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Evaluation of the possibility of using diatomite natural mineral as a composite agent in acrylic coating

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Abstract:

In the present study the possibility of the commercially available acryl and diatomite earth (DE) mineral as a composite coating for corrosion protection of Mg alloys has been evaluated. The acrylic coating is used as a top coating in a wide field of applications like automotive, aerospace, medicine and electronics where it shows beneficial properties. Diatomite-dispersed acrylic paint was applied over the substrate by conventional spray technique with an air pressure of 3 kg cm⁻². Firstly the acryl was mixed with hardener and then the DE was added to the mixture. Four types of coating with 0,2,4,8 g/L DE have been prepared. The results show that adding up to 4 g/L of the DE improved the corrosion resistance and produced a coating with acceptable surface roughness.

Keywords: acrylic coating, diatomite earth, natural mineral, corrosion protection

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1. Introduction:

Magnesium alloy is the lightest metallic structural engineering material [1] because of the high strength to weight ratio and is an alternative to steels, cast irons, copper-based alloys and aluminium alloys with respect to reducing emissions (light-weighting) [1-3]. However one of the main issues with Mg alloys are their high reactivity and poor corrosion resistance [4]. The main reasons for this are internal galvanic corrosion (caused by second phases) and the fact that the oxide/hydroxide film on Mg is less protective [5, 6].

Methods to improve the corrosion resistance of Mg alloy are therefore a very active field of research. Various coating technologies for improving the corrosion resistance of Mg and its alloys, such as chemical conversion coatings [7, 8], electroless nickel [9, 10], electroplating [11], anodising [12, 13], micro-arc oxidation [14, 15] and organic coatings [5] have all been used.

Polymers are the matrix component of paints used for all purposes, as in decorative and protective applications [16, 17]. Typically organic coatings consist of a binder or vehicle, pigments and additives such as dryers, hardening agents, stabilizing agents, surface activating compounds and dispersion agents [18]. These types of coatings act as a barrier layer to separate the substrate metal from its environment. The general process of coating a specimen with a polymer is to prepare a solution or an emulsion, apply it to the substrate and let it dry or cure (in the case of thermosetting resins). In general the industrial methods of coating metals with polymers are cheaper and easier than other types of coating such as conversion and plasma electrolytic oxidation (PEO) coating [19, 20]. One potential approach, that has not been widely investigated, is the employment of polymer coatings for the corrosion protection of magnesium.

Among the polymeric coatings, acrylic copolymer coatings have been widely used in maintenance paints due to their excellent weatherability, hardness, and water and alkali resistance [21, 22]. In acrylic coatings, the aqueous polymer latexes are responsible for binding the pigments and fillers and forming a homogeneous film with good adhesion to the substrate. However, acrylic-based coatings do not show high resistance to the diffusion of corrosive reactants such as water, oxygen and other corrosive ions. This has limited their application as corrosion protection coatings since it can result in the delamination and degradation of the coatings once the electrolyte solution reaches the metal-coating interface leading to corrosion of the metal [23]. Therefore it is necessary

to develop composite acrylic latex coatings by adding additives/fillers in order to improve the corrosion protection properties of these kinds of coatings.

Recently there have been several studies conducted on the utilisation of various nanoparticles as additives in organic coatings to improve their corrosion resistance [24-26]. Most of these additives are synthetic and expensive, require energy intensive manufacturing methods and create problems in terms of recovery at end of life. There is therefore an increasing demand for low cost, sustainable and cost-effective additives for organic coatings.

In this research the possibility of using natural minerals without any purification as an additive in acrylic coating was investigated to improve the properties of the organic coating, namely diatomite. Diatomite is a silica mineral composed of the fossilized skeletal remains of microscopic single celled aquatic plants called diatoms. Among thousands of forms of algae, a unique group, the diatoms or diatomaceous are able to absorb miscible silica from water at extremely low concentrations and metabolise and accumulate it as an external skeleton. Diatomaceous earth has high porosity, stable chemical properties, wear resistance and heat resistance, etc. it can provide excellent surface properties, as well as increasing the coating production capacity, thickening and adhesion. Because it has a larger hole size, the DE reduced coating drying time [27-29]. For this reason we choose this particle as an additive for preparation composite coatings.

2. Materials and method:

AZ31 Mg alloy was used as a substrate whose chemical composition is 2.8% Al, 1.1% Zn, 0.3% Mn and the remainder Mg. Specimens with dimensions 150 mm × 150 mm × 3 mm were prepared with 600, 1500 and 2000 grade SiC emery paper, followed by 5 min ultrasonic degreasing in acetone at room temperature and washed by distilled water.

Diatomite Earth (DE) was provided from Beg-Tug Mineral (Ankara, Turkey), whilst a commercially available acrylic coating with a hardener additive was used for coating the material. Firstly the acryl was mixed with the hardener and then the DE was added to the mixture. Four types of coating with 0,2,4,8 g/L DE were prepared. The DE was mixed using a magnetic stirrer for 15 minutes and then by applying ultrasound at 50 kHz at 480 W power for a further 15 minutes.

The Diatomite-dispersed acrylic paints were then applied over the substrate by conventional spray technique with an air pressure of 3 kg cm^{-2} .

The infrared spectra of the polymer was recorded on Thermoscientific Nicolet 380FTIR spectrometer in KBr medium at room temperature. The morphology of the pigment was analysed at a magnification of 1k using a Hitachi (Model S3000 H) Scanning Electron Microscope (SEM) by spreading the pigment over a copper block which was then sputtered with gold. A Nanosurfe Atomic Force Microscope (AFM) was used for surface morphology analysis whilst FTIR spectroscopy was employed to determine the polymer phase change.

The total thickness of the coating was $100 \pm 5 \text{ }\mu\text{m}$. Electrochemical studies were carried out using Autolab electrochemical device (PGSTAT204 - Compact and modular) and a standard three electrode cell in an aqueous solution of 3.5 wt. % NaCl. Pt wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The potentiodynamic polarization curves were recorded using a constant potential scan rate of 1 mVs^{-1} .

3. Results and discussion:

The chemical compositions of the as-received raw materials are given in Table 1. Fig. 1 shows the SEM of the DE used in this study whilst Figure 2 details its particle size analysis. The results indicate that the DE is a silicon oxide base mineral whilst the SEM of the particle shows particles with a large hole size which helps to reduce the drying time of the paint and the amount of resin required because of the high surface area (therefore also lowering costs). The particle size analysis indicates that more that 80 % of the particles have a size less than $30 \text{ }\mu\text{m}$.

Table 1: Chemical composition analysis of as received DE (wt. %)

	SiO ₂	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	K ₂ O	SO ₃	Loss on ignition
Diatomite	65.5	1.75	2.39	2.61	7.89	0.28	1.45	0.13	18

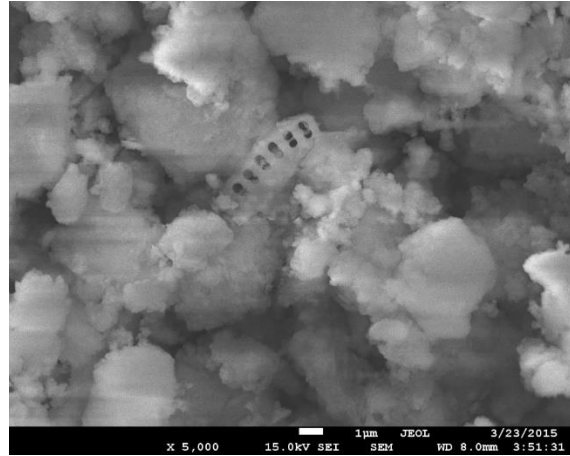


Fig.1. SEM images of the diatomite used in this study.

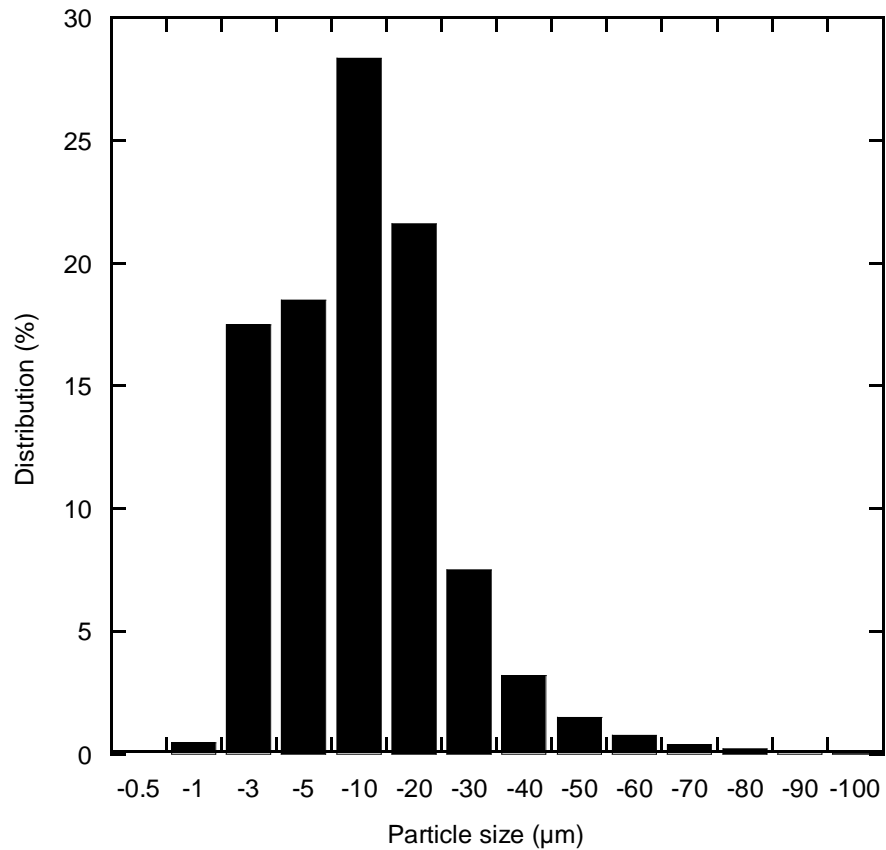


Fig. 2. Particle size analysis of the as-received DE.

Fig. 3 shows the infrared spectrums for the acrylic coating with and without DE. The acryl-DE composites show similar characteristic peaks. However, there is evidence of peak displacement

when DE particles are added to acryl. Additionally, in the case of acryl-DE composites, a broad peak appeared in 1064 cm^{-1} .

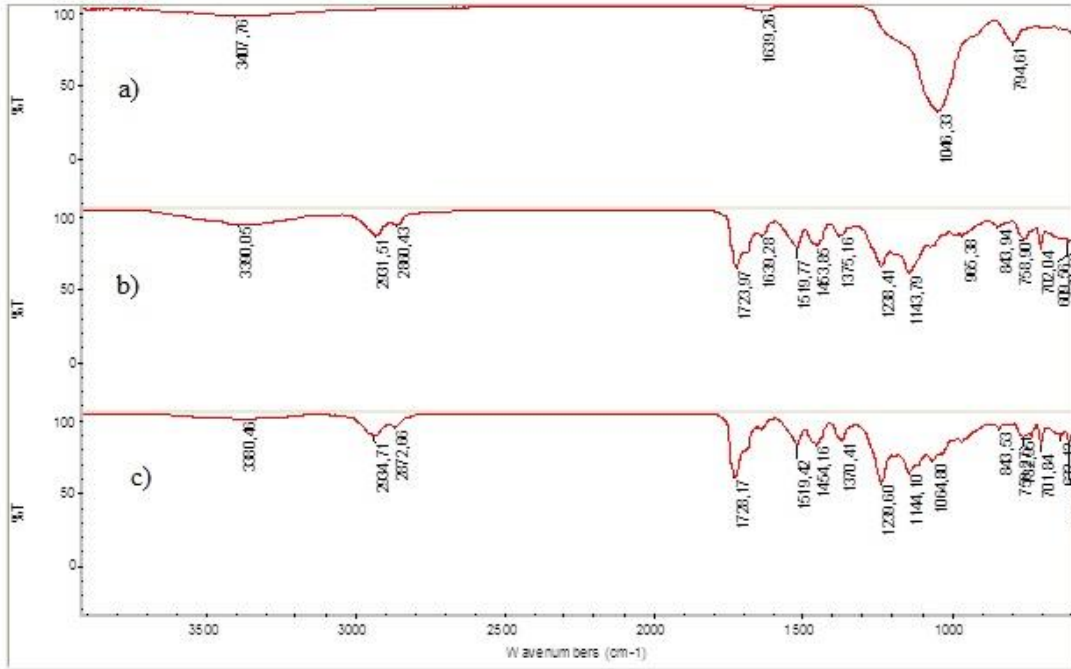


Figure 3. FTIR spectra of (a) DE, (b) Acryl alone and (c) Acryl/De composite

Fig. 4 shows the AFM image from samples of the untreated Mg and with different concentrations of DE in the Acryl coating. The roughness results are given in Table 2. It can be seen that by increasing the DE content the surface roughness is increased. As the DE concentration is increased up to 4 g/L the surface roughness does not increase significantly but a dramatic rise in surface roughness occurs when 8 g/L DE is added.

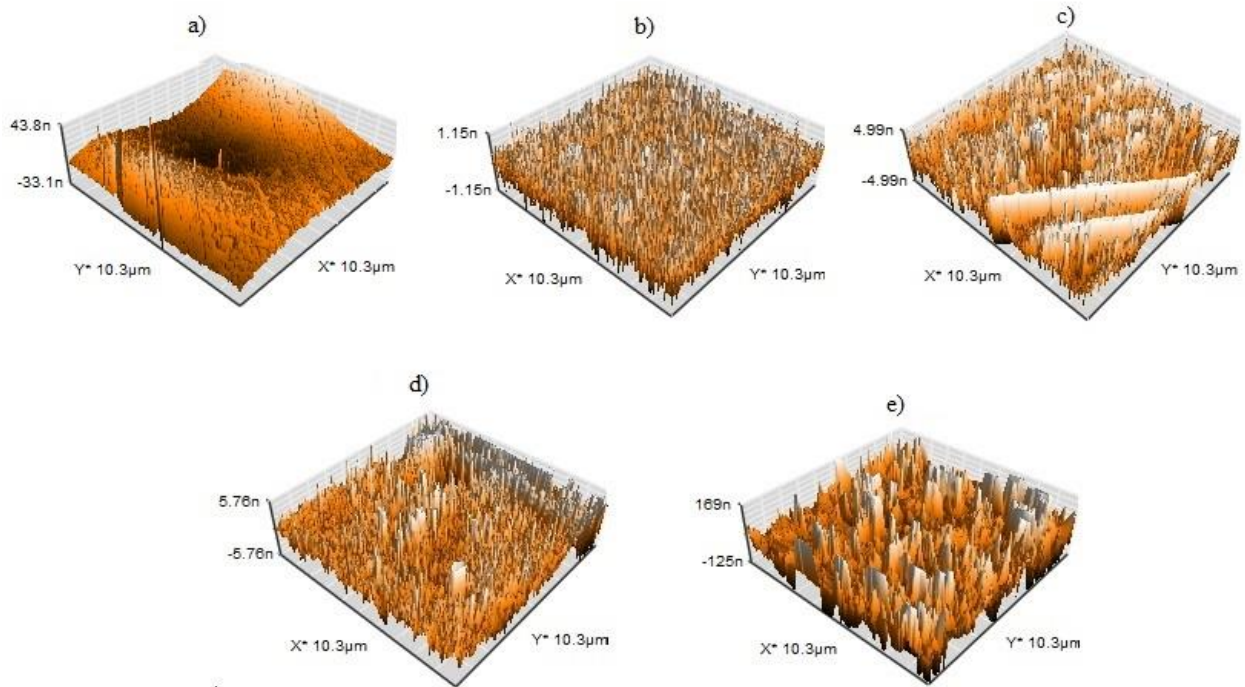


Figure 4. 3-D AFM images of uncoated a) Mg alloy and Mg alloy coated with Acryl coating with b) 0% c) 2% d) 4% and e) 8% concentrations of DE.

Figure 5 and Table 2 show the corrosion test results in simulated sea media. It can be seen that the corrosion potential of uncoated Mg is -1.54 V whilst that for the acrylic coating without additive and 2 g/L DE is approximately -1.40 V. The corrosion potential of the pure acryl coating is more positive than other samples and it shows that adding DE generally shifts the potential to more negative potentials, suggesting that the composite coatings are more active than pure acryl except when 2 g/L DE is added. As would be expected, the corrosion rate of the uncoated Mg samples are much higher than the coated samples. The corrosion rate (I_{corr}) of the coatings with 2 and 4 g/L DE is a factor of three times lower than the pure acryl coating and they therefore exhibit a relatively high corrosion resistance compared to the coating with 8 g/L DE. These results may suggest a synergistic effect between DE particles and acryl on corrosion protection and also uniform distribution of DE in low concentration. In the other word, presence of DE particles entrapped in acryl chain provide the reinforcement to acryl which reduce the degradation of polymer chain in saline condition[30]. Also it can be suggest that, because of high porosity, stable chemical properties of DE, DE and acryl molecules encapsulate with together and present a high dens structure to protect the surface and decreased diffusion of corrosive agent. The main

difference between the samples with 2 g/L and 4 g/L is their corrosion potential such that the acrylic coating with 2 g /L DE is more noble than coating with 4 g/l. This indicates that the DE shifts the potential to a more active potential. The corrosion rates for samples with less than 4 g/l DE were relatively similar. By increasing the DE content to 8 g/L the corrosion rate has been dramatically increased and this may be due to the formation of pores in the surface which would be expected to decrease the corrosion resistance. In addition, the high surface roughness (Table 2) shown on the sample with 8 g/L DE results in increased surface area and a higher probability of defects in the coating and therefore increased corrosion [31, 32]. Further consideration of the surface roughness results in Table 2 indicates that the acrylic coating decreases the surface roughness of Mg substrate. But as the DE concentration in acrylic coating increases, the surface roughness became higher due to the presence of DE on the surface of the coating. At high DE concentrations, the number of large particles on the surface increases leading to high surface impurities and low coating performance. The significant reduction in the corrosion current density (i_{corr}) in acrylic coated Mg alloy illustrate the effective corrosion protection performance of these coatings.

Table 2: Corrosion resistance and surface roughness data of prepared samples

Sample	R_a nm	E_{corr} v	I_{corr} μA	Corrosion protection efficiency %
Mg	52	-1.54	89	0.00
0 g/L DE	5	-1.42	0.77	99.13
2 g/L DE	8	-1.40	0.25	99.72
4 g/L DE	11	-1.54	0.22	99.75
8 g/L DE	186	-1.53	6.70	92.47

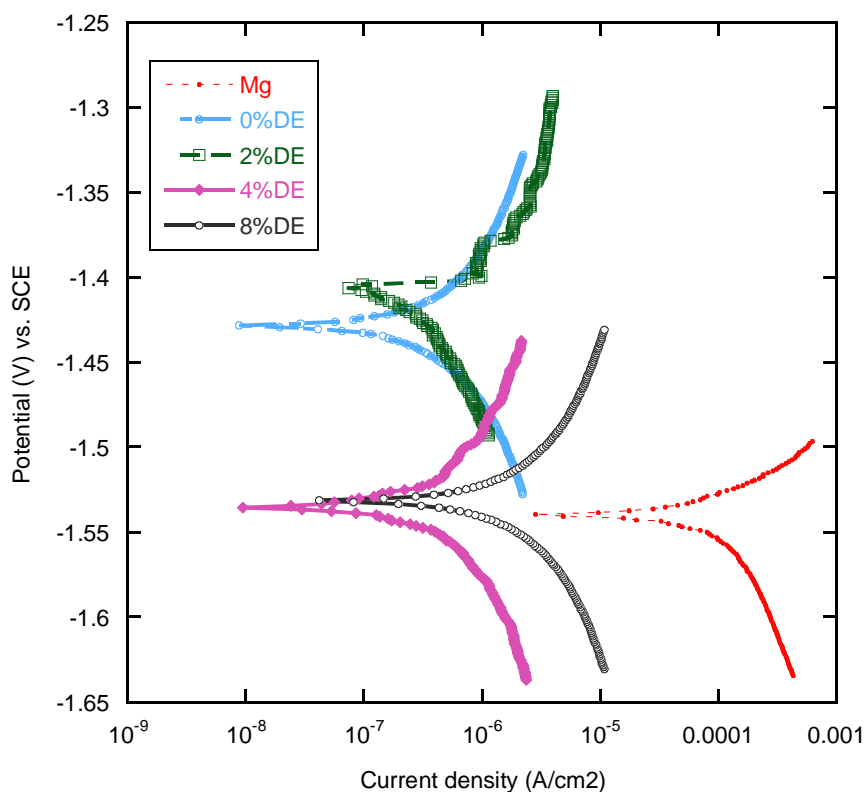


Figure 5. Polarization curves of different coatings.

Conclusion:

In this research a corrosion protective composite coating for magnesium alloy AZ31 with diatomite earth natural mineral without further purification in acrylic matrix has been described. The coated magnesium alloy showed the corrosion potential values in the noble direction due to the ability of the acrylic and composite to form a barrier coating. The corrosion rate (I_{corr}) of the coatings with 2 and 4 g/L DE is a factor of three times lower than the pure Acryl coating and therefore exhibit a relatively high corrosion resistance. The corrosion protection efficiency of the coating is found to be greater than 99%, which indicates the highly protective nature of the composite coatings.

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