Effects of TiO₂/SiO₂ reinforced nanoparticles on the mechanical properties of green hybrid coating

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ABSTRACT

Titanium and silica oxides nanoparticles were introduced into hybrid silica sol–gel/epoxy coating to enhance the mechanical properties of coatings. Titanium dioxide (TiO₂) and silica oxide (SiO₂) were chemically synthesised before adding to the prepared silica sol gel coating. X-ray diffraction (XRD), Energy-dispersive x-ray analysis (EDX) and Transmission Electron microscope (TEM) were used to characterize the prepared nanoparticles. The coating was then applied to 3003 aluminium alloy (AA3003) surface. The adhesion performance of different sol gel coating compositions was investigated using shear test to define the influence of nanoparticles on adhesive strength of the coating. The Rockwell C hardness test was used to study the micro-hardness of different compositions of sol gel coating. Also, contact angel was used to investigate the hydrophobicity of the coatings. The results showed that there was a significant improvement of the adhesion performance of hybrid silica sol gel coating due to addition of TiO₂ and the hydrophobicity of sol gel coating was increased due to addition of SiO₂ nanoparticles.

Keywords: Green coating; Sol gel; TiO₂; SiO₂; adhesion; contact angle; AA3003

1. INTRODUCTION

Hybrid silica sol gel coatings received a great interest during last decade due to their increasing applications and meeting the environmental requirements to be considered as a green coating. Moreover, it combines organic function into the matrix of inorganic silica. This advantage is allows to tailor the properties of coating such as flexibility, processability, hardness and temperature-resistance. However, there are some difficulties involved during of the sol gel processing such as complicated hydrolysis and condensation processes.

Silica sol gel coatings have been studied by numerous researchers reported that the combination of inorganic particles within its matrix lead to increase the mechanical properties of the coatings. Moreover, the introducing of nanoparticle within the sol gel matrix is presently one of explored areas in materials engineering. Conventionally micro-particles have been used within sol gel matrix to improve their mechanical performance[1]. The inorganic particles used as reinforcements that enhanced various mechanical properties of organic coatings, including scratch resistance[2], abrasion resistance, corrosion resistance [3], moisture resistance [4], heat stability, UV shielding [5] as well as other mechanical properties [6].

Nano-fillers have many advantages rather than micro-reinforcements for coatings materials; it offers better adhesion and consequently decreasing coatings thickness. These particles combine the inorganic matrix by enhancing the reactions of active surface groups of these particles and the silica sol gel functional groups.

This concept has recently been challenged by producing non-homogeneously matrix with some agglomerations due to introducing these particles [6]

The mechanical mixing of out situ prepared nanoparticles into silica sol gel coatings is believed to be a more appropriate method to improve homogeneity of the matrix. During this technique, nanoparticles are directly blended with precursors obtaining hybrid coating with no complicated chemical reactions.

Continuing my work [3,7] on hybrid sol gel coating, in the current study, the effect of adding titanium dioxide and silica oxide nanoparticles to silica sol gel coating and the consequences change in the mechanical properties of coating were investigated.

2. MATERIALS AND METHODS

2.1. Material

Aluminium alloy 3003 samples (obtained from Q-panel $15 \times 10 \times 0.15 \text{ cm}^3$) were cleaned with deionised water followed by ultrasonic cleaning in acetone and then dried for 30 min at 70°C before applying the coating at room temperature.

2.2. Preparation of hybrid sol-gel coating

The hybrid sol-gel (SOL) solution was prepared by an acid-catalyzed hydrolysis and condensation process using the following precursors; tetraethoxysilane (TEOS) and 3-Glycidyloxypropyl trimethoxysilane (GPTMS) purchased from Sigma Aldrich, USA. Bisphenol-A (BPA) was used as an organic cross-linking agent for the hybrid silica epoxy precursors. TEOS, GPTMS and BPA were mixed in ethanol with the molar ratio of 0.02: 0.09: 0.02: 5.0 respectively. The mixture was stirred for 60 min. before adding of the HNO_3 catalyst. The pH was adjusted by adding 0.1M HNO_3 to a value of 2. The mixture was then stirred vigorously at room temperature until it turned to a clear colorless homogenous solution. Then trimethylenediamine (TMDA) was added to accelerate the condensation reaction after hydrolysis. The TMDA/BPA mole ratio was adjusted to be 0.5 to form neat silica sol gel coating (SOL). For the different nanoparticles additives to hybrid sol gel coating, a similar procedure was carried out; with the exception that 0.05g of additive, TiO_2 and SiO_2 , is added in the 0.1M HNO_3 followed by sonocation for 2hrs before adding the acid to the precursor mixture forming TiO_2 /sol gel coating (SOT) and SiO_2 /solgel coating (SOS). All sols allowed to stand for 3 days before they were used to deposit a film on the Al alloy substrate. The coating was applied using a spray coating technique, following which the coating was dried at 80°C for 16 hours.

2.3. Preparation of SiO_2 nanoparticles

TEOS was added to a solution of water and ethanol. The molar ratio of TEOS: water: ethanol was kept constant at 0.1: 7.8:1 respectively. A solution was stirred for 30 min before adding to the dodecyl benzene sulphonic acid surfactant and ammonium hydroxide catalyst solution to initiate the synthesis of silica particles. The solution was kept stirred at room temperature for 12hrs. The solution was then dried using domestic microwave (800watt) for 10 min. before oven dry at 400°C for 3 hrs.

2.4. Preparation of TiO_2 nanoparticles

Titanium dioxide was prepared by hydrolysis and condensation of titanium tetra isopropoxide (TTIP). 5 ml TTIP is dissolved in 10 ml iso-propanol followed by adding of 0.01M nitric acid (HNO_3) drop wise with vigorous stirring in order reach a pH of 1.5. The solution continues to stir to form a homogenous semi-transparent sol. After 24hr, the

transparent TiO_2 sol was obtained. The gel was dried in microwave for 15min to get TiO_2 powder followed by calcinated at 450°C for 4 hrs to obtain desired TiO_2 nanoparticles.

2.5. Mechanical Testing

The mechanical properties of the coatings were evaluated in order to estimate the behaviour of the sol gel coatings with and without selected nanoparticles. Several mechanical tests have been used to evaluate different coatings. For each test triplicate samples were tested and the average test value calculated.

Hardness is the resistance of material for localized plastic deformation. The Rockwell C macro-hardness test has been performed according to the ASTM E18-12, while the Knoop indentation has been used to measure the micro-hardness according to the ASTM D1474-98. The Knoop indenter used in the form of a rhombic-based pyramidal diamond supplied a 100g test weight, and then the indent size is measured using a high magnification microscope. The cross hatch technique is used to evaluate the adhesion of a coating to the metallic surface according to scratch test (ASTM D3359). In this test, ten parallel scratches perpendicular to another ten parallel scratches are made on the coating film such that they reach to the surface of the substrate. The distance between each scratch is 1 mm. After the scratches were made, a standard adhesive tape is applied to the surface and removed subsequently. The tape is then visually inspected for the presence of any delaminated coating attached to the tape. The results of this test are counted in terms of the amount of the film removed from the coated substrate and are compared to data documented by the ASTM standard.

Lap shear test were applied according to ASTM D1002 as shown in Figure 1 where the geometry and dimensions of the joints are illustrated. The surface of the joined was first rinsed with tap water, air-dried at room temperature, followed by immersed in acetone and ultrasonic for 15 min, and then air-dried. This procedure was used for both joints of the aluminium sample. The sol gel coating was then applied on both surfaces by dip coating. The samples were then left for 8hrs to drying at 80°C . The joints were tested at room temperature, on Lloyd tensile machine having a capacity of 25kN and at a constant cross-head speed of 1mm/min. Lap shear strength data were taken as an average of at least three measurements.

Figure 1. Geometry and dimensions of lap joint.

Contact angles of different coating systems were measured from water drops using a goniometer and camera with SCA202 software. The angle between the baseline of the drop and the tangent at the drop boundary is measured and analyzed optically in static mode. All measurements were made using drops with a total volume of $2\mu\text{m}$ of distilled water with the needle of the syringe in the water drop and just above the solid surface. The contact angle was

recorded after it has reached a relatively constant value at room temperature in ambient air. The measurements were carried out at different 5 point on the surface of each sample and the average of these measurements was calculated.

3. RESULTS AND DISCUSSION

3.1. Nanoparticles characterization

EDX elemental analysis of prepared, TiO_2 and SiO_2 , is shown in Figures 2-a and 2-b respectively. the figure clarify that there is no other elements appeared during the preparation only few amount of carbon that appeared due to contamination of the sample during calcination and/or from the organic source of the prepared silicon oxide.

Figure 2. EDX analyses of the synthesized (a) TiO_2 and (b) silica oxide particles.

For more confirmation and investigation of the prepared particles, XRD technique was used. The XRD pattern of the prepared titanium dioxide, Figure 3-a, shows peaks at 2θ equal to 26, 38, 48, 54, 62 and 70 confirm the preparation of TiO_2 anatase phase [8] with few amount of rutile percent (18%) appeared at positions (2θ) = 28, 32, 37 and 42 [9]. Moreover, the XRD shows sharp peaks which may related to the high crystalline of the prepared TiO_2 . The XRD patterns of the prepared SiO_2 (Figure 3-b) showed a broad peaks at 2θ equal to 22.8 and small peaks at 26.6, 36.1 and 72.3 which confirm the preparation of Nanoparticles of SiO_2 [10, 11]. These broad peaks reflect the amorphous nature of the prepared silicon oxide particles. The particle size of the prepared TiO_2 powder was determined from the XRD pattern using Scherrer's equation [8].

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where d is the particle size, k is a dimensionless factor equal 0.9 [12], λ is the x-ray wavelength, β is the line broadening at the half maximum intensity and θ is the braggs angle, all these parameters are calculated directly from the XRD software. The calculated particle sizes of the TiO_2 sample was 27nm.

Figure 3. XRD patterns of the synthesized (a) TiO_2 and (b) SiO_2 particles.

Figure 4-a shows the TEM image of the prepared titanium dioxide. It is clear that the prepared TiO_2 particles are homogeneous and in the nano size range with an average particles size of 20nm. Moreover, parallel patterns appear within the particles which confirm the high degree of crystallinity [13]. Figure 4-b shows the TEM image of the prepared SiO_2 particles. It can be notice that, the particle size of silicon oxide is smaller (average particles size is 15 nm) than that of TiO_2 . In addition, SiO_2 particles do not show any parallel patterns which confirm the amorphous property of the SiO_2 . From the above results, it can conclude that the TiO_2 and SiO_2 particles are successfully prepared in the nano-size range.

Figure 4. TEM images of the synthesized (a) TiO_2 and (b) SiO_2 particles.

3.2. Mechanical characterization

The hybrid silica sol made from the hydrolysis and condensation of GPTMS and TEOS as the precursor in acid catalyzed condition. The introducing bisphenol-A is to connect the epoxy group where the epoxy functions of 3-Glycidyloxypropyl trimethoxysilane (GPTMS) chains

are opened and connected according to addition polymerization reaction with the bisphenol-A in the presence of TMDA catalyst as shown in equation (2). The existence of OH^{-1} group in the sol-gel coating (due to condensation processes) leads to formation of strong cross-linked bonds between the sol-gel coating and the metal surface [14]. These bonds increase in cross-linking during the high temperature curing process [15] which would significantly reflect on the superior adhesion of this type of coating with metal substrates. In addition the silanol groups (Si-OH) within silica sol gel coating forms a strong covalent bond with the aluminium substrates (Si-O-Al) [16, 17].

The stress-strain curves from the tensile tests shown in Figure 5 and the tensile strength of all coating systems are typically equal to 1.1 MPa. The addition of TiO_2 increase the failure elongation i.e. extend the plastic deformation of the hybrid sol gel, and the coating would be more rigid (i.e. increases the modulus of rigidity).

It can notice that the addition of SiO_2 improve the failure behaviour and makes the coating more ductile. It increases the modulus of elasticity and it would improve the impact properties of the sol gel coatings.

When the area under the stress-strain curve is calculated, it gives the toughness of these coatings system. The result, 0.84, 1.34 and 1.24 J/m^3 for SOL, SOT and SOS samples respectively. Moreover the proportional modulus of rigidity can be calculated by measuring the stress above which stress is not longer proportional to strain which is 0.11, 0.19 and 0.21 MPa for SOL, SOT and SOS samples respectively. It can conclude that both TiO_2 and SiO_2 nanoparticles improve the toughness and rigidity of the sol gel coatings. This behaviour of different coating systems would be reflected on the adhesion and hardness properties.

Figure 5. Stress-strain curves of different coating systems.

3.3. Contact angle

Contact angle measuring is used to determine the surface properties of solids and liquids using the pendant drop method. The contact angle is an important criterion for

determining the degree of flotation of particles. It is the easiest way to determine the hydrophobicity of a coating or a substance [18]. Hydrophobic and hydrophilic properties of surfaces can be evaluated using contact angle measurements. Hydrophilic materials have the contact angle below 90 deg., because a liquid spreads on the surface, while for highly hydrophobic substances the angle reaches even 110 deg.

The contact angles of different sol gel coatings system were measured as shown in Figure 6. It can be notes that the contact angle of SOL, SOT and SOS coatings are 92.8, 95.2 and 98.1 respectively. It can be seen that the contact angle increased by adding both TiO_2 and SiO_2 particles i.e. increasing hydrophobicity. In addition, the contact angle change by adding the TiO_2 particles is less than that of SiO_2 . It is well known that the silica particles increase the hydrophobic properties of coatings due to increase the surface roughness of the coating [19], however, titanium particles increase bonding within the sol gel matrix and so increase homogeneity which reflected in increasing the hydrophobic properties of coatings [20]. These properties would affect the adhesion of coating on the metal substrates as shown in the next section.

Figure 6. Contact angle of water droplet with the surface of (a) SOL (b) SOT and (c) SOS.

3.4. Mechanical Testing

The hardness of coated samples has been applied using the Rockwell C hardness test. Test samples have been tested under 150g loads. Average HRC value is 43 for the SOL coated samples and 48 and 43 for sol-gel coating with addition of SiO_2 and TiO_2 nanoparticles respectively.

Results of the Knoop indentation hardness test was carried out on three sample of each system of coating and the results are the average results. The Knoop indentation of different system are shown in Figure 7, where the average value for SOL, SOT and SOS coating systems are 296, 266 and 318 respectively. Since higher Knoop values indicate higher hardness, these

results suggest that the addition of SiO_2 significantly improve the coating hardness which is in agreement with the results of shear test. However, the SOS sample showed some cracks and delamination beside the indentation spot which reflect the bad adhesion of this coating sample.

Figure 7. Optical images of Knoop indentation of (a) SOL (b) SOT and (c) SOS coatings.

In order to study the adhesion performance of different coatings, the cross cut test has been applied to SOL, SOT and SOS coated AA3003 samples. The cross cut test images of SOL and SOT coated samples did not show any signs of delamination after performing the test ten times as shown in Figure 8-a and Figure 8-b. When performing the test on SOS samples, the sample exhibits distinguishable differences in behaviour when compared to that of the SOL and SOT samples, where delamination is visible at few scratch lines as shown in Figure 8-c. A 5B type of degree of adhesion (according to the ASTM D3359) was assigned to both SOL and SOT coatings deposited onto AA3003 substrates. This classification means that no area delamination of both coating systems. However, SOS coating has a 4B type of degree of adhesion which means the estimating amount of coating flakes detached at intersections from the substrate are less than 5%.

The SEM image of the scratched SOS sample, Figure 9, clarifies the delamination and cracks (arrows) due to scratching. This result is related to the increase of brittleness of sol gel coating due to addition of SiO_2 nanoparticles. From the above results it can be concluded that the addition of TiO_2 nanoparticles to the hybrid sol-gel coating has improved the adhesion, wettability properties of the hybrid sol gel coating, however, it decreases the hardness of the sol gel coating. In the other hand the SiO_2 decreases the adhesion properties of the hybrid sol gel coating and increases the hardness of those types of coatings.

Further studied is needed to investigate the effect of quantities of the nanoparticles on the mechanical properties of hybrid silica sol gel coatings.

Figure 8. Optical images of cross cut adhesion test of (a) SOL (b) SOT and (c) SOS.

Figure 9. SEM image of the scratched SOS sample.

4. CONCLUSION

1. Titanium dioxide and silica oxide were successfully prepared and TEM analysis confirm it is in the nano-size range

2. The prepared nano-particles were mixed within sol gel coating matrix before applied to AA3003 metal surface.

3. Shear test, cross cut test and contact angle showed that the addition of titanium dioxide to sol gel coating improve the hydrophobic and adhesion properties of the coating, however, it decreases the hardness of this type of coatings.

4. In addition the introducing SiO₂ to the coating improve hydrophobic and surface hardness but decreases the adhesion properties of the sol gel coating.

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References

- [1] S. Kermadi, N. Agoudjil, S. Sali, M. Boumaour, S. Bourgeois, M.C. Marco de Lucas, *Thin Solid Films*, 564 (2014) 170-178.
- [2] J. Xu, W. Pang, W. Shi, *Thin Solid Films*, 514 (2006) 69-75.
- [3] R. Akid, M. Gobara, H. Wang, *Electrochimica Acta*, 56 (2011) 2483-2492.
- [4] C. Decker, L. Keller, K. Zahouily, S. Benfarhi, *Polymer*, 46 (2005) 6640-6648.
- [5] H. Zhang, H. Zhang, L. Tang, Z. Zhang, L. Gu, Y. Xu, C. Eger, *Tribology International*, 43 (2010) 83-91.
- [6] H. Zhang, H. Zhang, L. Tang, L. Zhou, C. Eger, Z. Zhang, *Composites Science and Technology*, 71 (2011) 471-479.
- [7] H. Wang, R. Akid, M. Gobara, *Corrosion Science*, 52 (2010) 2565-2570.
- [8] M. Nasr, A. Abou Chaaya, N. Abboud, M. Bechelany, R. Viter, C. Eid, A. Khoury, P. Miele, *Superlattices and Microstructures*, 77 (2015) 18-24.
- [9] B.K. Mutuma, G.N. Shao, W.D. Kim, H.T. Kim, *Journal of Colloid and Interface Science*, 442 (2015) 1-7.
- [10] D. Adak, M. Sarkar, S. Mandal, *Construction and Building Materials*, 70 (2014) 453-459.
- [11] H. Banu Yener, Ş.Ş. Helvacı, *Separation and Purification Technology*, 140 (2015) 84-93.
- [12] P.K. Khanna, N. Singh, S. Charan, *Materials Letters*, 61 (2007) 4725-4730.
- [13] P. Simon, W. Carrillo-Cabrera, P. Formánek, C. Göbel, D. Geiger, R. Ramlau, H. Tlatlik, J. Buder, R. Kniep, *Journal of Materials Chemistry*, 14 (2004) 2218-2224.
- [14] M. May, H.M. Wang, R. Akid, *International Journal of Adhesion and Adhesives*, 30 (2010) 505-512.
- [15] J. Habsuda, G.P. Simon, Y.B. Cheng, D.G. Hewitt, D.A. Lewis, H. Toh, *Polymer*, 43 (2002) 4123-4136.
- [16] S. Hamdy, P. Butt, *Surface and Coatings Technology*, 201 (2006) 401-407.
- [17] V. Dalmoro, J.H.Z. dos Santos, E. Armelin, C. Alemán, D.S. Azambuja, *Applied Surface Science*, 273 (2013) 758-768.

- [18] M. Sakai, J.-H. Song, N. Yoshida, S. Suzuki, Y. Kameshima, A. Nakajima, *Surface Science*, 600 (2006) L204-L208.
- [19] T. Bharathidasan, S.V. Kumar, M.S. Bobji, R.P.S. Chakradhar, B.J. Basu, *Applied Surface Science*, 314 (2014) 241-250.
- [20] K.-R. Wu, J.-J. Wang, W.-C. Liu, Z.-S. Chen, J.-K. Wu, *Applied Surface Science*, 252 (2006) 5829-5838.

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