Influence of the Polyethyleneglycol Plasticizer on the Mechanical and Electrochemical Properties of Siloxane Hybrid Films Applied on Tinplate


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The coatings developed by sol-gel process have been proven to be an efficient alternative for corrosion protection of metal surfaces, especially to replace the chromate technique. The sol-gel processes have several advantages, such as their high purity and an excellent distribution of the components. The objective of this work is to characterize the hybrid films morphologically and electrochemically with different plasticizer concentrations, obtained by sol-gel process applied on tinplate. The film was prepared with two alkoxide precursor, 3-trimethoxysilylpropyl methacrylate (TMSPMA) and tetraethoxysilane (TEOS) with addition of cerium nitrate. The polyethyleneglycol (PEG) was added in four different concentrations and their effect on the film was evaluated. The morphological characterization was performed by scanning electron microscopy and profilometry. The electrochemical characterization was performed using the electrochemical impedance spectroscopy (EIS) and the scanning vibrating electrode technique (SVET). The results showed that the enhanced performance was obtained with the coating containing PEG 20 g.L\(^{-1}\) because the corrosion of the system, which was detected after 120 hours, showed only two small points of corrosion and only one active. The lowest amount of PEG improved the plasticity and the barrier properties of the hybrid film.

Keywords: tinplate; hybrid film; plasticizer; corrosion; SVET;
1. INTRODUCTION

The study of corrosion protection techniques on metal substrates is an area that is under continuous development. Technological progress has enabled advances in developing new protective materials whose barrier effect is able to prevent corrosion. Although the cromate technique has been used for decades for the protection of hybrid films, lately alternative coatings have been studied in order to avoid the presence of the highly toxical Cr\(^{3+}\) e Cr\(^{6+}\) ions [1-9].

The sol-gel process has been shown to be an effective alternative for the protection of metal surfaces. Through this chemical process it is possible to synthesize films under room temperature conditions on an industrial scale, with low-cost methods, such as spraying, dipping, spin coating and flow. Organic-inorganic hybrid materials have contributed significantly to the sol-gel process, as they are multi-functional with a wide range of properties and present several application possibilities. This process provides a good dispersion of the inorganic phase, even at a molecular level due to the physical and chemical properties such hybrids possess, besides processing capabilities provided by the colloidal state [1, 8, 9].

Organic molecules promote improvement in the matrix phase, for instance, they alter the mechanical properties, resulting in processability, molding needs for optical parts, control of the porosity and the adjustment of the hydrophobic/hydrophilic balance. Inorganic molecules improve thermal stability, modulate the optical index and confer magnetic, electrical and electrochemical properties [2, 8].

Other authors describe the application of sol-gel coatings on hybrid materials for corrosion protection of steel alloys and aluminum. They explain that this protection occurs through the covalent bonds between the inorganic parts of the organic-inorganic hybrid siloxane, making them suitable for conventional coatings [3, 8]. The organic different terminal groups of functionalized siloxanes have an important role in improving the coating adhesion in the inorganic network which is formed, and largely silicate provides mechanical strength and hydrophobicity to the coating [1, 3, 8, 10].

Early in the development of this technology, metallurgical industry of tinplate had as the main problem the complex nature of the system metal/coating/food substrate. The material does not have uniformity and during the manufacturing process it is necessary to apply a passivation treatment to prevent corrosion and adhesion of lacquer, in order to prevent the formation of tin oxide [2, 4-6, 11].

Packaging for food products requires a high performance of mechanical and physical-chemical characteristics, as they can not interact with the metal substrate. The film must have sufficient flexibility to avoid tearing, high adhesion to the substrate and appropriate wording to avoid contamination to food [10].

This paper deals with the behavior of the hybrid films obtained from sol-gel applied on tinplate with two alkoxides precursors, 3-trimethoxysilylpropyl methacrylate (TMSPMA) and tetraethoxysilane (TEOS) with the addition of cerium nitrate and polyethylene glycol (PEG 1500 g.mol\(^{-1}\)) to highlight the effect of plasticizer in the hybrid sol-gel film. The electrochemical and physicochemical properties of the films were evaluated.
2. EXPERIMENTAL

2.1. Metal substrate and surface preparation

Tinplate samples with dimensions of 20x40 mm were obtained from an industrial sheet, rinsed with acetone and dried. Then, the plates were degreased by a 10 min immersion in neutral detergent at 70°C, washed with deionized water and dried.

2.2. Synthesis of hybrid films

The silanes precursors used in this work, 3-(Trimethoxysilyl)propyl methacrylate (C<sub>10</sub>H<sub>20</sub>SiO<sub>5</sub>, TMSPMA) and tetraethoxysilane (C<sub>8</sub>H<sub>20</sub>SiO<sub>4</sub>, TEOS), were obtained from Aldrich with 98% purity. Polyethylene glycol (PEG, 1500 g.mol<sup>-1</sup>) plasticizers were obtained from Selectophore®.

The hydrolysis reactions were conducted with the silane precursors TMSPMA and TEOS, with 0.01 mol.L<sup>-1</sup> cerium nitrate addition (approximately 0.5%) as corrosion inhibitor. Ethanol and water were used as solvents. PEG was added to the sol formulation at four different concentrations: 0, 20, 40, 60 and 80 g.L<sup>-1</sup>. The hydrolysis time was 24 hours. The hybrid films were obtained by dip-coating that was performed at with draw speed of 10 cm.min<sup>-1</sup> and immersion time of 5 minutes. After the dip-coating process, the hybrid films were thermally cured at 60º C ± 2 for 20 minutes in a furnace. Figure 1 presents the flowchart of the process and Table 1 presents the description of the samples.

![Figure 1](image)

**Figure 1.** Experimental parameters of sol synthesis and procedure to deposit the coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR</td>
<td>Uncoated tinplate, without hybrid film – Reference</td>
</tr>
<tr>
<td>TP-0</td>
<td>Tinplate coated with hybrid film without PEG addition</td>
</tr>
<tr>
<td>TP-20</td>
<td>Tinplate coated with hybrid film with 20 g.L&lt;sup&gt;-1&lt;/sup&gt; PEG addition</td>
</tr>
<tr>
<td>TP-40</td>
<td>Tinplate coated with hybrid film with 40 g.L&lt;sup&gt;-1&lt;/sup&gt; PEG addition</td>
</tr>
<tr>
<td>TP-60</td>
<td>Tinplate coated with hybrid film with 60 g.L&lt;sup&gt;-1&lt;/sup&gt; PEG addition</td>
</tr>
<tr>
<td>TP-80</td>
<td>Tinplate coated with hybrid film with 80 g.L&lt;sup&gt;-1&lt;/sup&gt; PEG addition</td>
</tr>
</tbody>
</table>
2.3. Experimental techniques

A JEOL 5800 Scanning Electron Microscopy (SEM), coupled to an analysis equipment dispersive ray X (EDX), with an acceleration voltage of 20 kV carried out morphological characterization of surface and cross sections.

Sample surface roughness was determined by the CETR-PRO5003D profilometer. Three areas were analyzed in each sample to determine the average roughness (Ra). For this kind of analysis, some geometric parameters should be specified, as sample size, also known as cut off. These values were determined by the expected roughness as recommended by ISO 4288:1996.

Corrosion performance of the coatings was evaluated using open circuit potential (OCP) monitoring and electrochemical impedance spectroscopy (EIS), measurements were performed in a 0.05 mol.L\(^{-1}\) NaCl solution. This concentration is high enough to activate corrosion in a relatively short period of time, but low enough to discriminate the effects on the different samples [12, 13]. A three-electrode cell with a platinum wire counter electrode and saturated calomel electrode (SCE) reference electrode were used to perform the analyses. The working electrode area was 0.626 cm\(^2\). For the EIS measurements, the systems were monitored for 96 hours. The amplitude of the EIS perturbation signal was 10 mV and the studied frequency range was from 100 kHz to 10 mHz using a NOVA frequency response analyzer and an AUTOLAB PGSTAT 30 potentiostat.

The SVET equipment was manufactured by Applicable Electronics Inc. (USA) and controlled by the ASET 2.0 program developed by Sciencewares (USA). Scanning vibrating electrode technique (SVET) microelectrode was prepared from polymer insulated Pt-Ir microelectrodes produced by Microprobes Inc. (USA). A 10 – 20 µm diameter platinum black sphere was electro-deposited on the tip.

![Figure 2. Schematic representation of the tribologic test.](image)

While it was possible to vibrate the microelectrode in two directions, one parallel (x axis) and another normal (z axis) to the sample surface. Only signals from the normal field were considered in the present study. The frequency was 162 Hz and the amplitude of vibration was two times the tip diameter. The measured potential differences were converted to cathodic and anodic currents after a calibration routine was performed with a point current source (microelectrode with a tip of ~ 3 mm) driving a current of 60 nA at 150 µm from the vibrating probe [14, 15]. The calibration is valid for a
new solution, provided that the system is updated with its resistivity. The maps and lines were obtained at a plane 100 µm above the surface of the sample.

Wear tests were performed with a computationally controlled CETR UMT (Universal Micro Tribometer) tribometer with the type-setting ball on the plate. The wear test was conducted with reciprocal linear movement by a sphere of alumina with a 7.75 mm diameter. A constant force of 1.5 N, a frequency of 2 Hz and a track length of 2 mm were the wear tests parameters.

3. RESULTS AND DISCUSSION

3.1. Morphological and surface characterization

Figure 3 shows the SEM micrographs for the hybrid films, before the electrochemical tests and the layer thickness of the films were determined by cross-section SEM micrographs image analysis.

In Figure 3 the presence of cracks on the TP-40, TP-60 and TP-80 hybrid films can be observed. A more homogeneous and crack-less hybrid film was only obtained for PEG addition in a concentration of 20 g.L⁻¹. It seems that an excess in addition of plasticizer interferes with the hydrolysis of the alkoxide precursor, forming only dense interwoven PEG networks and causing cracks and delamination on the films [16].

![Figure 3](image)

**Figure 3.** Top micrographs (left column) and cross section (right column) micrographs obtained by SEM analysis for the hybrid films.

It is observed in Figure 3 that all films with PEG addition had an increased thickness compared to the film without PEG (TP-0). It seems that the addition of the flexibilizing agent promotes the formation of cross-linked PEG networks and, thus, an increase of the layer thickness [17]. This
increase in the layer thickness was proportional to the increase of the PEG concentration in the hybrid films.

Figure 4 shows images obtained by elemental distribution using EDS for cross sections of the hybrid films, which shows the hybrid film layer by mapping the element silicon as well as the substrate by mapping the elements tin and iron.

Figure 4. Elemental distribution of the cross-section of the samples studied

The addition of PEG (TP-20, TP-40, TP-60 and TP-80) provided an increase in thickness of all the films. According to Kulkarni et al. [17], that the addition of the flexibilizing agent in excess interferes with the hydrolysis of the alkoxide precursors, forming only dense interwoven networks of PEG and causing an increase in the thickness of the layer. It was observed that the TP-20 sample showed an uncracked film, while the other samples TP-40, TP-60 and TP-80 resulted in the formation of a film with cracks due to the cross-linked PEG chains.

Moreover, the monomer of ethylene oxide is characterized by a single site polymerization molecule and therefore during the curing process, each monomer of the polyethylene glycol can have only a covalent bond with TMSM which, in turn, has three groups hydrolysable. The TMSM copolymerization with monomers having ethylene oxide increases the formation of a hybrid composed crosslinked with polyethylene glycol chains, or no formation of dense intertwined strands of PEG around the particles siloxane.

However, these polymerization reactions only occur through weak bonds, or hydrogen bonds, without forming an effective barrier but a porous film and brittle as seen in SEM images before assay electrochemical test.

Figure 5 shows three-dimensional images obtained by profilometry for all systems studied and for system without coating. The determined roughness values are shown in Table 2.

The results showed that the films hybrids without PEG (TP-0), and with lower concentrations of PEG (PT-20) had lower roughness values (Table 2), ie, films that showed no cracks nor delamination (Figure 3) were less rough compared to the other films studied and uncoated tinplate. This indicates that the lower the amount of polymer chains, increasing the inorganic phase of the film and consequently the greater the presence of silicon groups. Furthermore, the increase of covalent bonds of the silanes precursors improves densification of the formed film and decreases the surface roughness system forming a more compact film. This demonstrates the synergistic effect of TMSM precursors TEOS and present in the hybrid film.
Figure 5. 3D images obtained by profilometry for the samples studied

Table 2. Samples roughness values, determined by profilometry analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ra (µm)</th>
<th>Rms (µm)</th>
<th>Peak to peak (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR</td>
<td>0.43 ± 0.27</td>
<td>0.51 ± 0.31</td>
<td>2.40 ± 0.83</td>
</tr>
<tr>
<td>TP-0</td>
<td>0.40 ± 0.31</td>
<td>0.50 ± 0.33</td>
<td>3.53 ± 0.37</td>
</tr>
<tr>
<td>TP-20</td>
<td>0.37 ± 0.17</td>
<td>0.48 ± 0.19</td>
<td>2.99 ± 0.24</td>
</tr>
<tr>
<td>TP-40</td>
<td>0.45 ± 0.34</td>
<td>0.59 ± 0.31</td>
<td>3.84 ± 0.49</td>
</tr>
<tr>
<td>TP-60</td>
<td>0.49 ± 0.22</td>
<td>0.60 ± 0.24</td>
<td>3.52 ± 0.27</td>
</tr>
<tr>
<td>TP-80</td>
<td>0.54 ± 0.26</td>
<td>0.76 ± 0.21</td>
<td>7.41 ± 0.34</td>
</tr>
</tbody>
</table>

3.2. Electrochemical characterization

Figure 6 shows the monitoring of OCP for 96 hours of immersion in 0.05 mol.L\(^{-1}\) NaCl. It was observed that all the samples showed small variations in potential. The TP-40, TP-60 and TP-80 samples showed similar behavior, starting with the most active potential and as from 24 hours immersion there was a decrease for less active potential. This decrease may be associated with the
resistance of the electrolyte through the films hybrids. After 48 hours of immersion, the potential became active again, this indicate that the electrolyte permeates through cracks in the coatings.

Moreover, the TP-0 and TP-40 samples showed more resistance to the electrolyte, due to the fact that these films present a barrier behavior, without cracks. The TP-20 sample presented a less active potential at the end of 96 hours of immersion, which show the good performance of this system.

**Figure 6.** Open circuit potential monitoring for 96 hours of immersion in a 0.05 mol.L\(^{-1}\) NaCl solution.

In Figure 7 appear the Bode impedance diagrams for the coated and uncoated samples by 24 and 96 hours of immersion in a 0.05 mol.L\(^{-1}\) NaCl solution.

On impedance plots, the TP-20 sample presented the highest values for phase angle and impedance modulus (Figure 7) throughout the whole experiment, compared to the other studied hybrid films (TP-40, TP-60, TP-80 and TP-0). The resistance of TP-20 achieved values 6 times higher in 24 hours immersion and up to 8 times higher in 96 hours with respect to the uncoated substrate. It demonstrates the protective action of this hybrid film against corrosion on tinplate. The good performance of this coating is associated with the fact that the small increase in branching, the radical ethylene oxide (20 g.L\(^{-1}\)) was sufficient to decrease the triorganosilane condensation reaction rate. The condensation of the tetrafunctional alkoxides was also delayed in the presence of this monomer (PEG), due to steric hindrance in the transition state. Hence, the film improved its compactness and, consequently, its anticorrosive properties.

However, resistance of the TP-20 sample decreased by half from 24 to 96 hours of immersion. It means that this system did not resist long times of immersion, possibly because of its small layer thickness.

Hybrid films with higher PEG concentration (TP-40, TP-60 and TP-80) showed the lowest values of resistance, phase angle and impedance modulus. It indicates that excessive branching in the formulation prevented the formation of siloxane groups from silanol species and consequently there is
the formation of irregular films with low corrosion resistance. Also, regarding the existence of cracks on the surface, there was electrolyte passing through the film and provoked corrosion.

**Figure 7.** Bode diagrams for uncoated and hybrid-film-coated tinplate at (a) 24 and (b) 96 hours of immersion in 0.05 mol.L⁻¹ NaCl.

Table 3 present the electrical component values obtained by equivalent electrical circuit fitting from the experimental EIS data for the hybrid films TP-0, TP-20, TP-40, TP-60 and TP-80 and for 96 h of immersion in a 0.05 mol.L⁻¹ NaCl solution. The percent errors shown in brackets in Table 3 were less than 5% in most of the cases, demonstrating the suitability of the circuit. These models use a combination of resistances, capacitances and other electrical elements, which have a clear physical meaning, related with the response of the electrochemical system [18]. In this paper two equivalent electrical circuit models were used and appear in Figure 8.

**Table 3.** Equivalent circuit elements for samples. Percent error value is given in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>TP-0 sample</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (h)</td>
<td>$R_{el}$ (Ω.cm²)</td>
<td>$R_{MF}$ (kΩ.cm²)</td>
<td>$CPE_{MF,Q}$ (µF.cm²)</td>
<td>$CPE_{MF,n}$</td>
<td>$R_{LF}$ (kΩ.cm²)</td>
</tr>
<tr>
<td></td>
<td>1h</td>
<td>229 (2.2)</td>
<td>1114 (4.4)</td>
<td>6.28 (1.7)</td>
<td>0.74 (0.9)</td>
<td>6.69 (4.9)</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>238 (1.3)</td>
<td>312 (1.8)</td>
<td>10.01 (0.9)</td>
<td>0.75 (0.7)</td>
<td>5.44 (3.3)</td>
</tr>
<tr>
<td></td>
<td>48h</td>
<td>220 (1.4)</td>
<td>115 (1.4)</td>
<td>11.30 (1.8)</td>
<td>0.73 (4.7)</td>
<td>2.58 (7.3)</td>
</tr>
<tr>
<td></td>
<td>72h</td>
<td>226 (4.8)</td>
<td>58.0 (5.1)</td>
<td>11.08 (1.4)</td>
<td>0.74 (0.9)</td>
<td>0.99 (7.7)</td>
</tr>
<tr>
<td></td>
<td>96h</td>
<td>218 (2.3)</td>
<td>44.8 (2.1)</td>
<td>16.02 (1.7)</td>
<td>0.69 (1.1)</td>
<td>0.51 (4.1)</td>
</tr>
</tbody>
</table>

**TP-20 sample**
In the circuits, $Re$ represents the electrolyte resistance. Also capacitors were substituted by constant phase elements (CPE) in order to take into account the non-ideality of the systems.

Figure 8-a best fitted to systems TP-20 during the whole experiment and TP-40, TP-60 and TP-80 at 72 h of immersion. In this circuit (Figure 8-a), $R_HF$ and $CPE_{HF}$ represent respectively, the resistance and the constant phase element associated to the hybrid film barrier effect. This behavior was also observed by other authors [19, 20] indicating the hybrid films retarding the corrosion processes on the metallic substrate.

The circuit corresponding to Figure 8-b best fitted to samples TP-0 for all the studied immersion times and for the samples TP-20 and TP-60 at 96 hours of immersion. In these cases, two relaxation constants were observed. The high frequency constant indicates a phenomenon associated to the hybrid film barrier effect. The low frequency constant can be associated to the formation of oxides for TP-0 and TP-20 samples, maybe through passivation. In the TP-60 sample that low frequency phenomenon can be related to corrosion produced by electrolyte permeation through the cracks on the film surface (Figure 3).
Henceforth, it is recommended for the metallic substrate to be coated with hybrid films with a small PEG concentration, like the TP-20 sample, in order to enhance the corrosion protection and prevent cracks and delamination. The TP-20 hybrid film resistance (R_{HF}) can be estimated by the Nyquist diagram at the end of the experiment, wherein the system resistance values are found to be about 125 kΩ.cm² for 96 h of immersion.

![Equivalent circuits](image)

**Figure 8.** Equivalent circuits for a) TP-20 sample throughout the whole experiment and TP-40, TP-60 and TP-80 until 72 h of immersion, and b) for TP-0 sample throughout the whole experiment and TP-40, TP-60 and TP-80 at 96 h of immersion.

Figure 9 shows the evolution of the coating properties, i.e. the resistance as a function of immersion time. Generally, the resistance values show a decrease during the first hours of immersion; this occurred more significantly on the TP-0 hybrid film. Hence, this can be the development of conductive pathways inside the hybrid film, according to what was analyzed by some authors [21].

![Graph](image)

**Figure 9.** Evolution of the hybrid films resistance for samples studied in a 0.05M NaCl solution with the immersion time.
The evolution of the coating resistance is a major characteristic of the barrier properties of a protective layer [22]. It can be observed that the TP-0 and TP-20 samples exhibited the highest values resistance after 24 and 96 hours of immersion relative to other samples (TP-40, TP-60 and TP-80); which can be associated to the fact that the small increase in branching radical ethylene oxide (20 g.L$^{-1}$) was sufficient to decrease the triorganosilane condensation reaction rate. The condensation of the tetrafunctional alkoxides was also delayed in the presence of this monomer (PEG), due to steric hindrance in the transition state.

Subsequently, the resistance of the TP-40 and TP-60 samples decreases slowly over an immersion time of 96 hours, which reflects the stability of the coating and good barrier properties [23]. In contrast, the TP-0 coating rapidly lost its barrier properties in 24 hours of immersion. This rapid decrease is related to the formation of new defects and pores in the coatings [24].

Figure 10. Images obtained after 96 hours of electrochemical impedance for the hybrid film samples.
Figure 10 presents images for all studied hybrid films after 96 hours of electrochemical impedance. According to this figure, hybrid films TP-40, TP-60 and TP-80 samples showed more corrosion product, confirming the results obtained in the electrochemical tests.

The TP-20 hybrid film showed the least corrosion product, which was expected due to the good performance of this film in EIS tests. The sample without PEG addition, TP-0 had a good electrochemical performance too, due to its compact structure, as in Figure 3 XRD and NMR suggest and because of its hydrophobicity [25] as suggested by FTIR spectra and wettability. For both samples, electrolyte permeation was hindered by the film presence on the substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Immersion Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 h</td>
</tr>
<tr>
<td>TR</td>
<td>![Image]</td>
</tr>
<tr>
<td>TP-60</td>
<td>![Image]</td>
</tr>
<tr>
<td>TP-20</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

**Figure 11.** Surfaces and SVET maps of TR, TP-60 and TP-20 samples, after 24 h and 120 h of immersion in 0.05 M NaCl.

The closer analysis with a magnifying lens allowed detecting more corroded spots than those observed by the bare eye. The localized nature of the corrosion was analyzed with the SVET. This technique uses a vibrating electrode to measure local potential differences in solution, related to the currents flowing between the anodes and cathodes on the surface. It is therefore possible to map the corrosion activity in terms of distribution of anodic and cathodic regions and their evolution in time and space. Figure 11 shows surface images and SVET maps of the bare substrate (TR), a lower
coating (TP60) and the enhanced coating system (TP20). Corrosion of tinplate was detected since the beginning of immersion, with localized anodic spots and the remaining area being cathodic. In 24 hours of immersion, 8 pits were observed in an area of 16 mm². After 120 hours, some of the original pits became inactive and corrosion moved to other areas. Anodic activity was located in a substantial fraction of the area, with abundant accumulation of corrosion products. The rest of the surface presented cathodic activity with currents around -2 µA cm⁻². Interestingly, a slight higher cathodic activity was measured above the inactive pits. This may be due to the deposit of iron corrosion products, of different natures, that may increase the cathodic activity through a local higher surface area or a catalytic enhancement of the oxygen reduction reaction.

The maps for TP60 show a trend similar to the base substrate and after 120 h the activity was even more localized, with intense pits. The enhanced performance was obtained with the coating containing 20 g L⁻¹ of PEG. Corrosion was detected only at the second day of immersion with a small pit. After 120 hours this system displayed just two small points of corrosion, only one active.

3.3. Mechanical characterization

Figure 12 shows the coefficient of friction (COF) and the sliding time for all hybrid films and for the tinplate substrate. The initial values are low and when the film rupture occurs, which is at a different time for each film, the COF increases abruptly. Which corresponds to the onset of wear on the metallic substrate. PEG concentration in samples TP-20, TP-40 and TP-60 led to higher film durability. In addition, higher wear resistances were observed.

![Figure 12](image_url)

**Figure 12.** Coefficient of friction (constant force: 1.5 N; frequency: 2 Hz; track length: 2 mm) of the specimens covered with hybrid films.

Although the TP-80 sample had the highest layer thickness (Figure 3), this hybrid film broke very fast due to the plasticizer addition. These cross-linked PEG chains structures become more
crystalline and thus more brittle. This decreases the plastic deformation of the film, lowering its resistance to wear. That is why this sample had a poor performance in mechanical resistance. However, compared to TR, the TP-80 COF was lower.

The TP-0 sample had low COF values (Figure 12) compared to the TR sample. These results indicate that at high concentrations, PEG polymerization during the condensation reactions promoted the formation of a more fragile structure, which undermine its performance against the wear test.

The TP-20 and TP-80 samples did not achieve good results in the mechanical tests. Because the layer thickness is still lower than in the TP-40 and TP-60 samples that resisted respectively the to wear test two and three more times. It is possible to state that there is a compromise between the layer thickness, which is induced by the PEG introduction to the formulation, in this case up to a determined concentration corresponding to 60 mg.L⁻¹.

4. CONCLUSION

Results showed that the TP-20 hybrid film had the enhanced performance in the electrochemical tests. This behavior is associated with the small increase of the branch of PEG, which was enough to decrease the trifunctional and tetrafunctional alkoxide condensation rate. For this reason, PEG steric hindrance promoted the formation of a more compact film. PEG addition at low concentration influenced the polymerization degree, controlled the amounts of trifunctional and tetrafunctional species in the structure and settled a compromise of compactness.

Curing temperature of 60 °C was appropriated since it did not cause cracks on the hybrid film, neither in the case of the absence of the plasticizer. This is the reason why TP-0 and TP-20 samples did not suffer electrolyte permeation through the film.

From the presented results, it is concluded that the hybrid film with the enhanced performance was TP-20 (20 g.L⁻¹ PEG). The results showed that the lowest amount of PEG in the hybrid film promoted, in addition to improving its plasticity and flexibility, improvements in the barrier properties of the film.

The results obtained by SVET for TP60 show a trend similar to the base substrate and after 120 hours the activity was even more concentrated, with intense pits. The enhanced performance was obtained with the coating containing PEG 20 g.L⁻¹. Corrosion was detected only at the second day of immersion with a small pit. After 120 hours this system displayed just two small points of corrosion, only one active.

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