3.1 INTRODUCTION

The present research work is focusing on the application of coatings on the improvement of mechanical properties of ABS rapid prototypes used in automobile components. The aim of the study has arrived by adopting suitable plating metals on the ABMSM30 rapid prototypes to replace the metal based components in automobile vehicles. In order to understand the functions of coated ABS M30 RP components, coatings on ABMSM30 plastics prepared by injection molding were studied and comparisons on results have been done. The experimental procedures used in this unique approach of electro/electroless plating process on ABMSM30 rapid prototypes are discussed in detail.

The mechanical properties of the coatings have been determined by weight gain studies, Vicker’s micro hardness test (ASTM E-384), Tensile strength (ASTM D638), Taber wear (ASTM D-4060) and controlled metal dissolution [potentiodynamic polarization measurements, impedance studies and salt spray test (ASTM B-117)] were carried out to assess the mechanical properties of the metallized ABMSM30 rapid prototypes and injection molded ABS plastics. Surface morphological studies were carried out using X-ray diffraction (XRD) technique, Surface roughness measurements, X-ray photo electron spectra (XPS) studies and Scanning electron microscope (SEM) images.

3.2 MATERIALS AND METHODS

3.2.1 SELECTION OF THERMOPLASTIC ABS M30 FOR RP PROCESS

For electrochemical measurements like potential-current studies and impedance measurements, 1 cm² area of metalized ABMSM30 RP and ABMSM30 IM specimens were employed as working electrode, platinum(3 cm²) as auxiliary electrode and saturated calomel electrode as reference electrode respectively.

All glasswares were of Borosil make used in electrochemical cells and electrode were of imported from Sinsil instruments, USA.
A single pan with 1mg accuracy digital balance was used for weight gain measurements to understand the plating rate resulted from this method. A digital pH meter (Elico, India) was used to note the pH values of the plating formulations adopted in the study. The above experimental setup was employed for developing hard coatings on ABS M30 RP and ABS IM plastics. The metallization involves the application of coatings on the development of holograms, chassis, and automobile dash board used in automobile components. The figurative models of metallized engine oil tank cap and metallized electronic housing automobile components used for in this present investigation are shown below.

Fig.3.1 Metallized engine oil tank cap

Fig.3.2 Metallized electronic housing made of RP
Reason for selecting the automotive components

Component I - Metallized engine oil tank cap

- Mild steel cap is widely used in vehicle engine oil tank.
- However, the present mild steel cap undergoes corrosion from road mud and salt (particularly chloride ions) and cause damage on the surface of steel cap and causes injury during maintenance.
- The alternate candidate for the protection of mild steel cap involved was Zinc alloy plating which is having anti-corrosion characteristics.

Anomaly of the present system:

- However, the mass production of Zinc alloy plating based mild steel cap is highly expensive and withstand only limited period (2 years).

Remedial measures of the above defect:

the use of metallized RP/IM based engine oil tank cap with an inherent corrosion resistant coating is the only way to enhance the life time with improved mechanical properties have to be applied

Component II – Metallized electronic housing

- Galvanized (zinc coated Mild steel) electronic housing is interior part widely used as holder/container in automobile sensor and electronic devices.

Anomaly of the present system:

- Galvanized electronic housing is more susceptible to corrosion and form rust that leads improper seating and malfunctioning of automobile sensor and electronic devices.

Remedial measures of the above defect:

- In order to avoid the deterioration of Galvanized electronic housing when exposed to humid environment, the use of metallized RP/IM parts with improved mechanical properties have to be applied.
The reason for choosing the metalized ABS M30 plastics prepared by RP and IM process is due to the fact that after coating, the automotive components are exerting cushioning effect when any impact by means of application of external load. This has led to improve the strength and weight ratio of the uncoated ABS M30 plastics. Also, this finds an alternate application for replacing metallic components/metals used in automobile parts in vehicles.

Hence, the present research concerns on the metallization of ABS M30 plastics prepared by RP and IM processes that lead to improvement in mechanical properties and an alternate to metallic parts of automotive vehicles as given below:

1) Thickness of coatings above 150 µm is to be achieved which is an industrial requirement in automobile industries.

2) Enhancements in tensile strength, flexural strength, hardness, wear resistance, and corrosion resistant after metallization process are to be explored.

3) The new plating formulation for RP and IM parts based on electroless Ni, electrodeposition of Cu, electrodeposition of Ni, and electrodeposition of trivalent Cr are to be studied.

3.2.2 CHOICE OF PLATING CHEMICALS USED

All the chemicals used for formulating coatings were of analytical grade reagents. Names of the chemicals with their manufacturer are listed below:

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chromium Sulphate purified</td>
<td>Merk (1)</td>
</tr>
<tr>
<td>2. Nickel Chloride</td>
<td>S.d. fine chem. Limited</td>
</tr>
<tr>
<td>3. Sodium Hypo phosphite</td>
<td>Merk-schuchardt</td>
</tr>
<tr>
<td>4. Sodium Succinate</td>
<td>Fisher</td>
</tr>
<tr>
<td>5. Nickel sulfate heptahydrate</td>
<td>Ranboxy</td>
</tr>
<tr>
<td>6. Copper sulphate pentahydrate</td>
<td>Fisher</td>
</tr>
<tr>
<td>7. Sulphuric acid</td>
<td>Fisher</td>
</tr>
<tr>
<td></td>
<td>Chemical Name</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------</td>
</tr>
<tr>
<td>9</td>
<td>Boric acid</td>
</tr>
<tr>
<td>10</td>
<td>Ammonium thiocyanate</td>
</tr>
<tr>
<td>11</td>
<td>Glycolic acid</td>
</tr>
<tr>
<td>12</td>
<td>1,3 Butyn-diol</td>
</tr>
<tr>
<td>13</td>
<td>ABS M30 polymer</td>
</tr>
<tr>
<td>14</td>
<td>Furosemide</td>
</tr>
<tr>
<td>15</td>
<td>Sodium gluconate</td>
</tr>
<tr>
<td>16</td>
<td>Tri Sodium citrate</td>
</tr>
</tbody>
</table>

### 3.2.3 FORMULATION COATING CHEMICALS

For any metallization process, proper method of formulation and preconditioning of plating chemicals to avoid the entry of foreign particles are imperative to achieve coatings with superior mechanical properties to cater the needs of automobile parts.

#### 3.2.3.1 PREPARATION OF ELECTROLESS FORMULATION

About four plating formulations have been arrived by following standard plating steps suing trial and error method. The formulations are presented in the table 3.1.
Table 3.1 Formulations of electroless Nickel baths

<table>
<thead>
<tr>
<th>S.No</th>
<th>Trial for electroless nickel</th>
<th>Optimized electroless nickel coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NiCl₂ = 32 g/l</td>
<td>NiSO₄·6H₂O = 35 g/l</td>
</tr>
<tr>
<td></td>
<td>NaH₂PO₂ = 25 g/l</td>
<td>NaH₂PO₂ = 27 g/l</td>
</tr>
<tr>
<td></td>
<td>Na₃.citrate = 45 g/l</td>
<td>Tri Potassium Citrate = 50 g/l</td>
</tr>
<tr>
<td></td>
<td>Furosemide = 0.3 mg/l</td>
<td>Dextrin = 2 g/l</td>
</tr>
<tr>
<td></td>
<td>pH = 5.5</td>
<td>NaNO₃ = 1 g/l</td>
</tr>
<tr>
<td></td>
<td>Temperature = 85⁰C</td>
<td>pH = 5.83</td>
</tr>
<tr>
<td></td>
<td>Plating time = 6 hrs.</td>
<td>Temperature = 85±2⁰C</td>
</tr>
<tr>
<td></td>
<td>Nature of deposit = Loosely</td>
<td>Coating thickness = 150 microns</td>
</tr>
<tr>
<td></td>
<td>adherent.</td>
<td>Nature of deposit = Strong and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>adherent.</td>
</tr>
<tr>
<td>2.</td>
<td>NiSO₄ = 30 g/l</td>
<td>NiSO₄·6H₂O = 35 g/l</td>
</tr>
<tr>
<td></td>
<td>NaH₂PO₂ = 25 g/l</td>
<td>NaH₂PO₂ = 27 g/l</td>
</tr>
<tr>
<td></td>
<td>Na₃.citrate = 25 g/l</td>
<td>Tri Potassium Citrate = 50 g/l</td>
</tr>
<tr>
<td></td>
<td>Furosemide = 0.3 mg/l</td>
<td>Dextrin = 2 g/l</td>
</tr>
<tr>
<td></td>
<td>Na.succinate = 20 g/l</td>
<td>NaNO₃ = 1 g/l</td>
</tr>
<tr>
<td></td>
<td>pH = 5.5</td>
<td>pH = 5.83</td>
</tr>
<tr>
<td></td>
<td>Temperature = 85⁰C</td>
<td>Temperature = 85±2⁰C</td>
</tr>
<tr>
<td></td>
<td>Plating time = 5 hrs.</td>
<td>Coating thickness = 150 microns</td>
</tr>
<tr>
<td></td>
<td>Nature of deposit = Loosely</td>
<td>Nature of deposit = Strong and</td>
</tr>
<tr>
<td></td>
<td>adherent.</td>
<td>adherent.</td>
</tr>
</tbody>
</table>
Plating time = 5 hrs.
Nature of deposit = Loosely adherent.

About 35g of nickel sulphate and 27 g of sodium hypo phosphite were accurately weighed and transferred in 1000 ml clean beaker and stirred with minimum quantity of double distilled water. To this tri potassium citrate (50 g/l), Dextrin (2 g/l) and sodium nitrate (1 g/l) were added. The contents were made up to 1000ml using standard measuring flask with double distilled water. The oily substances and colloidal minute particles present in the formulation were removed by filtration. The formulated plating bath was preserved in a closed container at room temperature. The stock solution was analyzed for the Nickel and Phosphorus contents by Atomic absorption spectra (AAS), Pinnaacle 900 AA spectrometer made of Perkin Elmer, USA.

Figure 3.3 Pinaacle 900 AA spectrometer for compositional analysis of coatings
Before carrying out electroless plating of nickel, ABS M30 plastics were etched in hydrogen peroxide (2% v/v), water dip, sensitized in stannus chloride+HCl (2.5 v/v) and then activated in Palladium chloride solution (0.1%). After washing, the activated thermoplastics were introduced into electroless nickel plating. The plating was carried out from 0.5 hours to 5 hours. If the time of electroless deposition is about 5 hours, the thickness of coatings will be 150 microns in the above developed formulations. The higher thickness of nickel-phosphorus on thermoplastics was found to enhance the mechanical properties than the uncoated plastics.

In order to utilize the coated thermoplastics (both ABS M30 RP & ABS M30 IM) in automobile parts and as an alternate to metallic components, the following scheme of plating formulations have been developed and their results are extensively discussed in chapter 4.

The optimized bath for obtaining copper, coatings on metallic components are given below:

**Electroplating of Copper**

\[ \text{CuSO}_4 \cdot 6\text{H}_2\text{O} = 200 \text{ g/l} \]

\[ \text{H}_2\text{SO}_4 = 50 \text{ g/l (weight per ml = 1.82 g)} \]

4-mercapto pyridine (brightener) = 0.03 g/l

Sodium laurel sulphate (wetting agent) = 0.05 g/l

Current density = 50 mA/cm²

\[ \text{pH} = 1.5 \]

Plating time = 1 hour

Thickness = 50 microns

**Electroplating of Nickel**

\[ \text{NiSO}_4 \cdot 6\text{H}_2\text{O} = 120 \text{ g/l} \]

\[ \text{NiCl}_2 = 25 \text{ g/l} \]

Boric acid = 60 g/l

Cetyl Tri Methyl Ammonium Bromide (CTAB) = 3 g/l

Ammonium Sulphate = 5 g/l

Sulfamerizine (Brightner) = 0.5 mg/l

Bath parameters:
pH = 4.3  
Current density = 45 mA/ cm$^2$  
Plating time = 90 min.  
Thickness = 130 microns  
Anode =Ni plates of size 100 x 300 mm  
Cathode = ABS M30 plastics coated with electrodeposited copper on EN.

**Electroplating of Chromium**  
CrCl$_3$.6H$_2$O = 90 g/l  
Sodium formate = 50 g/l  
Gly oxylc acid = 7 g/l  
Potassium chloride = 72 g/l  
Sulfamerizine (Brightner) = 1 mg/l  
1,3 Butyn-diol = 1 g/l  
Bath parameters:  
pH = 3  
Current density = 100 mA/cm$^2$  
Plating time = 10 min.  
Thickness = 10 microns  
Anode =Lead plates of size 100 x 300 mm  
Cathode = Nickel plated ABS plastics coated with electrodeposited copper on EN.

The above formulations pertained to decorative chrome plating for plastics especially ABS M30, wherein chromium plating has been carried out on the following sequences of plating process.

1. Top layer – Cr coatings (10 microns) – Very bright coatings  
2. Inner top layer – Ni coatings (120 microns) – Bright coatings  
3. Middle layer – Copper coatings (10 microns) – Bright  
4. Inner layer – Electroless nickel (10 microns) – Semi-bright  

The resultant surface layers are a metallic hybrid of various plating processes.  
This coatings exhibited outstanding micro hardness, taber wear resistance, tensile
strength and corrosion resistance that are comparable to conventional hard chrome plating on metals.

3.2.4 PREPARATION OF ABS M30 RAPID PROTOTYPES

The required ABS M30 rapid prototypes were prepared by using Fortus 900mc system (Stratasys, Inc). Building parameters accommodated a slice height of 0.254 mm, a solid-normal part interior style with contour width of 0.508 mm, negative air gap of -0.0002 mm and a part raster width of 0.508 mm. A -0.0002 mm negative air gap was used for these samples to obtain strong bonding between the ABS fibers.

Fig 3.4 Fortus 900mc FDM Machine

Slicing was performed with Insight 6.4.1 and all test specimens were fabricated. Test specimens were designed so that their dimensions after bonding were equivalent to those of an ASTM D638 Type I specimen (Figure 1b).
Figure 3.5 Tensile Dog Bone Specimens as per ASTM D-638 Standard

Fig. 3.6 shows the Metallized Injection Molding Specimen

Fig. 3.7 Metallized FDM based specimen
3.3 EVALUATION OF METALLIZED THERMOPLASTICS COATINGS THROUGH DIFFERENT TECHNIQUES

3.3.1 WEIGHT-GAIN METHOD

Thermoplastic specimens as described earlier of size 20 x 50 x 2 mm³ were used in the plating process. They were polished with fine grit paper and degreased using trichloroethylene to remove oil and greases. Thermoplastic specimens were pretreated in acid bath followed by alkaline bath and washed with tap water. They were rinsed in double distilled water and dried. The initial weight of panel was recorded using digital weighing balance machine. The same operating conditions were used for coating on automobile components made of ABS M30 RP and IM components. Then, both plastic components were introduced into the plating solution under optimized conditions of the bath. The rate of deposition was calculated using the following formula:

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

Where,

- \(W\) – Weight of the deposit (g)
- \(D\) – Density of the deposit (g/cm³)
- \(T\) – Plating duration (h)
- \(A\) – Surface area of the specimen (cm²)

The above experiments were conducted for developing coatings on automobile components made of thermoplastics. The following factors were analyzed with the above experiments.

3.3.2 MICRO HARDNESS MEASUREMENTS

Micro hardness measurements for both ABS M30 RP and IM metalized plastic specimens (20 x 50 x 2 mm³) were made by Vickers’s harness tester [fig 3.8] as per ASTM E-384 with a load of 100 g. A diamond shaped indentation was made on each sample at 6 different places and the average values of hardness were measured from the diagonal of indentation on Vicker’s scale using the formula.

\[
V.H.N = \frac{(1854 \times \text{load})}{d^2}
\]

Where \(d\) = diagonal of the indenter
However, the instrument displayed V.H.N directly using digital read out.

![Vickers Hardness Tester](image)

Fig. 3.8 Vickers Hardness Tester

### 3.3.3 TABER WEAR RESISTANCE MEASUREMENT

The taber wear resistances of the metalized ABS M30 specimens of size 100 x 100 x 4 mm$^3$ were measured as per ASTM D-4060 through Taber abraser. The abrading wheels were allowed to rotate on the coatings at a load of 500 g. Before the start of the experiment the specimen were accurately weighed. Then, the wheels were allowed to rotate against the deposit for 1000 cycles with the above load. After that the specimens were removed and weighed again. The experiment was repeated for another 1000 cycles on the specimens. The average weight loss was taken as the Taber wear index or Abrasion resistance.

Taber wear index = Average weight loss (in mg) for 1000 cycles

### 3.3.4 CORROSION RESISTANCE MEASUREMENTS

The electrochemical potential-current measurement (Tafel plots) and impedance studies were made with the metalized plastic surface of 10 mm$^2$ area (working electrode), 30 mm$^2$ of platinum electrode (counter electrode) and saturated calomel as reference electrode in three electrode cell assemblies. The block diagram for this study is given in fig 3.9.
3.3.4.1 POTENTIAL-CURRENT MEASUREMENTS

A constant quantity of 250 ml of 3.5% NaCl (sea water) solution was taken in a 500 ml beaker. The working electrode, reference electrode and the counter electrode were assembled in position and the connections were made. Initially, the potential is noted which is recorded as OCP. From OCP, polarization studies were performed using Sinsil Model 604E Electrochemical Analyzer [fig 3.10] imported from USA. The readings were obtained by ranging the potential values from OCP ± 1000 mV with scan rate 1 mV per second for the coated plastic surfaces.

The corrosion kinetic parameters such as \( E_{\text{corr}} \), \( I_{\text{corr}} \), anodic and cathodic Tafel slopes \( (b_a \) and \( b_c) \) were measured.

The reduction in potential values of Tafel slopes gave an idea that whether the metalized surfaces have reduced the oxidation of coatings from surface or involved in reducing chlorine gas evolution.
Figure 3.9 Block diagram of potentiodynamic polarization setup

U = Universal programmer
P = Potentiostat
R = X-Y Recorder
WE = Working electrode
RE = Reference electrode
CE = Counter electrode

Figure 3.9 Block diagram of potentiodynamic polarization setup
3.3.4.2 IMPEDANCE MEASUREMENT

The SINSIL Model 604E electrochemical analyzer as mentioned above was used for this measurement in the frequency range of 100 kHz to 0.01 Hz under potentiostatic conditions using 3.5% NaCl as corrosive medium. The impedance measurements were carried out on the metalized ABS M30 prepared by RP & IM processes at room temperature.

A semi-circular plots correspond to Nyquist plot was recorded for all coated plastics. From the Nyquist plot, the charge transfer resistance ($R_t$) and double layer capacitance ($C_{dl}$) values were calculated. The block diagram used for the impedance analyzer is shown in figure 3.11.
The electrical equivalent circuit for the corroding system is given below:

![Circuit Diagram](image)

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

Fig 3.11 block diagram used for the impedance analyzer

The cell impedance consists of real part ($Z'$) Vs imaginary part ($Z''$). A plot of real part ($Z'$) Vs imaginary part ($Z''$) gives a semicircle which cuts the real axis at higher and at low frequency $Z$ corresponds to $(R_S + R_t)$. The difference between the two values gives $R_t$. The double layer capacitance can be determined from the frequency at which $Z''$ is maximum from the relation

$$Z''_{(\text{max})} = \frac{1}{2\pi C_{dl} R_t}$$
3.3.4.3 SALT SPRAY ANALYSIS FOR CORROSION RESISTANCE OF METALIZED ABS M30 SAMPLES

The salt spray test of the metalized ABS M30 RP and IM were conducted in SF 850 salt spray cabinet as per ASTM B-117 in 3.5% NaCl to understand the corrosion resistance of the coatings in aggressive environment i.e. sea water medium. The corrosion degree of the samples was evaluated by average weight loss which was visibly noted by the appearance of formation of red rust spots on the coated samples used under annealed conditions. This test has established that the corrosion resistance of the coatings is higher
in sea water medium as validated results for potentiodynamic polarization and A/C impedance test.

3.3.5 SURFACE MORPHOLOGICAL STUDIES OF METALIZED THERMOPLASTICS

3.3.5.1 X-RAY DIFFRACTION STUDIES
The X-ray diffraction patterns for the metalized AB S M30 RP and IM surfaces were made using X’ pert pro XRD,(make- Panalytical, USA). These measurements help to explain the intermetallic phases formed in the coatings. The X-ray diffraction patterns were obtained with Cu Kα radiation in the above instrument (Figure 3.13) with the step of 0.02°. XRD patterns were recorded for different depth profiles employing grazing incidents X-ray technique.

3.3.5.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPIC STUDIES (FE-SEM)
The cross sectional morphology of the metalized ABS M30 RP and IM were examined under high magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits using a field emission scanning electron microscope. The scanning electron microscope, which makes use of reflected primary electrons and secondary electrons, enable one to obtain information from regions that cannot be examined by other studies.

The deposited specimens of various metalized ABS M30 RP and IM coatings were cut into 10 x 10 mm² size and mounted suitably and examined under the microscope. Since, the substrate is plastic, a thin layer (0.01 microns) of Au (gold) was applied to measure the kinetic energy of electron beam emitted by metallic species during FE-SEM analysis. The SEM photographs were taken by using Carl-Zeiss S-3000 model with an acceleration voltage range of 20,000 V and in the magnification range of 1000. (Figure 3.14).
Figure 3.13 Instrument for XRD measurement

Figure 3.14 Instrument for SEM measurement
3.3.6 X-RAY PHOTOELECTRON SPECTRA STUDIES (XPS)

The surface characterization measurements were carried out on metallized samples having surface area of 10 x 10 mm$^2$ using X-ray photoelectron spectra also known as Electron Spectroscopy for Chemical Analysis (ESCA) in a physical electronics PHI 5600 ESCA system (Figure 3.11) with Al K$_\alpha$ monochromatic source was used to obtain oxidation states of species along with chemical composition of surfaces. The binding energy values were calculated with a precision of ±0.2 eV. For this measurement, the samples were mounted in to an ultra high vacuum chamber at 10$^{-9}$ Torr housing the analyzer. Prior to mounting, the metallized samples were placed in the preparation chamber for 6 hours in order to remove any volatile species exist on the surface. The Block diagram of XPS used in this research is shown in fig 3.15.

Figure 3.15 Block diagram for XPS analysis
3.3.7 ULTIMATE TENSILE STRENGTH OF METALLIZED ABS M30 PLASTICS (RP & IM)

All specimens were conditioned at 23 ± 2 °C and 50 ± 5% relative humidity for at least 40 hours prior to tensile testing. Tensile tests were conducted on an Instron 8801 system as given in fig 3.16 (Instron®, Model XX01, UK make) following guidelines provided in ASTM D638. A 10kN load cell was utilized while employing a deformation cross-head speed of 5 mm/min. Each material and bonding method was tested using at least 5 specimens to report an average modulus of elasticity, ultimate strain, and ultimate stress. The tensile tested specimens of metallized ABSM30 are shown in fig 3.17.

Fig. 3.16 Instron UTM Testing Machine with extensometer

Fig. 3.17 Electrodeposited Tensile Specimens as per ASTM D638 standard after tensile testing.
3.3.8 SURFACE ROUGHNESS TESTER MEASUREMENTS

Fig 3.18 Surface finish measurements using Mahrs surface roughness tester