsaari S. Synth Met 1999;102:1394–5.
[31] Dominis AJ, Spinks GM, Wallace GG. Prog Org Coat 2003;48(1): 43–9.
[32] Peltola J, Cao Y, Smith P. Adhesives Age 1995;38(5):18–20.
[33] May CA. Epoxy resins: chemistry and technology. 2nd ed. New York: Marcel Dekker, Inc; 1988.
[34] Wei Y, Wang J, Jia X, Yeh J-M, Spellane P. Polymer 1995;36(23): 4535–7.
[35] Fahlman M, Jasty S, Epstein AJ. Synth Met 1997;85:1323–6.
[36] Brusic V, Angelopoulos M, Graham T. J Electrochem Soc 1997; 144(2):436–42.
[37] Fahlman M, Guan H, Smallfield JAO, Epstein AJ. 56th Ann Tech Conf–Soc Plast Eng 1998;2:1238–41.
[38] Ahmad N, MacDiarmid AG. Synth Met 1996;78:103–10.
[39] Liu L-M, Levon K. J Appl Polym Sci 1999;73:2849–56.
[40] Mirmohseni A, Oladegaragoze A. Synth Met 2000;114:105–8.
[41] Wang J. Synth Met 2002;132:53–6.
[42] Lu JL, Liu NJ, Wang XH, Li J, Jing XB, Wang FS. Synth Met 2003; 135-136:237–8.
[43] Angelopoulos M, Ray A, MacDiarmid AG, Epstein AJ. Synth Met 1987;21(1):21–30.
[44] Tiitu M, Volk N, Torkkeli M, Serimaa R, ten Brinke G, Ikkala O. Macromolecules 2004;37(19):7364–70.
[45] To be submitted.
[46] Park JR, MacDonald DD. Corros Sci 1983;23(4):295–315.
[47] Tiitu M, Talo A, Blomqvist K, Jussila M, Ikkala O. US Patent 6500544 B1, 2002.