

Mechanical properties of electroless nickel coated ABS M30 plastics prepared by rapid prototyping process

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Abstract

Electroless nickel coating on rapid prototyped ABS M30 plastics was successfully developed. Micro hardness studies indicated that the coatings are enhancing the strength of plastics. The corrosion resistance of coated surface was evaluated in sea water medium using electrochemical techniques. The EN surfaces improved the ultimate tensile strength in comparison with ABS M30 plastics. The appearances of spherical particles of Ni–P are visible in FE–SEM images. The results are presented and discussed.

Keywords Electroless nickel, ABS M30, corrosion resistance, tensile, SEM

Introduction

Electroless nickel–phosphorus deposition is an established industrial practice as a protective and decorative coating in various industries due to its superior corrosion and wear resistance, excellent uniformity, wide range of thickness as well as mechanical and physical properties. Extensive research has been carried out on the characterization of the electroless nickel deposition process. Corrosion properties of

electroless Ni-P deposition depend mainly on phosphorus content and the corresponding structural and mechanical state. Micro porosity, roughness and inhomogenities due to internal stress within the Ni-P deposited layer are affected by the substrate pretreatment method.

Brenner and Riddell first developed autocatalytic nickel deposition using a sodium hypophosphite bath [1]. There are numerous parameters affecting the electroless nickel process temperature, pH, nickel ion concentration, reducing agent concentration, the loading in the bath and agitation affect the nickel deposition rate[2–3]. Electroless nickel deposition bath is known to have a major problem of sudden bath decomposition, which results in an increase in the operating cost of the process and the generation of environmentally hazardous waste [4]. Electroless Ni-Co-P electrolyte solution containing sodium citrate and lactic acid as complexing agents in order to obtain a relatively high deposition rate [5]. The coatings can be tailored for desired properties by selecting the composition of the coating alloy, composite and metallic to suitable specific requirements [6]. Another serious consequence of phosphite presence in the EN solution is its effect on the internal stress of Ni-P deposit. As the phosphite concentration increases, the internal stress becomes more tensile [7]. The tensile stress is harmful to many applications such as corrosion and memory disk. However, metallization of ABS plastics prepared through RP process is still at entry level. The presence of honey comb structure of ABS obtained by RP method is claiming that metallization on it will improve the mechanical properties considerably better than the injection molded plastics.

The developed coatings are expected to increase hardness and tensile strength. The performance of coatings is to be screened by weight gain studies, Vickers hardness test, Tensile strength, corrosion resistant measurement by tafel polarization and AC impedance methods. The uniformity of the surface is a desirable factor for improvement on mechanical properties for metalized ABS M30 which will be determined by micro structural analysis using FE-SEM images.

Experimental Procedure

The bath developed in the present study had the following ingredients.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O} = 35 \text{ g/l}$

$\text{NaH}_2\text{PO}_2 = 27 \text{ g/l}$

Tri Potassium Citrate = 50 g/l

Dextrin = 2 g/l

$\text{NaNO}_3 = 1 \text{ g/l}$

pH = 5.83

Temperature = $85 \pm 2^\circ \text{C}$

Plating time = 2 hours (25 microns per hour)

Coating thickness = 50–54 microns

Evaluation of Electroless nickel coatings on ABS M30 through various measurement

Weight-gain method

ABS M30 plastics prepared by RP process with size 20 x 50 x 2 mm³ were employed in the EN plating bath. They were mechanically polished with fine grit paper, washed with distilled water and then degreased by acetone. It is again washed and etched in 2% HCl and 1% H₂O₂ solution. Then the plastics were sensitized and activated by adopting the procedure as reported earlier[8]. The initial weight of ABS M30 plastic was measured using electronic weighing machine. Then the plastics were subjected to EN plating. The rate of deposition was calculated using the following formula:

$$\text{The rate of deposition } (\mu\text{m/h}) = \frac{W \times 10^4}{D A T}$$

Where,

W – Weight gain of the deposit (g)

D – density of Ni-P in the coating (g/cm³)

T – plating time (h)

A – Surface area of the ABS M30 (cm²)

Micro hardness measurements

Micro hardness measurements for all the as metalized ABS M30 (20 x 50 x 2 mm³) were determined adapting ASTM E-384 procedure by Vicker's hardness tester with a load of 100 g. A diamond shaped indentation was made on each EN coated ABS M30

plastics at eight different points and the average of hardness was measured as given below:

$$\text{V.H.N} = (1854 \times \text{load}) / d^2$$

where d = diagonal of the indentor

Corrosion resistance measurements

The potentiodynamic polarization and impedance studies were carried out on metalized ABS M30 plastics with the electroless nickel coated area of 1 cm^2 exposed surface (test electrode) in sea water medium, 5 cm^2 of platinum electrode (counter electrode) and saturated calomel as reference electrode in three electrode cell setup.

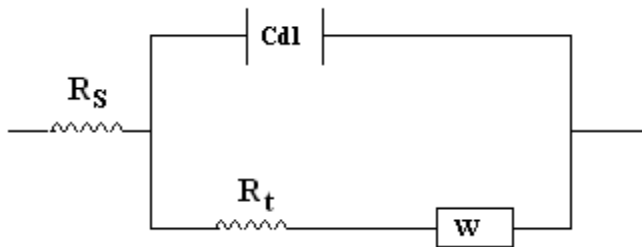
Tafel polarization studies

A constant quantity of 250 ml of sea water (3.5% NaCl) solution was accurately measured and used as electrolyte for this study. The working electrode, reference electrode and the auxiliary electrode were arranged in the electro chemical workstation (Sinsil Model 604E, USA) and the readings were measured by changing the potential values $\pm 300 \text{ mV}$ from open circuit potential at a sweep rate $1 \text{ mV} \cdot \text{second}^{-1}$ for the metalized ABS M30 rapid prototypes.

The corrosion kinetic parameters such as E_{corr} and I_{corr} , were determined. The decremental values of E_{corr} and I_{corr} confirmed that the coatings are protecting the etching of plastics from the attack of aggressive chloride ions[9–13].

Impedance measurement

AC impedance was performed using Nyquist plots in the frequency range of 10 kHz to 0.01 Hz under potentiostatic conditions using sea water as electrolyte for EN. The impedance measurements were carried out on test surface at room temperature. The Randell's electrochemical equivalent circuit[14] was adopted which is highly suitable system for corrosion resistance surfaces as reported by Raja et.al.[15]



- R_s – Solution resistance
- R_t – Charge transfer resistance
- W – Warburg impedance
- C_{dl} – Double layer capacitance

The circuit composed of real impedance (Z') and imaginary impedance (Z''). A plot of real impedance (Z') Vs imaginary impedance (Z'') showed a uncompleted semicircle which is the characteristics of EN coatings as reported earlier[16]. The formation of Warburg impedance equivalence were arrived by analyzing the plots to identify the best fit for corrosion resistant surfaces. A capacitance is created between EN coatings and electrolyte which is measured as double layer capacitance at coating/solution interface.

The higher value of frequency was used to calculate C_{dl} using the following relation of equation.

$$C_{dl} = \frac{1}{2\pi Z''_{\max} R_t}$$

Tensile strength measurements

This experiment was carried out using Instron 8801 as per ASTM D638 at a strain rate of 2 mm/min.

Scanning electron microscopic studies (SEM)

The cross-sectional micro structural images of EN coated ABS M30 plastics were examined using FE-SEM analyzer. The EN coated test electrodes were prepared for size 1 cm² and placed firmly on test plate pre-coated with Au to make a conducting surfaces on ABS M30 rapid prototypes.

Results and Discussions

Weight gain studies

The results of electroless nickel coatings on ABS M30 plastics obtained by weight gain method and eddy current tests are placed in Table 1. It has been noticed that the incorporation improves the micro hardness values. The addition nickel coatings on fiber matrix enhanced the tensile strength because of its higher anti-galling effect than uncoated plastics. The rate of deposition for EN was calculated as 50µm at the plating duration of 2 hours.

Micro hardness measurements

The hardness of the electroless nickel coated ABS M30 plastics was measured by Vicker's hardness tester is given in Table 2. The higher hardness is due to the presence of non-metallic phosphorus in Ni matrix.

Corrosion resistance studies

Tafel polarization studies

The corrosion resistance experiments were carried out for EN coatings on ABS M30 plastics has been done by employing current–voltage measurements using polarization studies. The shift of Potential to less negative direction by coating indicated the corrosion protection nature of the surface. Also I_{corr} values have reduced to a greater extent by EN coatings and the results are presented in table 3.

Electrochemical Impedance Spectroscopy (EIS) studies

The calculated impedance values of EN coated ABS M30 plastics in 3.5% sea water medium are indicated in the table 4. It is cleared that R_t values are increased at the expense of double layer capacitance. The reduction in C_{dl} values have been accounted for the system following Warburg's impedance. It is evident that EN coatings on ABS M30 plastics prepared by FDM RP method can be useful for electronic circuits as this coatings exhibit EMI shielding effect due to the presence of phosphorus in Ni matrix.

Tensile strength measurements

The table 5 indicates that at strain rate of 2.48 in the case uncoated plastics resulted maximum stress at 27.78 MPa. For EN coated plastics, the rate of strain started at 2.48% and at 2.51%, the ultimate tensile strength of 28.94 Mpa was achieved due to presence of Ni–P coatings on ABS M30 Rapid prototypes. Hence it is understood that EN coated surfaces can be used as intermittent layers for developing surface finishing for automobile components.

Scanning Electron Microscopic studies

Figure 1 indicates the cross-sectional SEM images of EN coatings obtained from citrate based bath. The appearance of layered structures with hanging of spherical particles aggregation indicating that the presence of Ni-P in the coatings. This entire coatings micro structures seem to be a caterpillar resting on a leaf. The black images are the conductive gold coatings on ABS M30 plastics. The top layer in the image is the indicative of reflected X-rays in SEM instrument and not on the coating systems.

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Conclusion

An attempt has been made successfully to develop non magnetic coatings based on EN on ABS M30 plastics. The EN coatings improved hardness, corrosion resistance and tensile strength of ABS plastics. SEM images confirmed the existence of Ni-P in ABS polymer matrix. This investigation was found useful to develop an EMI shielding coatings for and PCB.

References

- [1]. 'Nickel and Chromium plating', J.K. Dennis, T.E. Such.. Butterworth & Co, Londres 1972.
- [2]. 'Effects of electroplating on the mechanical properties of stereolithography and laser sintered parts', N.Saleh, N.Hopkinson, R.F.M. Hague, S.Wise, Rapid Prototyping Journal, 10, 5, pp305–315, 2004.
- [3]. 'Intergrated used of rapid prototyping and metal plating technique for development of micro air vehicles', U.Chandrasekhar, K. Venkatesh, K. Elangovan, T.Rangaswamy, Int. J. of Engg. Sci. and Tech., 3, 1, pp188–193, 2011.
- [4]. 'Study of electroless nickel plating on PerFactory rapid prototype model', J.C. Rajaguru, C.Au, M. Duke, J. of Achiv. In Mater. and Manuf. Engg., 55, 2, pp782–789, 2012.
- [5]. 'Description and modeling of the additive manufacturing technology for aerodynamic coefficients measurement', S. Daneshmand, C. Aghanajafi, J. of Mech. Engg., 58, 2, pp125–133, 2012.
- [6]. 'Electroless copper deposition on aluminium-seeded ABS plastics', D.Li, K.Goodwin, C. Lu Yang, J Mater Sci., DOI 10.1007/s10853-008-3031-1.
- [7]. 'Surface modification with copper by electroless deposition technique: an overview', K.G. Mishra, R.K. Paramguru, African J of Pure and Appl. Chem., 4, 6, pp87–99, 2010.
- [8]. 'Corrosion inhibition of mild steel in 1M H₂SO₄ by Ampicillin as an inhibitor', S. Hari Kumar, S. Karthikeyan, P.A. Jeeva, Journal of Corrosion Science and Engineering, Vol.16, 2013.
- [9]. 'Quantum mechanical approach for electroless plating process', S. Karthikeyan, P. A. Jeeva, S. Narayanan, K. N. Srinivasan, X. Hu, Surface Engineering, 28, 10, pp 743–746, 2012.
- [10]. 'Electrodeposition of copper', Hans-Gerhard Creutz, Roy W. Herr, US4110176 A, US 05/793,701, 1978.
- [11]. 'Impedance measurements for electroless nickel plating process', S. Karthikeyan, K.N. Srinivasan, T. Vasudevan, S. John, Port. Electrochim. Acta, 24, 4, pp405–413, 2006.
- [12]. 'Ethane-2- thioamido-4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide: A novel inhibitor for the corrosion of mild steel in 1N HCl' , S.

Karthikeyan, N. Arivazhagan, S. Narayanan, Journal of Corrosion Science &Engineering, Vol.16, 2013.

[13] 'Performance characteristics of 1, 3-diorthotolyl thiourea on the corrosion of mild steel in 5% NaCl', S. Karthikeyan, N. Arivazhagan, D. Ramkumar, S. Narayanan, Journal of Corrosion Science &Engineering, Vol.16, 2013.

[14]. '4-Chloro-2-((furan-2-ylmethyl) amino)-5-sulfamoylbenzoic Acid (FSM) and N-(Isopropylcarbamoyl)-4-(m-tolylamino) Pyridine-3-sulfonamide (TSM) as Potential Inhibitors for Mild Steel Corrosion in 1 N H₂SO₄ Medium. Part I', S. Harikumar, S. Karthikeyan, Ind. Eng. Chem. Res. , 53, 9, pp 3415-3425, 2014.

[15]. 'Corrosion and hardness characteristics of metalized ABS plastics prepared by FDM rapid prototyping process', K. Raja, C.D. Naiju, S. Narayanan, P.A. Jeeva, S. Karthikeyan, Journal of Corrosion Science &Engineering, Vol.17, 2013.

[16]. 'Torsemide and Furosemide as Green Inhibitors for the Corrosion of Mild Steel in Hydrochloric Acid Medium', S. Harikumar, S. Karthikeyan, Ind. Eng. Chem. Res., 52, 22, pp 7547-7469, 2013.

Table 1 The results of weight gain studies and eddy current test obtained for EN coated ABS M30 plastics

S.No.	Deposition timings (hrs)	Thickness (μm)		Inference
		Weight gain method	Eddy current test	
1.	2	50	49.8	Uniform coating thickness

Table 2 Micro hardness values for EN coatings on ABS M30 plastics

S.No.	Coatings	Hardness (V.H.N) Load:100g
1	EN coated ABS M30	437

Table 3 Current–Potential results for the rapid prototyped ABS M30 in sea water medium

Nature of substrate	Corrosion kinetic factors		Tafel slopes	
	Ecorr (mV)	Icorr (μA)	ba	bc
EN Coated ABS M30	–560	1.82	82	110

Table 4 Impedance values of EN coatings ABS M30 plastics

Nature of deposit	Rt (Ohm.cm^2)	Cdl ($\mu\text{F. cm}^{-2}$)
EN coatings on ABS	800	1.28

Table 5 The results of tensile test obtained for EN coated ABS M30 plastics

S.No.	Nature of substrate	Tensile strain at Maximum Load (%)	Tensile stress at Break (Standard) (MPa)
1.	Uncoated	2.48	27.78
2.	Coated	2.51	28.94

Legends for figure

1. FE-SEM image of EN coated rapid prototyped ABS M30

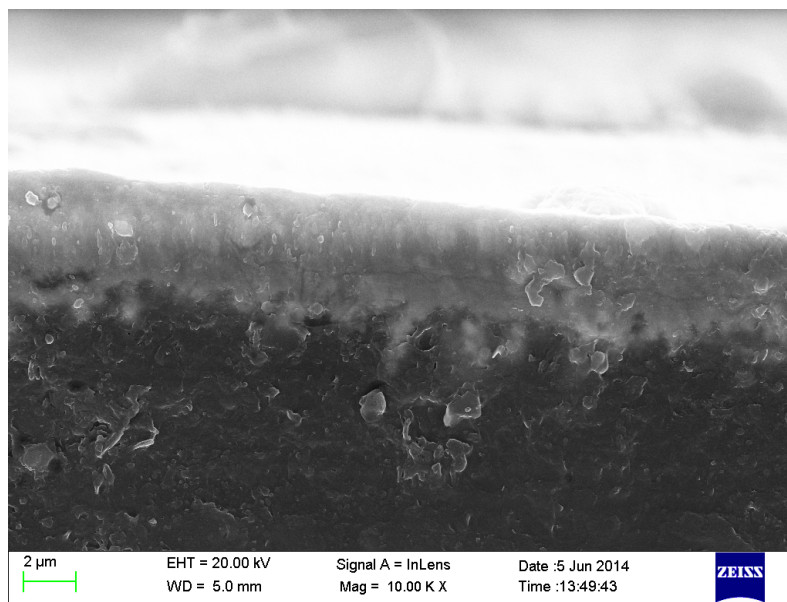


Figure 1