Effect of the NCO/OH Molar Ratio on the Physical Aging and on the Electrochemical Behavior of Polyurethane-Urea Hybrid Coatings

Mara Cristina Lopes de Oliveira[1], Renato Altobelli Antunes[2,], Isolda Costa[3]*

[1] Electrocell Ind. Com. Equip. Elet. LTDA, Technology, Entrepreneurship and Innovation Center (CIETEC), 05508-000 São Paulo-SP, Brazil
[2] Engineering, Modeling and Applied Social Sciences Center (CECS), Federal University of ABC (UFABC), 09210-170, Santo André-SP, Brazil,
[3] IPEN/CNEN-SP, Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, SP, Brazil
[*]E-mail: Renato.antunes@ufabc.edu.br

Low volatile organic compounds (VOCs) coatings are increasingly attractive due to both environmental concerns and high protective performance. High solid systems play a central role in this scenario. In this work, 100% solids polyurethane-urea hybrid coatings have been prepared. The coatings were prepared using methylene diphenyl ***diisocyanate*** (MDI) for the synthesis process and different NCO/OH molar ratio. The effects of the structural characteristics on the physical aging behavior and on the electrochemical response of the hybrid coatings were evaluated using differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS). The results showed that the coating with the highest NCO/OH ratio presented the best combination of properties, showing low susceptibility to physical aging and high corrosion resistance.

1. INTRODUCTION

The increasing demand for high chemical and mechanical resistance associated with more restrictive environmental regulations have driven the development of new coating systems in the paint industry over the last two decades [1,2]. Low volatile organic compound (VOC) emission has become a must-attend issue for contemporary coating systems [3]. Waterborne and high solids coatings have emerged as the main technological targets in this scenario [4,5].

Polyurethanes (PU) are a versatile class of polymer considered as indispensable components in coatings due to the possibility of tailoring properties according to the application [6]. Several authors have explored the design of different molecular architectures for the PU backbone in order to achieve specific characteristics such as flexibility, thermal stability and corrosion resistance [7,8]. The chemistry of polyurethane coatings is extensively known. These polymers are obtained by reacting a polyol with an isocyanate in the presence of a suitable catalyst. The specific isocyanate and polyol used in the synthesis process determine the properties of the final product [9]. Isocyanates are characterized by the NCO chemical group and are related to hard segments on polyurethane polymer molecules. Polyols are OH containing groups and account for the soft segments of the polymer molecule [10]. Polyurea coatings are produced from the reaction of an isocyanate group with a polyamine (amine-terminated resin). They are chemically related to polyurethanes with the difference that the curing component is not a hydroxyl containing group. The presence of amine as a reactant makes the curing of polyureas faster than that of polyurethanes [11]. Polyurethane-urea hybrid coatings are a subclass of polyurethanes. They are produced when diamines or water are used as chain extenders during the synthesis process [12]. The interest in this type of coating resides in the fact that improved mechanical properties have been reported in comparison with conventional polyurethanes, thus enhancing the overall performance of the organic film [13].

The performance of polyurethane and polyurethane-urea hybrid coatings depends on the type of diisocyanate and on the NCO/OH molar ratio [14,15]. Negim et al. [16] showed that tensile strength, hardness and tear strength of water dispersion polyurethanes increased with the NCO/OH ratio whereas the elongation at break and viscosity decreased. Mishra et al. [15] observed that the thermal stability of PU-based coatings was also improved for higher NCO/OH ratios. This behavior is associated with the enhanced formation of molecular groups such as allophanate or biurate linkages along with the urethane/urea hard components [17]. Although the structure-property relationship of polyurethane and polyurethane-urea coatings has received much attention in the literature, investigations on the effect of structural parameters on the electrochemical behavior of these materials are scarce.

Physical aging is a fundamental phenomenon concerning the physical stability of organic coatings. It is defined as a spontaneous relaxation process of a coating taking place in its glassy state [18]. It is time-dependent process spanning from days to months. Aging results in the densification of the organic film, thus influencing several physical properties such as permeability, enthalpy and entropy which decrease as the phenomenon evolves [19]. Differential scanning calorimetry (DSC) is a powerful technique to study the physical aging of polymeric materials as it gives direct information about the enthalpy relaxation resulting from this process [20]. In spite of the relevance of this phenomenon to the performance of thermosetting coatings, it has been hardly investigated for polyurethane-urea systems. Furthermore, the correlation of physical aging with the corrosion protection ability of organic films is not encountered in the literature.

This work aims to fulfill this gap by investigating the physical aging and corrosion behavior of polyurethane-urea coatings synthesized using MDI as diisocyanate and with different NCO/OH molar ratios. Electrochemical impedance spectroscopy (EIS) was used to investigate the corrosion response of the different coating systems upon immersion in a saline solution for up to 100 days. The aging

behavior was studied using DSC. The coatings were further characterized by Fourier transform-infrared spectroscopy (FTIR) and thermogravimetric analysis in order to give a detailed assessment of their structure and thermal stability.

2. EXPERIMENTAL

2.1 Materials

Methylene diphenyl diisocyanate (MDI) and polytetramethylene glycol (PTMEG; molecular weight = 1000 g.mol^{-1}) were supplied by Basf. Diethyltoluene diamine (DEDTA, supplied by Brenntag Brasil) was used as both curing agent and chain extender. The coatings produced in this work are 100% solid films and, thus, no solvents were used in the synthesis process.

2.2 Preparation of the polyurethane-urea hybrid coatings

In the first step, a NCO-terminated prepolymer was prepared by carrying out the reaction in a 500 mL three necked round bottom flask equipped with a thermometer, dropping funnel and by continuously purging with nitrogen flow. The reaction was carried out over a digital magnetic heating/stirrer instrument. Initially, a fixed weight of PTMEG was heated at 45 ºC to melt inside the round botton flask. MDI was added drop-wise through a dropping funnel to the flask at 60 ºC and the addition was continued for 30–40 min. After complete addition, the reaction was carried out for another 2 h at 70 ºC. Next, the reaction was completed by adding a blend of PTMEG and DETDA to the prepolymer at specific concentrations to achieve the polyurethane-urea hybrid coatings with NCO/OH molar ratios of 0.8, 1.0 and 1.2. The nomenclature of the different coatings was given based on the initial letter of the diisocyanate used in the synthesis process, followed by the NCO/OH molar ratio as a subscript number. Thus, the coating designated as M$_{0.8}$ is referred to the film produced using MDI as diisocyanate and with a NCO/OH molar ratio of 0.8.

2.3 Characterization methods

Infrared analysis of the different coatings was conducted using Shimadzu FTIR8201PC equipment. The samples for the FTIR analysis were translucent films casted onto glass plates before curing. After curing, the films were removed from the plate and submitted to the FTIR analysis. The spectra were determined over the range of 4000-400 cm^{-1}. Thermal stability of the different coatings was assessed using thermogravimetric analysis (TGA). The measurements were carried out in a Shimadzu TGA50 under nitrogen atmosphere in the temperature range 20 ºC-600 ºC using a heating rate of 10 ºC.min^{-1}. The weight of the samples was approximately 8 mg.

Samples of the different coatings were aged in a kiln at 80 ºC for 1, 2, 3, 8 and 10 days under static air. The physical aging behavior of each sample was investigated using DSC. The measurements

were carried out in a Shimadzu DSC60 equipment at a heating rate of 10 ºC.min^{-1} from 30 ºC to 300 ºC under synthetic air.

The electrochemical behavior of the different coatings was assessed using EIS. The measurements were performed in a Autolab PGSTAT100 potentiostat/galvanostat equipped with a frequency response analyser (FRA) module. The tests were conducted using a three-electrode cell arrangement with a platinum wire as auxiliary, standard calomel electrode (SCE) as reference and polyurethane-urea coated SAE 1020 carbon steel as the working electrode. All tests have been conducted in naturally aerated NaCl 3.5 wt.% solution at room temperature. All results were obtained in potentiostatic mode and at the corrosion potential (E_{corr}). The amplitude of the perturbation signal was 10 mV, and the investigated frequency range was from 100 kHz to 2Hz with an acquisition rate of 12 points per decade. The electrochemical behaviour was evaluated until 100 days of immersion.

Additionally, the capacitance variation with immersion time was evaluated as a means of estimating the water uptake of the coating as a function of the immersion time. It is reported that the capacitance of an organic film increases when it absorbs water [21]. The capacitance value was determined based on the procedure proposed by Castela et al. [22]. The capacitance values were calculated using equation (1), where C is the capacitance, f is the frequency and Z" the imaginary impedance value at each specific frequency.

$$C = 1/2\pi f Z" \quad (1)$$

By plotting the capacitance versus frequency it is possible to evaluate the trend to a limiting capacitance value as the frequency increases. An approximately constant capacitance value may be determined. This stable value may then be used as a reference to compare coatings water absorption at different immersion periods. In this work the reference capacitance value was taken at 48 kHz.

3. RESULTS AND DISCUSSION

3.1 FTIR analysis

Figure 1 shows FTIR spectra of the polyurethane-urea hybrid coatings with different NCO/OH ratios. Strong absorption bands in the frequency range between 4000 cm^{-1} and 2500 cm^{-1} are associated with stretching vibrations resulting from the bonding between hydrogen and other atoms with low mass [23]. O-H and N-H stretching vibrations in polyurethane-urea hybrid coatings can be found in this region [24]. The strong band between 2000 and 2500 cm^{-1} is due to stretching vibrations of the NCO urethane group, associated with the presence of some unreacted NCO in the organic film [25]. It is seen that the most intense bands in this region occur for the film with the highest NCO/OH ratio. These bands are present in the spectra of all the samples, independently of the NCO/OH ratio. Stretching vibrations of the C=O carbonyl group of the urethane bond can be found in the region between 1700 and 2000 cm^{-1} [26].
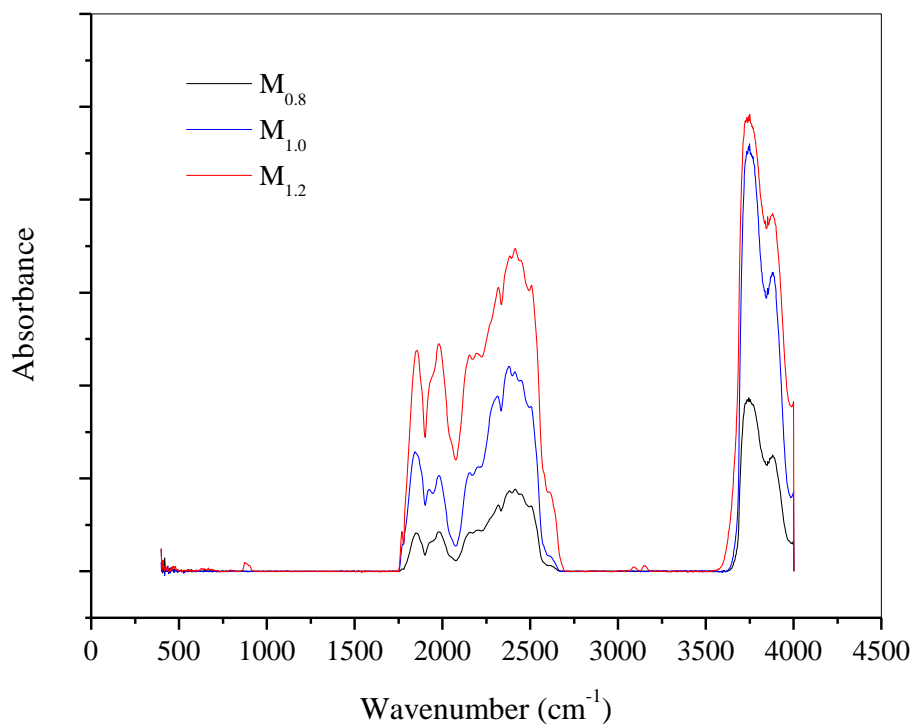
Figure 1. FTIR spectra of the polyurethane-urea hybrid coatings produced using MDI as diisocyanate with different NCO/OH ratios.

3.2 Thermal stability

TGA thermograms of the polyurethane-urea hybrid coatings are shown in Fig. 2. The thermal decomposition occurs in two stages. James and Jayakrishnan [27] have also observed a two-step decomposition profile in the TGA thermograms of a polyurethane-urea elastomer. The thermograms in Fig. 2 are similar, indicating that the thermal stability was little affected by the NCO/OH molar ratio. The literature presents variable data on the thermal stability of polyurethanes and polyurethane-urea coatings due to the wide variety of systems that can be synthesized depending on the isocyanate, polyol, curing agent and chain extenders that can be used. Zevenhoven [28] reports that the initial thermal decomposition of polyurethane elastomers is in the range of 110 ºC to 270 ºC, depending on the composition and method of analysis. According to Monteavaro et al. [29] the urethane bond is relatively unstable and its dissociation occurs between 150-220 ºC. In this work, the initial decomposition temperature was approximately 320 ºC for the coatings with NCO/OH ratios of 0.8 and 1.0 and 330 ºC for the coating with NCO/OH ratio of 1.2. MDI-based systems are reported to have good thermal stability due to the high chemical functionality of MDI which leads to higher crosslinking density [30].
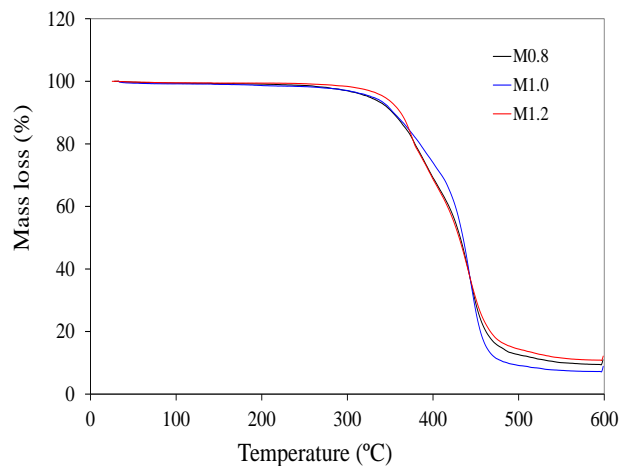
Figure 2. TGA thermograms of polyurethane-urea hybrid coatings with different NCO/OH ratios.

3.3 Physical aging

DSC thermograms (heat flow versus temperature) of the polyurethane-urea hybrid coatings with different NCO/OH ratios and aged at 80 ºC under static air for different aging times are shown in Fig. 3. Van der Linder et al. [31] described the quantification of physical aging of organic films through DSC measurements. The analysis is based on the enthalpy relaxation (endothermic peak) that represents the decrease of enthalpy (ΔH) during physical as the sample is heated after being aged. The value of ΔH is associated with the neat endothermic peak area and can be easily determined using the software that controls the DSC equipment. An increase of the endothermic peak area with aging time denotes that the coating is susceptible to physical aging.

The results shown in Fig. 3 evidenced that the thermograms of the $M_{1.2}$ coating did not present any endothermic peak. This indicates that this material was not susceptible to physical aging under the testing conditions employed in this work. The $M_{0.8}$ and $M_{1.0}$ coatings, in turn, presented endothermic peaks with a maximum at around 247 ºC for all the aging times. It is noteworthy, though, that the area of these peaks was not significantly altered with aging. Hence, in spite of the higher susceptibility to thermal decomposition in comparison with the $M_{1.2}$ coating, $M_{0.8}$ and $M_{1.0}$ were also little affected by physical aging. The absence of enthalpy relaxation associated with the thermogram of the $M_{1.2}$ coating demonstrates that physical aging of the polyurethane-urea hybrid coatings tested in this work becomes lessened for increasing NCO/OH ratios. This result corroborates those obtained by TGA which showed that the highest thermal stability was achieved for the $M_{1.2}$ film. The increase of the NCO/OH ratio in the pre-polymer leads to a higher content of hard segments in the molecule of the polymeric film, thus leading to improved thermal stability and resistance to deterioration by physical aging [17].
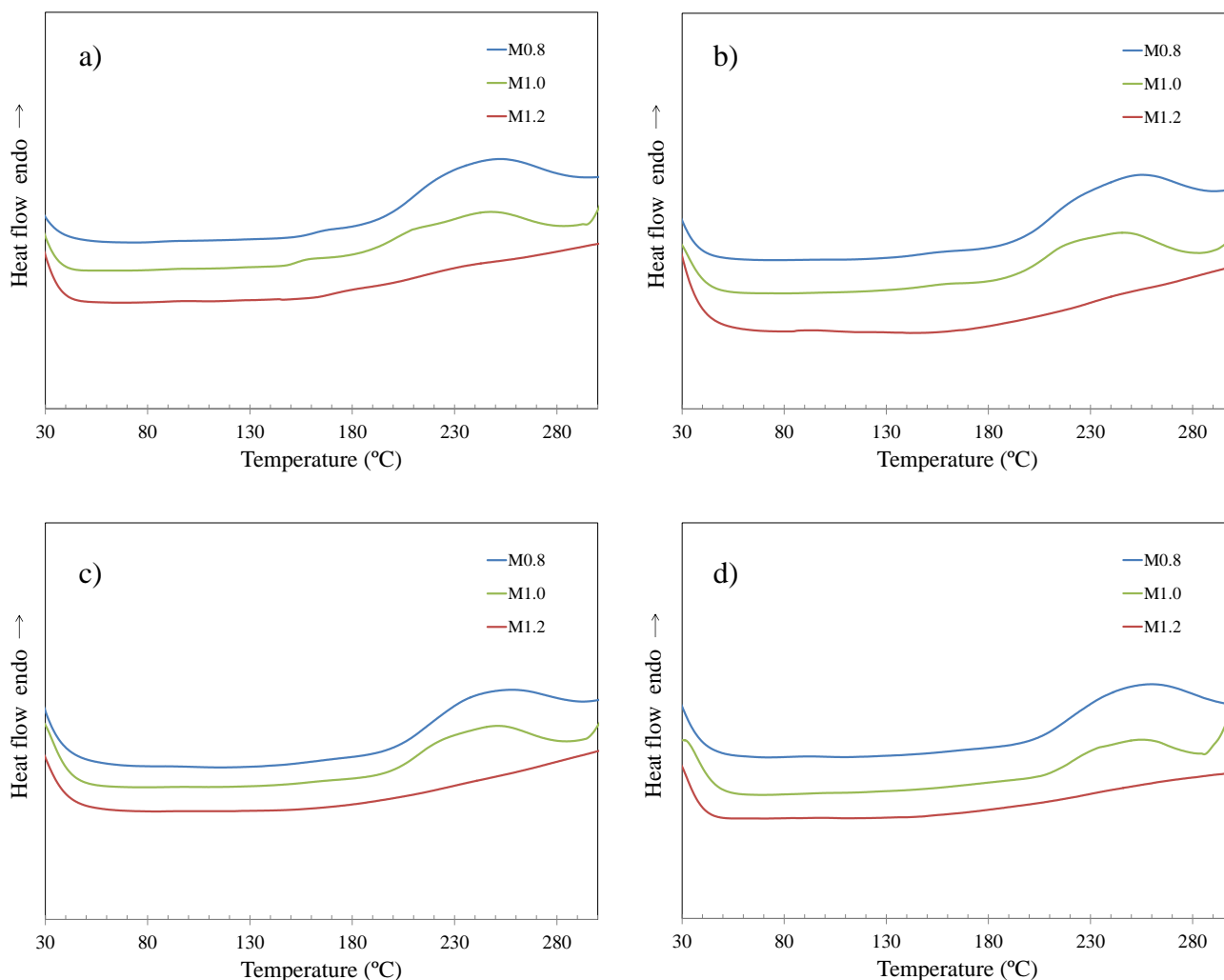
Figure 3. DSC thermograms (heat flow versus temperature) of the polyurethane-urea hybrid coatings with different NCO/OH ratios and aged at 80 ºC under static air for different aging times: a) 1 day; b) 3 days; c) 8 days; d) 10 days.

3.4 EIS measurements

The EIS spectra (impedance modulus vs. frequency) of the polyurethane-urea-coated steel samples obtained during exposure to naturally aerated 3.5 wt.% NaCl solution at room temperature are shown in Fig. 4 for selected periods of immersion. The impedance modulus can be associated with the corrosion resistance of organic films [32,33]. Impedance values above 10^7 $\square$.cm^2 are indicative of coating with high corrosion protection ability [34]. The EIS plots shown in Fig. 4 reveal that the impedance values remained relatively unchanged over the whole test, independently of the NCO/OH ratio of the coating. Even after 100 days of immersion, the $M_{0.8}$ and $M_{1.0}$ coatings presented impedance values only slightly below 10^8 Ω.cm^2, suggesting high corrosion resistance for all coatings tested. The impedance values of the $M_{1.2}$ coating exceeded 10^8 Ω.cm^2, pointing toward a superior corrosion protection ability of this film in comparison with the coatings with lower NCO/OH ratios. This behavior was observed for all immersion periods and sustained after 100 days. This result can be

correlated with the physical aging behavior studied by DSC (section 3.3). The increase of the NCO/OH provided high resistance to aging. According to Negim et al. [16], polyurethane-based polymers present progressively higher hydrophobicity as the NCO/OH ratio increases. Hence, it is expected that the impedance response of the coating with the highest NCO/OH ratio would reflect such hydrophobicity, yielding the best anticorrosion performance. In this regard, EIS proved to be a reliable method for evaluation of the NCO/OH ratio effect on the electrochemical behavior of the polyurethane-urea hybrid coatings. Furthermore, physical aging and electrochemical response are well correlated for the coatings prepared in this work.
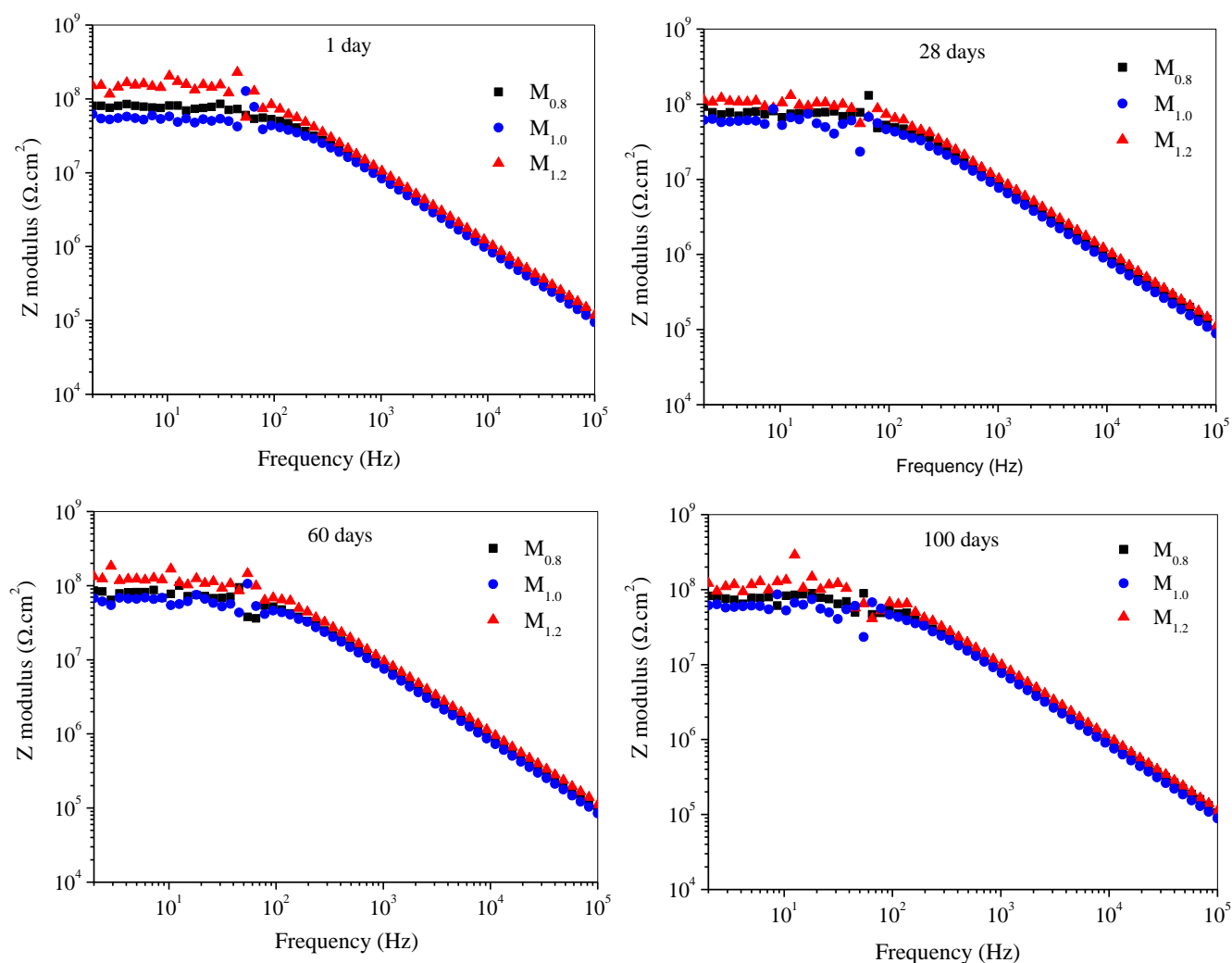

Figure 4. EIS plots (impedance modulus vs. frequency) of the polyurethane-urea-coated steel samples obtained during exposure to naturally aerated 3.5 wt.% NaCl solution at room temperature for selected periods of immersion.

In order to give a further insight into the effect of the NCO/OH ratio on the EIS response of the polyurethane-urea hybrid coatings the capacitance values of each film were determined according to the methodology described in section 2.3. An example of this procedure is shown in Fig. 5 for $M_{0.8}$ immersed during 28 days in NaCl 3.5 wt% solution at room temperature. The capacitance at 48 kHz

was found to be 1.45×10^{-11} F.cm^{-2}. By applying this procedure to each sample the capacitance evolution with time has been determined. The results are shown in Fig. 6.
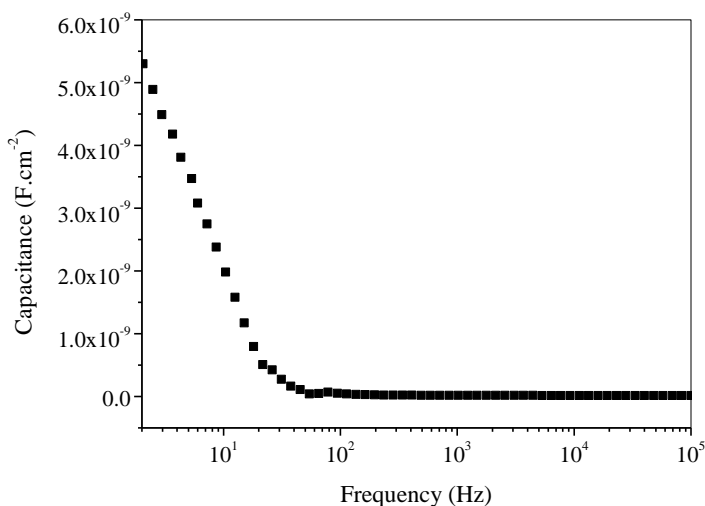

Figure 5. Capacitance variation with applied frequency for $M_{0.8}$ immersed during 28 days in NaCl 3.5 wt% solution at room temperature.
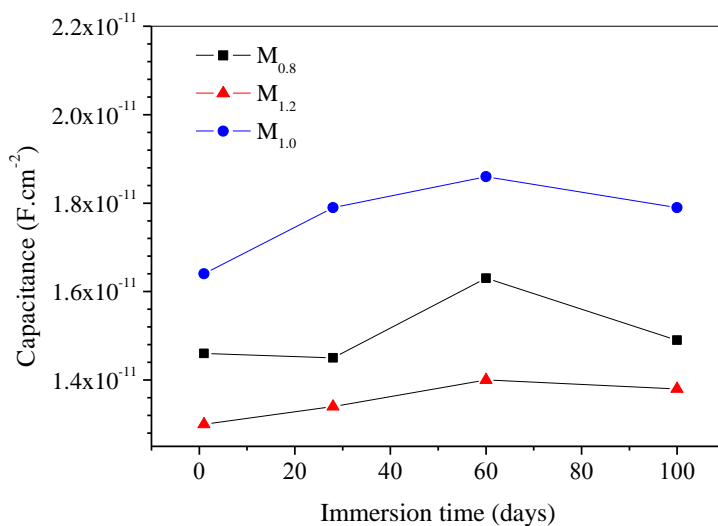

Figure 6. Capacitance evolution with immersion in 3.5 wt.% NaCl solution at room temperature.

The increase of capacitance with time for the initial stages of immersion has been correlated with the degradation of organic coatings due to water uptake and development of defects such as delamination [35,36]. In this regard, the coating performance against corrosion is related to low capacitance values. The magnitude of the capacitance values found in this work (10^{-11} F.cm^{-2}) is in good agreement with the literature and indicates a relatively high corrosion resistance [22] of the three different coatings tested. Yet, as clearly seen in Fig. 6, the NCO/OH ratio influenced the capacitance response of the polyurethane-urea hybrid coatings. The lowest capacitance values were observed for

the $M_{1.2}$ films which presents the highest NCO/OH. The $M_{0.8}$ coating presents intermediate capacitance values whereas the $M_{1.0}$ yielded the highest capacitances. This trend was observed for all the immersion times. These results agree well with the findings from the EIS plots shown in Fig. 4. Furthermore, it is interesting to note that the $M_{1.2}$ coating presented only small variations of the capacitance values with time in comparison with the coatings with lower NCO/OH ratios. This suggests that an increase of the NCO/OH ratio would be beneficial to avoid coating degradation, corroborating the results obtained by DSC which revealed the low susceptibility of the $M_{1.2}$ coating to physical aging.

4. CONCLUSIONS

Polyurethane-urea hybrid coatings with different NCO/OH molar ratio have been prepared and then characterized by FTIR and TGA. The thermal stability, as determined by TGA measurements, increased with the NCO/OH ratio. Moreover, the NCO/OH molar ratio strongly affected the physical aging and the electrochemical behavior of the polyurethane-urea hybrid coatings. DSC measurements revealed that the coating susceptibility to physical aging was small independently of the NCO/OH. However, the coating with a NCO/OH of 1.2 was not affected by physical aging whereas the coatings with ratios of 0.8 and 1.0 showed a small susceptibility to this phenomenon. EIS plots and capacitance analysis led to similar conclusions, indicating that the NCO/OH ratio of 1.2 provided the best anticorrosion performance. The results reveal that physical aging and corrosion resistance are well correlated for the polyurethane-urea hybrid coatings. In this context, the NCO/OH molar ratio should be carefully designed when preparing such materials in order to achieve the best combination of properties.

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