RESEARCH ARTICLE

PMMA-TIO$_2$ NANOCOMPOSITE COATING ON COPPER SUBSTRATE FOR CORROSION PROTECTION.

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Manuscript Info	*Abstract*
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The main aim of this work is to enhance the surface protection of copper substrate from corrosion, by dipping process in nanocomposite PMMA-TiO$_2$. Dipping method at constant dipping speed is applied to produce nanocomposite coat on copper substrate. The microstructure and morphology of the polymer nanocomposite coating, which includes different concentration of nanoparticles (NPs) of titanium dioxide filler (0, 1, 2 wt. %) as the reinforcing phase in PMMA matrix, was studied using SEM, AFM and FTIR. Corrosion measurement by Tafel polarization test was applied by using 3% NaCl solution. Finally, Vickers microhardness and contact angles were conducted on the nanocomposite coating surface. The results verified the formation of PMMA-TiO$_2$ nanocomposite coating. The corrosion test illustrated that the lower corrosion rate was achieved at 2wt% TiO$_2$ NPs. The results of the microhardness and contact angle showed that these properties depend heavily on the addition TiO$_2$ NPs. with the best condition attained at the 2wt% TiO$_2$ NPs.

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Introduction:-

Copper (Cu) and copper alloys are widely used in a variety of products that enable and enhance our everyday live, because they have excellent thermal and electrical conductivity, good formability and strength, good resistance to fatigue and corrosion, and known as nonmagnetic metal [1]. Excellent corrosion resistance, high thermal and electrical conductivity are properties that copper in its pure unalloyed state has. Various types of pure copper grades are differing in the amount of impurities. Applications requiring high ductility and exceptional conductivity using oxygen-free coppers [1].

There are numerous industrial methods to coat nanocomposite films, such as electro plating or spraying. However, the application of such methods is limited by the expensive, complex and time-consuming processes [2]. Nanocomposite are materials having at least one phases with dimensions equals to less than 100 nm materials and have very good performance. Nanocomposite coatings using dipping process one of successful method that was used in the previous years, the second phase can be nitride particles (BN) [3], or hard oxide (TiO2) [4], etc.

Poly methyl methacrylate (PMMA) is an important thermoplastic polymer that is transparent to visible light with a glass transition temperature of ~100 ℃ [5]. It presents very good strength-to-weight ratio and unaffected by moisture.

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Most outer surface of the copper tube in air conditioning systems undergo corrosion and copper is more prone to corrosion because it is the most metal used in this application under severe environmental conditions such as air, moisture and rain [6,7, 8]

There are several parameters that influence the rate and nature of the corrosion reactions and these include the material, the properties of the material and the environment, the chemical composition, the constituents, and the temperature [9].

In this work polymer Matrix Nanocomposites (PMMA) coating was used containing dispersed second-phase particulates (TiO2). Because of its variety of desirable properties, involving good mechanical properties, perfect transparency in visible regions, acceptable thermal stability, good weatherability, non-toxicity and compatibility with ceramic, PMMA has been choose as the main matrix for the preparation of polymeric nanocomposites [10]. Sol gel and automation dipping process will be used for preparation and coating of nano ceramic oxide on copper substrate.

The aim of this work is to enhance the surface protection of copper substrate from corrosion, by dipping process in nanocomposite PMMA-TiO2.Dipping method at constant dipping speed is applied to produce nanocomposite coat on copper substrate.

Experimental work:-
Materials:-
Pure Copper rod (99.9 Cu %) of 25.4 mm diameter and 3mm thickness are used as a substrate. The copper specimens were grinding using (320, 600, 800) grit silicon carbide grinding papers and polished with diamond paste, then the specimens washed with distilled water and finally rinsed with acetone in an ultrasonic bath for 15 min .

PMMA and its hardener used as matrix, Titanium dioxide (TiO_2 NPs) with 43nm particle size are used as reinforcement.

Methods
Titanium dioxide (TiO_2) was prepared from $TiCl_4$ solution [11]. TiO_2 NPs with 1% and 2% concentration are added to the PMMA solution and blended with the hardener at weight ratio 25:1. The amounts of PMMA and TiO2 NPs for the coating are shown in table 2.1.The preparation of nanocomposite coating was initially done after the mixing of mixture manually for 1 minute. Fig.1 shows nanocomposite solution at different concentration of TiO_2 NPs. Three sample were used for applying (PMMA: TiO_2) nanocomposite coating by dipping process on the pure copper substrate. This process was done at speed 200 mm/min with the automatic method with dwell time of 10 seconds. The samples were left for curing at atmosphere condition for 1 hour.

Table 1:-Preparation of nanocomposite of PMMA/TiO_2

No.	PMMA (wt %)	TiO_2 (wt %)
sample 1	100	0
sample 2	99	1
sample 3	98.00	2
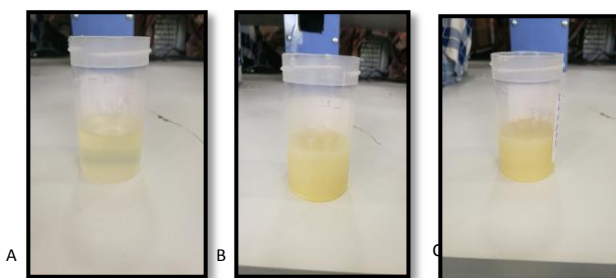
Fig.1:-Nanocomposite solution for: a: pure PMMA, b: 1%TiO_2, c: 2%TiO_2

Instrumentation

The surface morphology of the coating was investigated by using scanning electron microscope (SEM) and particle size measurement by using atomic force microscopy (AFM).

The microhardness of the samples was determined using a micro- hardness tester. Vickers micro hardness measurements were taken using a 4.9N load for each sample.

The hydrophobic property was measurement by contact angle test. For this test, a small liquid droplet resting on a flat a horizontal testing substrate was used.

Conventional three-electrode cells were used for Tafel polarization test. The first using copper samples as working electrodes, the second using Ag/AgCl as reference electrode, and the last using platinum as a counter electrode, the three electrodes immersed in a neutral solution. In this testing, fresh solutions of NaCl 3% were used for all the electrochemical tests. Also 1cm^2 areas were left for exposure to the electrolyte.

Result and Discussion:-

SEM analysis

Fig. 2a shows the SEM image of sample with PMMA coating only. Flat surface and relatively homogeneous morphology are seen. This feature is in agreement with that seen by Anita et al. [12]. Figures 2b&c shows image of coated substrates with PMMA/TiO$_2$ nanocomposites containing 1% and 2 % TiO$_2$ NPs respectively. The TiO$_2$ NPs with 2% addition are better distributed in the PMMA matrix than 1% addition. Although TiO$_2$ particles are in the nano scale range, the SEM image show that some other TiO$_2$ NPs tolerate some agglomeration with a maximum size of 300 nm. This agglomeration is attributed to the fact that, the mixing was carried out by hand and the viscosity of the PMMA was too much, which is lead to form different shapes of NPs in some regions which take place in a whole matrix and occupy the spaces among the molecules. The TiO$_2$ NPs appeared as bright point in the PMMA matrix. This good distribution of TiO$_2$ NPs helps to improve the nanocomposite ehavior.
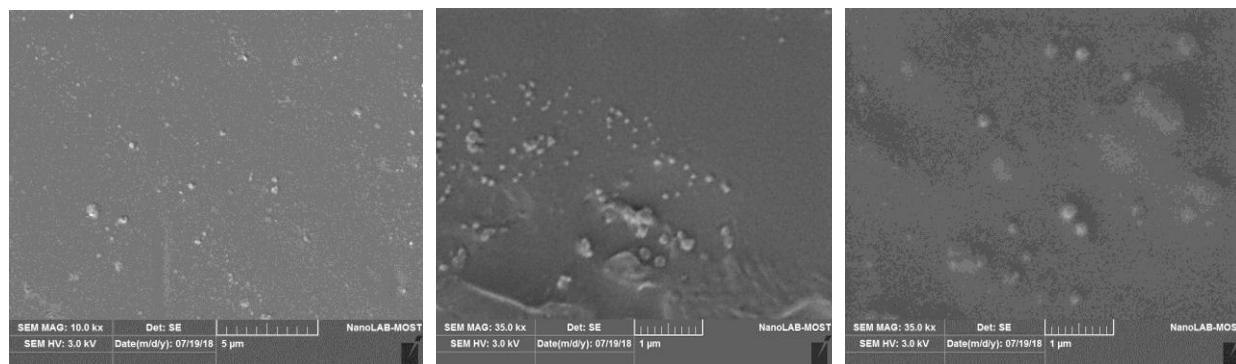
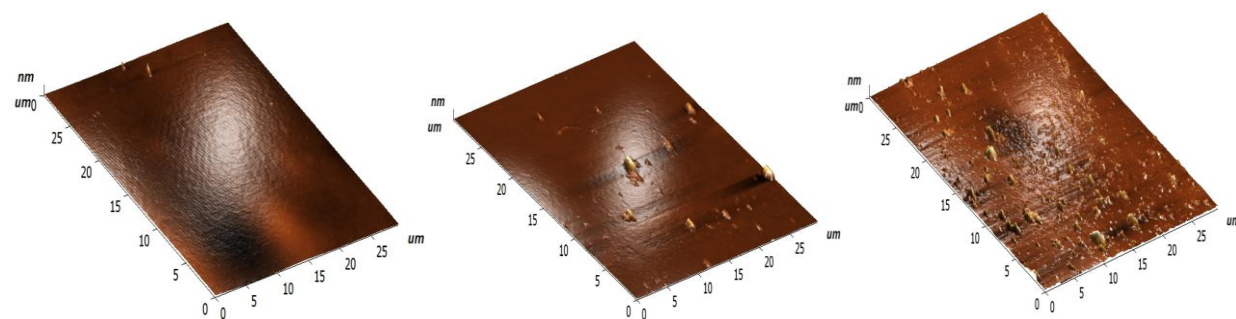**Fig.2:-**SEM images for: a: sample1, b: sample2, c: sample3

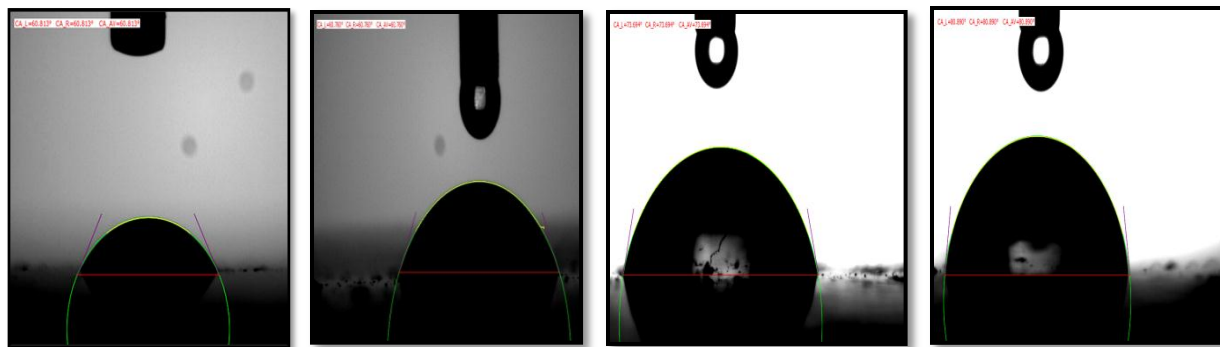**Fig. 3:-**AFM image for: a: sample1, b: sample2, c: sample

Fig. 4:-Contact angle for: A- uncoated substrate, B-sample1, C- sample 2, C- sample 3

AFM analysis

As shown in fig.3a, the PMMA coating (sample 1) has a smooth surface with very low root mean square roughness (R_{MS}) and surface average roughness (R_A) 0.266nm and 0.206nm, respectively. No pits or pin holes are observed in the AFM topographical image of the PMMA film.

Sample 2 with 1% TiO_2 NPs (fig. 2b) indicates that the R_A and R_{MS} are transformed to 0.466 and 0.599 nm respectively compared with PMMA coating.

Figure 2c shows that the TiO_2 NPs are uniformly distributed in the PMMA matrix, which is in agreement with the SEM morphology in Fig.2. The R_A and R_{MS} of the nanocomposite coatings are 3.238 nm and 5.3 nm, respectively. These results indicate that the surface roughness of PMMA/TiO_2 nanocomposites is increased with increasing TiO_2 NPs concentration. The nanocomposite particles size is in the range from 50 to 280 nm, this is attributed to the large agglomeration of NPs and there is agreement with the result of SEM.

Contact angle

The obtained data of contact angle measurements (fig. 4& table 2) show that the hydrophobic property has diminished with the addition of TiO_2 NPs, where the contact angle (CA) is increasing with the increase of the TiO_2 NPs. The surface tension decreased with increasing TiO_2 NPs and leads to reduce surface wetting [13]. From figure (4b), the PMMA showed hydrophilic natural with of 61° on its smooth surface this result showed good agreement with Feng et al [14].The same result is obtained for uncoated sample (fig. 4a) .This result leads to the fact that, at lower CA values, the surface will absorb more water molecules and the corrosion of the materials is increased.

Table 2:-Contact Angle Measurement

item	Contact angle
uncoated	61
Sample1(coated with PMMA only)	61
Sample2 (coated with PMMA and 1% TiO_2)	74
Sample3 (coated with PMMA and 2 % TiO_2)	81

Tafel polarization investigation

Fig.5 and table 3, which represent the corrosion characteristics for all samples that the anodic part (especially the passivation region) is more passive and passivation current is more close to cathodic current, i.e. the oxidation reaction on the metal surface is retarded and more difficult to reduce passivation current. The increasing in passivation is related to increasing in TiO_2 NPs concentration in PMMA coated layer. When the concentration was 0% (sample 1) the corrosion rate was 1.263×10^{-2} mm/y while when the concentration was 2% (sample 3) the corrosion rate was 2.159×10^{-4} mm/y and the corrosion rate gradually decreased with increasing the TiO_2 NPs concentration in PMMA coated layers.

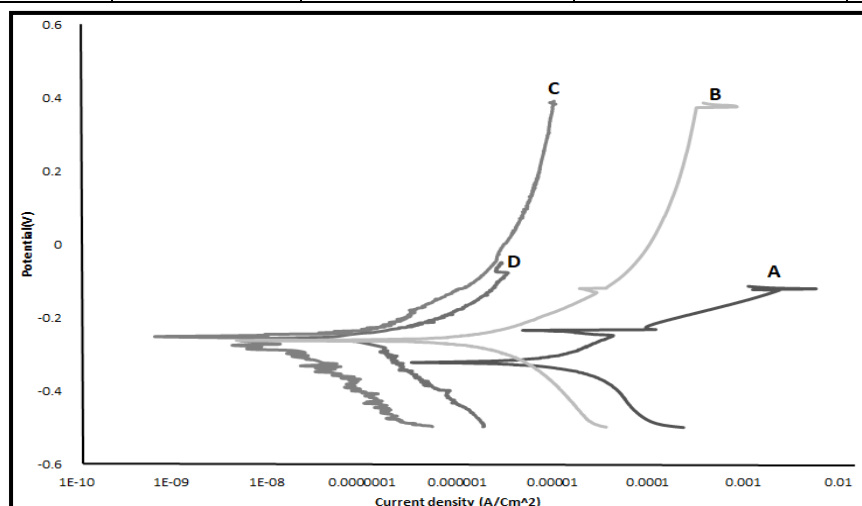| Item	E corr. (volt)	I Corr. (Amp/cm^2)	C.R (mm/y)	I Passive (Amp)
uncoated	-0.320	6.38×10^{-6}	0.740×10^{-1}	2.0×10^{-3}
sample 1	-0.260	1.09×10^{-6}	1.263×10^{-2}	2.5×10^{-4}
sample 2	-0.253	7.20×10^{-8}	0.834×10^{-3}	3.0×10^{-6}
sample 3	-0.269	1.86×10^{-8}	2.159×10^{-4}	1.1×10^{-5}

Fig.5:-The polarization curve (Tafel) for different coating on copper surface, A: uncoated, B: Sample1, C: Sample2, D: Sample3

Table 3:-The Corrosion Characteristics For Sample At Dipping Speed 200mm/Min.

Vickers microhardness

As shown in table 4, the microhardness value of samples was improved with addition TiO_2 which is changed from 80 for pure copper to 126 with 2%TiO_2 within nanocomposite coating. This increment in TiO_2 is due to the fact that TiO_2 nanoparticles have good resistance to penetration of load of hardness indenter and acting as rigid bodies in the PMMA matrix. Hence the microstructural bonds between PMMA and TiO_2 endure the applied force instead of base matrix alone.

Table 4;-Mean average value of Vickers microhardness

item	uncoated	sample1	sample 2	sample 3
Values (HV)	90	80	117	126

Conclusions:-

The produced PMMA-TiO_2 nanocomposite coating in this study improves the corrosion resistance and mechanical behavior of the surface of copper substrate. The findings of this study are summarized as below:

1. Corrosion protection is increased with increasing TiO_2 in the formed composite layer under constant dipping speed of coating (200 mm/min). The coatings containing 2wt% TiO_2 exhibited the highest corrosion resistance, with corrosion rate of 2.159×10^{-4} mm/y.
2. Vickers microhardness of coated Cu substrate are higher than that of uncoated copper one. There is a maximum increase of microhardness from 90 for pure copper to 126 HV with the addition of 2% TiO_2 NPs.
3. The hydrophobic property of surface improved with increased TiO_2 NPs, where the value of contact angle for nanocomposite coatings with 2% TiO_2 is 81° while that for uncoated Cu substrate is substrate 61°.

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