STUDY ON CORROSION PROTECTION OF NANOCOMPOSITE LAYERS (EPOXY RESIN/ MWCNTs) BASED DIP-COATING ON MG ALLOY AM50

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Abstract
Mg and its alloys have been attracted a lot of attention in many sectors of engineering applications, such as automotive, aircraft, electronics, handled or household industry. These are due to lightweight and superior specific strength of magnesium alloy. However, the low corrosion resistance of Mg alloys making their difficult to apply in many engineering application. The present investigation evaluates nanocomposite layers which were prepared by adding a multi walled carbon nanotubes (MWCNTs) to an epoxy resin aiming to study the resulting corrosion mechanism and corrosion performance of Mg alloy AM50. The pure polymer layer was investigated and compared between the nanocomposites containing different CNTs (0.5, and 1.5 wt %). Distribution behavior of carbon nanotubes in the epoxy matrix was examined through forced scanning electron microscopy (FESEM). The results demonstrated that, the CNTs demonstrated a good dispersion inside the polymer matrix. Both nanocomposite and pure coated samples showed good adhesive properties subsequently resist to aggressive corrosion environmental for a long period.

1. Introduction
Because of the rapid development in automotive, aircraft, and electro industry the use of light alloys and their development is extensively increased. This increase is especially evident in the use of light magnesium alloys. The advantage of the Mg-alloys is in the mass/strength ratio, i.e. small mass of final products and their good mechanical properties. The magnesium alloys find principal use in non-structural application although the structural uses are expected to grow in importance in the future. On the other hand, magnesium and its alloys are highly susceptible to dissolution in aqueous environment; especially in those containing aggressive electrolytes such as chloride ion, mainly due to their very low corrosion potential [1]. Keeping these problems in view an immense effort has been devoted to improve the general corrosion resistance of magnesium based alloys, such as decreasing impurity level [2], adding superior corrosion resistance materials and producing a more homogeneous microstructure [1]. Nevertheless, the aforementioned processes couldn’t able to avoid internal or/and external galvanic corrosion. The
reactivity of magnesium surface is considered high; therefore, surface modification can be considered as an ideal way to improve the corrosion resistance, avoid severe localized corrosion on magnesium surface and decrease the interlocking between the magnesium substrate and aggressive environment, particularly by organic coatings. Organic coatings can act as a barrier layer to separate the substrate metal from its environment. Earlier workers [3],[4], [5],[6], [7], have conducted different studies on pure polymeric coatings of magnesium based alloys, but very encouraging results were not obtained where they cannot meet the appropriate corrosion protection requirements. The main drawback of the plain organic coatings is that they do not show any admirable resistance against the diffusion of water molecules within the organic coating. That informs the plain organic coating bulk materials deposited on magnesium alloy doesn’t have enough strength to resist for long period in contact with the substrates.

Not only the aforementioned, in fact, Polymers contain a very low concentration of free charge carriers and are therefore generally good electrical insulators. Epoxy resins were used as suitable matrices in several areas of industry, such as the aerospace industry in the fuselage and the facing layers of airliners and such as microelectronics in the insulators between adjacent planes of multilayers printed circuits board. Coating materials based on epoxy resins (EP) have gained considerable importance in many areas of technology and daily life. This is due, on the one hand, to the fact that epoxy resins can be processed relatively simply and safely and, on the other hand, to the good mechanical and chemical property level of the cured epoxy resin. This versatility in formulation made epoxy resins widely applied industrially for surface coating, adhesive, painting materials, composites, etc[8]. But there are instances when an increased conductivity of the metal coating by polymer is warranted, such as in applications that require electrostatic dissipation (antistatic materials) or electromagnetic radiation shielding.

The electrical conductivity of an insulating polymer can be altered by adding conducting particles like carbon black particles,1-8 carbon fibers,9 metallic fillers,10,11 or intrinsically conducting polymers.12-14 The conductivity of the composite material can thus be controlled by properly choosing the components, their shape, and their relative concentrations. Carbon nanotubes (CNTs) are increasingly attracting scientific and industrial interest by virtue of their outstanding characteristics. The CNT walls resemble rolled-up graphite-like sheets with strong covalent sp² bonds. According to their graphitic structure, CNTs possess high thermal conductivity and an electrical conductivity that can be either semi-conducting or metal like. The Young's modulus of carbon nanotubes can be as high as 1000 GPa, which is approximately five times higher than steel. The tensile strength of carbon nanotubes can be up to 150 GPa, around 40 times higher than steel. Several researches have investigated that incorporation CNTs into epoxy resin enhanced the impact strength, thermal stability, scratching effect, moisture resistance and electrical properties.

The present study focused on the corrosion performance of the plain EP and EP/CNTs nanocomposites conducted layer deposited on magnesium substrates. We report our experimental results on the dependence of filler content and interval immersion time in 3.5 % NaCl solution.
Table 1 Chemical compositions of the substrate in weight percentage-%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>Mn</th>
<th>Zn</th>
<th>Si</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
<th>Be</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM50</td>
<td>4.9</td>
<td>0.45</td>
<td>0.2</td>
<td>0.047</td>
<td>0.0009</td>
<td>0.008</td>
<td>0.004</td>
<td>0.001</td>
<td>Bal</td>
</tr>
</tbody>
</table>

2. Experimental
2.1. Materials
EP resins (HTC-667C) with hardener dicyandiamide (HTC-667C) both were supplied by IGT, Korea and were used as a matrix. The glass transition temperature and density of the neat resin were around 85 °C and 1.175 g/cc, respectively. MWNTs (CVD method, purity > 95%, diameter 15-25 nm, length 5-20 µm), were obtained from NanoLab (Boston, MA). Ethanol (Samchun, Korea) was used to alter the dispersion of CNTs inside the polymer matrix. Sodium chloride was purchased from Showa, Japan. CNTs and all the reagents were used as received. Magnesium alloy AM50 was used as a substrate and was cut into square pieces (12 x12 mm² and 2 mm in thickness). The chemical compositions of AM50 are typically shown in Table 1.

2.2. Preparation of EP/CNTs nanocomposites solution
For the preparation of the colloidal solution, MWCNTs (0.5 and 1.5 % w.w-1 in relation to the epoxy matrix) were dispersed in ethanol using magnetic stirring for more than 24 h. In total, four three formulations (1 pristine EP solutions and 2 colloids) were prepared and investigated as coating layers on Mg-alloy substrate. The amount of acetone used, 15% w.w-1 in relation to the epoxy matrix, was chosen in order to minimize viscosity and yet avoiding the use of a large amount of solvent.

The colloidal solution was heated to 60 °C under atmospheric environment for 18 h and then continues for 4 h at 70 °C under vacuum to remove most of the solvent. Further, the solution was sonicated (Sonic Vibrator, 500 W and 20 kHz) for one hour under vacuum at 70 °C. To evaluate the removal of all solvent, the samples were weighed before the addition of ethanol and before coating. Nevertheless, acetone traces could still be found in the nanocomposites. Then, the dispersions were left under vacuum for 4 more hours at room temperature and under stirring. Later, the hardener was added (4:1 w.w-1). Neat epoxy resin samples were also prepared following the same route for comparison.

2.3. Coating
For the samples preparation, the samples were mechanically polished with 800-2000 grit waterproof adhesive paper and then polished with 1 µm diamond grinding. Thereafter the
samples were sonicated in acetone for 5 min and distilled water and finally dried under vacuum. The pre-treated samples were kept over a hot plate at 200 °C for 10 min to eliminate the moisture and entrapped air from the surfaces of substrate. Coating was conducted by dipping the AM50 substrates into the aforementioned solution at ambient temperature and environmental condition (Fig.1). The treated magnesium bars were immersed into prepared solutions for 25 s to allow the wetting. In order to obtain a stain-free surface, the specimens were slowly pulled out of the solution with a speed of 2 mm/s.

2. 4. Coating characterization
2.4.1. Scanning electron microscopy observation
Prior to the SEM observation all the coated samples before and after immersion test were sputtered with platinum by a passage of a current to provide a conductive surface. The morphologies of the surfaces were observed in a scanning electron microscope (SEM) (JEOL JSM 820, Cambridge) using acceleration voltage 15 kV, to obtain the best resolution.

2.5. Immersion tests
The corrosion behaviour of the coated samples was further investigated by immersion tests. The coated and uncoated magnesium bars were conducted in aqueous 3.5 wt% NaCl solution, 3 specimens for each sample were immersed in 200 ml of solution. a change on the visual aspect with immersion time was observed by SEM. The electrolyte was saturated with atmospheric oxygen without stirring during the experiments. The temperature was maintained at room temperature during the test.

Figure 1 Schematic diagram shows the coating process
3. Results and discussion

Flat and smooth surface to allow the formation of defect free coatings must be prepared in the case of the coating method which can be considered as limitations concerning on the shape and roughness of the substrate surface. In the previously publication by [14], the corrosion resistance obtained with spin coated substrates pre-treated with acids was much inferior to that of ground ones due to roughness effects. An interesting method to address this problem is the dip coating method. The dip coating process consists in bringing a substrate into a solution, maintain it there for a reasonable time to allow wetability, withdrawn it from the solution and let it dry. By this process, the coating thickness can be controlled by several ways such as, withdraw speed, solution concentration and by the number of dipping-withdraw cycles. Besides the possibility of increasing thickness, this method allows the simultaneous coating of both sides of a coupon and the coating of non-flat substrates. One drawback of this method is the solution flow during the drying step that could induce non uniformity of the thickness.

3.1. CNTs dispersion

To check the dispersion, as well as the reinforcing mechanism of carbon nanotubes in CNTs reinforced epoxy resin composites, the fracture surfaces of samples were observed by FESEM. Fig.2 typically demonstrates the CNTs dispersion within the EP matrix. It is clearly shown from this figure that the nanotubes showed relatively homogeneous distribution (Fig.2B). the possible reason for getting the uniformity due to the sequential of the solution preparation as a aforementioned. It is know very well that, the good dispersion of CNTs have a strong affinity for enhanced the characterization of the prepared composites. Many research efforts have been directed towards producing CNT/polymer composites for functional and structural applications . Ma and et.al have decided that, the electrical conductivity, optical, thermal and mechanical properties, such as toughness, strength and tensile modulus can be enhanced with improvement the distribution of nanotubes. Accordingly, it is speculated that the good distribution of CNT inside the epoxy matrix is able to optimize both electrical conductivity and corrosion behavior of plain EP layer on magnesium substrate.

Figure.2 FE-SEM observation for CNTs dispersion inside the polymer matrix (A) at low magnification, (B) high magnification
3.2. Immersion test

The surface appearance in SEM after immersion the samples in 3.5 % NaCl solution are typically presented in Fig.3. In most cases, the corrosion of magnesium and magnesium alloys initiates from localized corrosion, but sometimes the localized corrosion is shallow and widespread. The corrosion morphology of magnesium and magnesium alloys depends on the alloy chemistry and environmental conditions. For example, atmospheric corrosion is uniform in usual industrial atmospheres, whereas corrosion is usually localized for immersed conditions. Our results are in agreement with this theory, where after immersion in salt solution for 6 h the uncoated samples showed severe localized corrosion. With further immersion time (24 h) the corrosion attacks the entire appeared are as shown in Fig.3B. On the other hand, the protected samples with epoxy resin and advanced nanocomposites layer showed a promising protection especially for CNTs/EP layer on magnesium substrate. As indicates in the figure, the coated samples with plain epoxy established a pin holes with the polymer layer that is likely due to the evaluation of hydrogen gas underneath the protected layer. Subsequently, the composite layer was able to provide strength enough to damp the hydrogen gas underneath the layer. Another layer, possible the composites samples had a strong ability to avoid the water molecular diffusion through the polymer matrix composite.

Figure 3. samples surface morphology in SEM after immersion in NaCl solution (A and B) uncoated (C and D) plain polymer (D and E) composites coated samples
4. Conclusions

Our results showed that the incorporation of carbon nanotubes into the EP coating magnesium bar significantly increased the corrosion resistance. The improvement in corrosion resistance is due to the CNTs acting as physical barriers to the corrosion process by filling in crevices, gaps and micron holes on the surface of the EP coating. Another reason is that the CNTs uniformly distributed in the EP coating and increased corrosion potential of the composite coating towards more positive values, restricting localized corrosion, and result in possibly homogenous corrosion. This study opened a new route for industrial in anti-corrosion region.

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