Chapter III

EXPERIMENTAL WORK

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The fundamental mechanisms involved in the degradation and failure of coatings are affected by its behavior towards moisture, corrosion agents, various environmental influences, and finally the changes in the internal physical structure of the coatings [121]. All these factors influence the durability of organic coatings, as a result, evaluation of coating efficiency has been an active subject among technologists for a number of years. In the present study the electrochemical behavior of carbon steel and evaluation of EPDM / PE blend coatings are studied.

3.1. Materials:

3.1.1. Carbon steel:

Carbon steel alloy is the most common structural material that can be used in industrial applications such as space craft, stacks, petroleum pipelines, and most marine structures [122]. Specimens of X- 52 A carbon steel petroleum pipeline were used as metallic substrate, they were obtained from Petroleum Pipeline Company, Cairo, Egypt.

The chemical composition of carbon steel used is given in Table (3.1).

Table (3.1) - Composition of carbon steel alloy

Element	C	Mn	P	S	Fe
Amount %	0.28	1.25	0.04	0.05	98.38

The shape of the working sample used for electrochemical measurements is a 3 cm long block cylinder with a diameter of 0.9 cm, and the sample used

for weight loss test is a square shaped sheet of 1 cm side length. After cutting, all the test specimens were surface - ground manually on successively finer silicon carbide papers to a 600 grit finish on all faces, degreased with acetone, rinsed in tap and distilled water respectively, and finally dried in warm air.

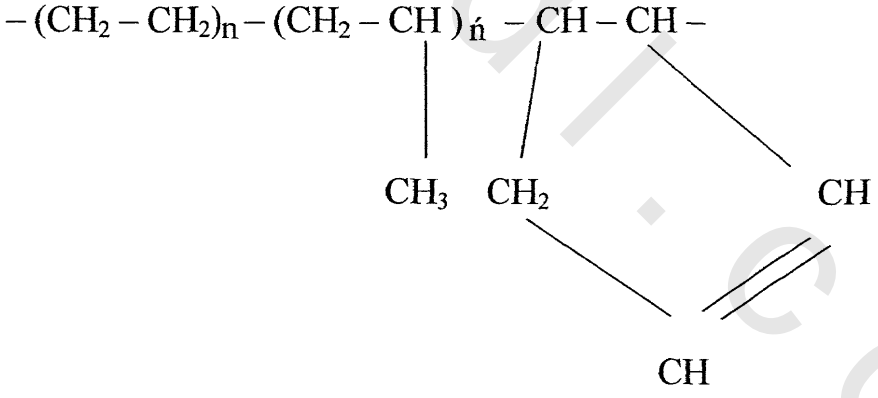
3.1.2. Rubber:

Ethylene / propylene rubbers are copolymers that consist of randomly distributed alternating blocks of ethylene and propylene. There are two main types produced commercially [123]:

a- Saturated copolymers vulcanizable with organic peroxides.

b- Terpolymers containing a small proportion of diene to confer unsaturation and make sulfur vulcanization possible. This type is called ethylene propylene diene monomer (EPDM), which is the raw rubber used in this work.

The chemical structural unit of (EPDM) is:



ethylene propylene diene

Where, n and n / = 10 - 20

The commercial grade of (EPDM) used in this work is Vistalon 5600. Some physical properties of this raw rubber are listed in Table (3.2) [123].

Table (3.2) - Specifications of (EPDM)

Specifications	*EPDM*
Grade	Vistalon 5600
Color	Light gray
Diene content (%)	4-7
Oil content	Nil
Ethylene content (%)	60
Mooney viscosity M_L (1 + 8 min.) at 122 °C	65 - 75
Specific gravity (g / cm^3)	0.85
Modulus at 300 % elongation (MPa)	9.5
Tensile strength (MPa)	10
Coefficient of linear expansion ($^oC^{-1}$)	(2.3 - 2.4) x 10^{-4}
Significant stiffening begins at	50 °C
Glass transition temperature	–50 - –58 °C
Brittleness temperature	– 90 °C

EPDM has many unique properties which make it well accepted by the rubber industry. The predominantly saturated nature of EPDM has led to it's considerable resistance to many chemicals. A qualitative indication of this resistance is given in Table (3.3) [123].

Table (3.3) – EPDM resistance to chemical agents

Chemical agent	*Resistance*
Ozone	Excellent
Oxygen	Excellent
Water	Excellent
Alkalis	Excellent
Acids, dilute	Excellent
Acids, concentrated	Fair – good
Animal oil	Fair
Vegetable oil	Fair

3.1.3 Thermoplastic:

Low-density polyethylene (LDPE) is the thermoplastic used in this work, where some of its important parameters are listed in Table (3.4) [124].

Table (3.4): Some parameters of low density polyethylene (LDPE)

Parameters	*LDPE*
Specific gravity (g / cm^3)	0.91 – 0.94
Glass transition temperature	about - 80 °C
Molding temperature	about 250 °C
Annealing temperature	100 °C
Crystalline melting point, T_m	100 – 125 °C
Swelling %	(15 – 40)
Dielectric constant	2.2 at 10^3 HZ
Dissipation factor	0.0003 at 10^3 HZ
Volume resistivity	10^{16} Ω. cm

LDPE film has a good balance of mechanical properties, and it is a good barrier to water and water vapor, also, its resistance to acids, alkalis, and inorganic salt solutions is high [125].

3.1.4. Carbon black:

Most rubber articles produced are compounded with carbon black (CB) as a filler typically in the amount of at least 50 parts of carbon black per hundred parts of rubber by weight (50 phr). There are far too many types of carbon black available to the rubber compounder [126], the most common ones are high abrasion furnace (HAF), semi-reinforcing furnace (SRF), general purpose furnace (GPF), and fast extrusion furnace (FEF), where the last one is the type used in this work. FEF black is characterized by medium particle size and by giving moderate abrasion resistance and improved processing.

3.1.5. Curing agents:

The curing system used is sulfur system, which is composed of:

i) Activator (stearic acid + zinc oxide)

ii) Accelerators [2 – dibenzothiazole disulphide (MBTS), tetra methylthiuram disulphide (TMTD) and phenyl – β naphthyl amine (PBN)].

iii) Elemental sulfur.

Also, dioctylphthalate (DOP) and processing oil are used as softeners.

3.1.6. Adhesive:

Many types of adhesives are currently in use and there is no adequate single system of classification for all products[127]. The adhesives industry has generally employed classification based on end - use such as metal- to-metal adhesives, wood adhesives, general-purpose adhesives, paper, and packaging.

Parlock (PC 17) is the adhesive used in this study, it is a specially bonding agent developed only for EPDM compounds. Parlock pc - 17 should be applied in combination with PM - 05 primer, and this recommended system has proved to have excellent resistance against corrosion. Some technical data concerned parlock are listed in Table (3.5).

Table (3.5) - Technical data of parlock

Composition	*Polymers and fillers dispersed in xylene*
Color	Black
Viscosity 4 mm ford – cup	80 - 120 s
Specific Gravity	0.91 -0.95 g / cm^3
Flash point	24 °C
Solid content	16 - 18 % by weight

3.1.7. Test media:

The tests were carried out in natural seawater, which have been brought from Mediterranean Sea. The concentration of cations in seawater were analyzed by ICP technique and the concentration of Cl^- ion was determined by ion chromatography DIONEX 600 – ASTM , D 4327 , The results obtained are given in Table (3.6).

Table (3.6) - Constituents of sea water (concentration in ppm)

Fe^{2+}	Li^+	Na^+	Mg^{2+}	Al^{3+}	K^+
< 0.0054	0.539	11572	1848	< 0.0014	543
Ca^{2+}	Cu^{2+}	Sr^{2+}	Ba^{2+}	Mn^{2+}	Cl^-
571	< 0.0029	7.60	< 0.0035	< 0.007	25215

3.2. Blend Preparation and Vulcanization:

Blends of PE and EPDM in different proportions were prepared in a Brabender Electronic Plasticcorder at a temperature of 170 °C which was adjusted to be above the specific melting temperature of PE, and rotor speed of 30 rev/min. Thereafter, the curing agents were mixed with the PE / EPDM blend at a temperature not exceeding 70 °C on a two - roll mill, the blend was passed through the rolls twice without banding at a roll opening of about 0.2 mm and then it was banded with a mill opening of about 1.5 mm, 3-4 cuts were made every ½ minute alternatively from each side.

The composition of working blends, is given in Table (3.7).

Table (3.7) - Composition of the working polymer blends.

Ingredients	*Blend (1)*	*Blend (2)*	*Blend (3)*	*Blend (4)*	*Blend (5)*
EPDM	100	90	80	70	60
LDPE	0	10	20	30	40
Stearic acid	2	1.8	1.6	1.4	1.2
ZnO	5	4.5	4	3.5	3
Processing oil	30	27	24	21	18
DOP	0	1	2	3	4
FEF	70	70	70	70	70
MBTS	1.5	1.35	1.2	1.05	0.9
TMTD	1.5	1.35	1.2	1.05	0.9
PBN	1	0.9	0.8	0.7	0.6
S	3	2.7	2.4	2.1	1.8

The weight of the blends was checked after mixing to ensure that the loss in weight does not exceed 5%. The compounded blend was left at room temperature

over night before vulcanization. Then vulcanization was carried out over 170 °C ± 2 °C at 4 MPa for 25 minutes. The stock was sheeted out and compression molded in an electrically heated hydraulic press (Fig.3.1). The optimum cure time was derived from the oscillating disc rheometer (Mönsanto ODR - 100) measurements[128].

3.3. Preparation of Coated Samples:

Using compression molding, EPDM / PE coatings were applied on carbon steel block cylinders in three different thickness 1, 2, and 3 mm with pretreatment the metal with adhesive in certain samples, and without applying adhesive in other groups of samples, to detect the effect of adhesion on the efficiency of coatings in corrosion protection.

3.4. Methods of Investigations:

3.4.1. Electrochemical measurements:

The change in electrode potential for series of uncoated and coated carbon steel specimens was observed for 24 months of immersion in natural sea water. Measurements were carried out monthly to evaluate both the corrosion behavior of bare carbon steel and the corrosion protection efficiency of the coatings. Two different techniques were carried out, open circuit, and potentiodynamic. For electrochemical measurements, the cell was conventional three electrodes pyrex vessel converter with Pt wire counter electrode, saturated calomel electrode (SCE) as a reference electrode and carbon steel (either bare or coated) as working electrode (Fig. 3.2) . The volume of immersion solution was 100 ml for each test

The potentiodynamic current - potential curves were recorded by changing the electrode potential automatically from – 1000 up to + 1000 mV (SCE) with scan rate of 25 mVs^{-1} using Potentiostate – Galvanostate (EG & G model 273). All measurements were carried out in freshly seawater at room temperature.

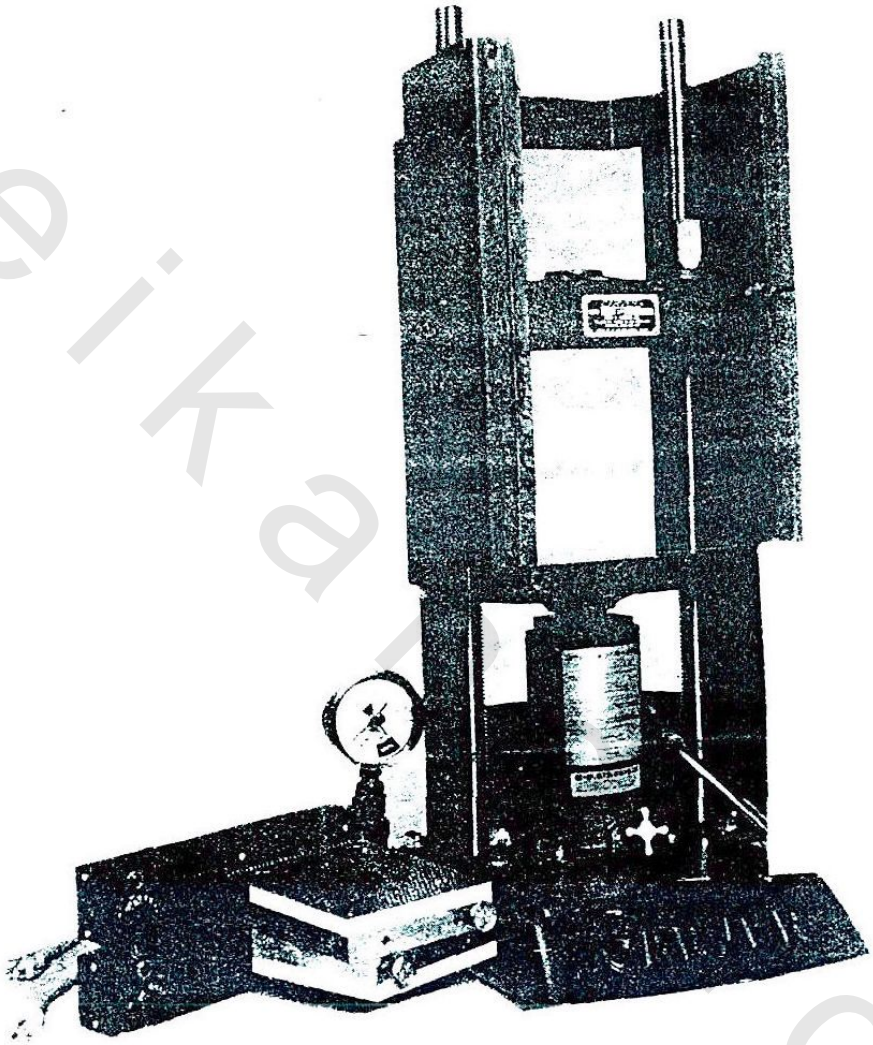


Fig. (3.1) – Hydraulic Press used for vulcanization of EPDM/PE blends and for preparation of coated samples.

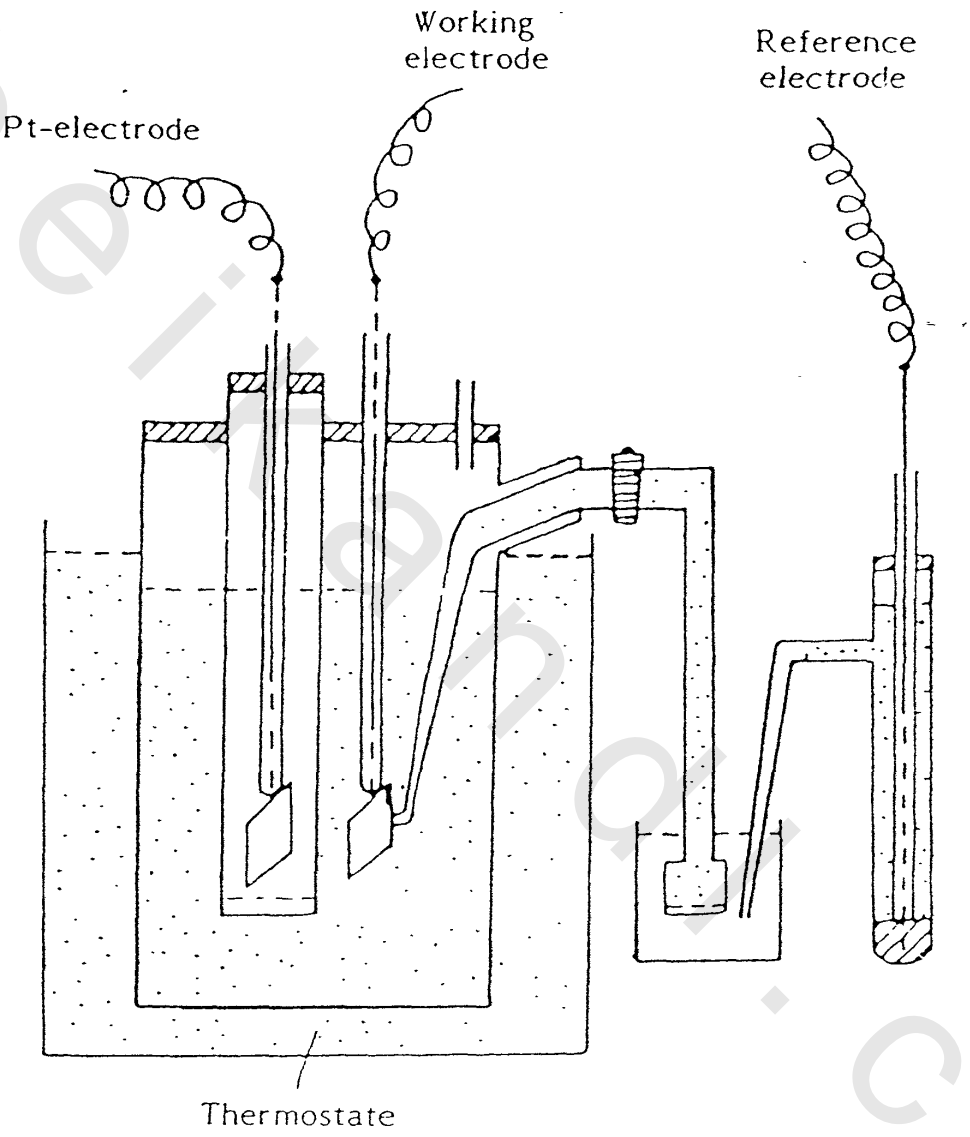


Fig. (3.2) – The electrolytic cell used for electrochemical measurements.

3.4.2. Gravemetric techniques :

(a) Weight loss test:

Uncoated carbon steel specimens (flat sheets) were prepared as mentioned previously, then weighed and immersed in natural sea water at room temperature. After two weeks the first specimen was removed from the solution, then washed with distilled water, alcohol, and acetone after that it was dried and reweighed. The weight loss of specimen was deduced by subtraction of its final weight from the initial one. The same procedure was followed for the other specimens at two weeks interval over a period of 48 weeks.

(b) Swelling test :

Swelling tests were conducted on the polymer blends without a metallic substrate in order to avoid ambiguity due to metal loss or corrosion product formation. The blends were prepared as previously stated, after curing they were cut into thin discs of radius 5 mm and with thickness 1, 2 and 3 mm. The samples were weighed, using an electronic balance, then they were immersed in natural sea water. The samples were reweighed weekly over 40 weeks. Before weighing, the samples were removed from the solution with tweezers, rinsed with distilled water and blotted dry to remove any excess water. The water uptake by the sample can be defined as the amount of water absorbed at a certain moment of time per unit weight of dry polymer. The swelling degree (Q %) was calculated as follows:

$$(Q)\,\% = \frac{W_t - W_i}{W_i} x\ 100 \qquad (3.1)$$

where, W_t is the weight of the sample at a certain moment of time and W_i is the initial weight of the same sample.

3.4.3. Mechanical measurements :

Stress - strain behavior in uniaxial tension was measured using a Zwick universal testing machine (model 1445) (Zwick, Germany). Dumbbell shaped specimens were cut from blends sheets according to ASTM 415 - 80 using a steel die of standard width 4 mm, length 50 mm, and 2 mm thick.. The thickness of the test specimens was determined by a gauge graduated to one hundredth of mm. .The tensile strain (ε) and tensile stress (б) were calculated as follows :

$$\varepsilon = \frac{L - L_o}{L_o} \qquad (3.2)$$

$$б = \frac{F}{A} \qquad (3.3)$$

Where, L_o, L are the lengths of undeformed and deformed samples, F is the force, and A is the cross sectional area of strained samples obtained from the relation:

$$A = \frac{L_o\ A_o}{L} \qquad (3.4)$$

Where ,A_o is the cross sectional area of unstrained sample.

From stress – strain diagrams, we can deduce many useful parameters such as tensile strength, modulus of elasticity, elongation at break, permanent set, and toughness.

3.4.4. Electrical conductivity measurements:

The rubber specimens used for electrical conductivity measurements have circular shape of radius 1.2 cm and thickness of about 0.6 cm. The electrodes were made from brass, covering the opposite major surface of the specimen over the circular area ; (the brass electrodes were attached to the rubber specimens

during the vulcanization process) [129]. The cell used for the measurements of electrical conductivity is shown in Fig (3.3). The sample holder consists of two parallel plates of brass with 1 cm diameter, and the lower is supported with a light pressure spring. The circuit used for the measurements is shown in Fig (3.4). This circuit incorporated a digital electrometer type (Keithley 616), with a range varying from 10^{-15} up to 10^{-1} A. and a smoothly variable power supply, up to 300 V.

The electrical conductivity, (σ), was determined from the relation

$$\sigma = \frac{I.t}{V_s A} \qquad (3.5)$$

where t is the thickness of the sample in cm, A is the surface area of the electrode in cm^2, V_s is the applied voltage on the sample in volt, and I is the current in ampere. Electrical conductivity of the different composites was measured at various temperatures from 25° up to 140°C. The sample temperature was measured by using copper - constantan thermocouple located near the center of the sample surface.

3.4.5. Spectroscopic measurements :

As the appearance of the surface generally changes during weathering, therefore, microscopic information is very useful to examine the degree of degradation. Also, such study is helpful to determine the mechanism of failure. The surface of the samples was examined by the following techniques :

(a) Scanning electron microscopy (SEM) :

SEM has been demonstrated to be extremely useful tool for characterizing coatings, substrates, interfaces and also, for organic coating failure analysis. [130] The morphology of both the blends and the substrate was examined using SEM, JEOLJSM – 5400. The test was performed on several immersed carbon steel specimens at 0, 3, 6, 9, and 12 month interval to detect the effect of corrosive test

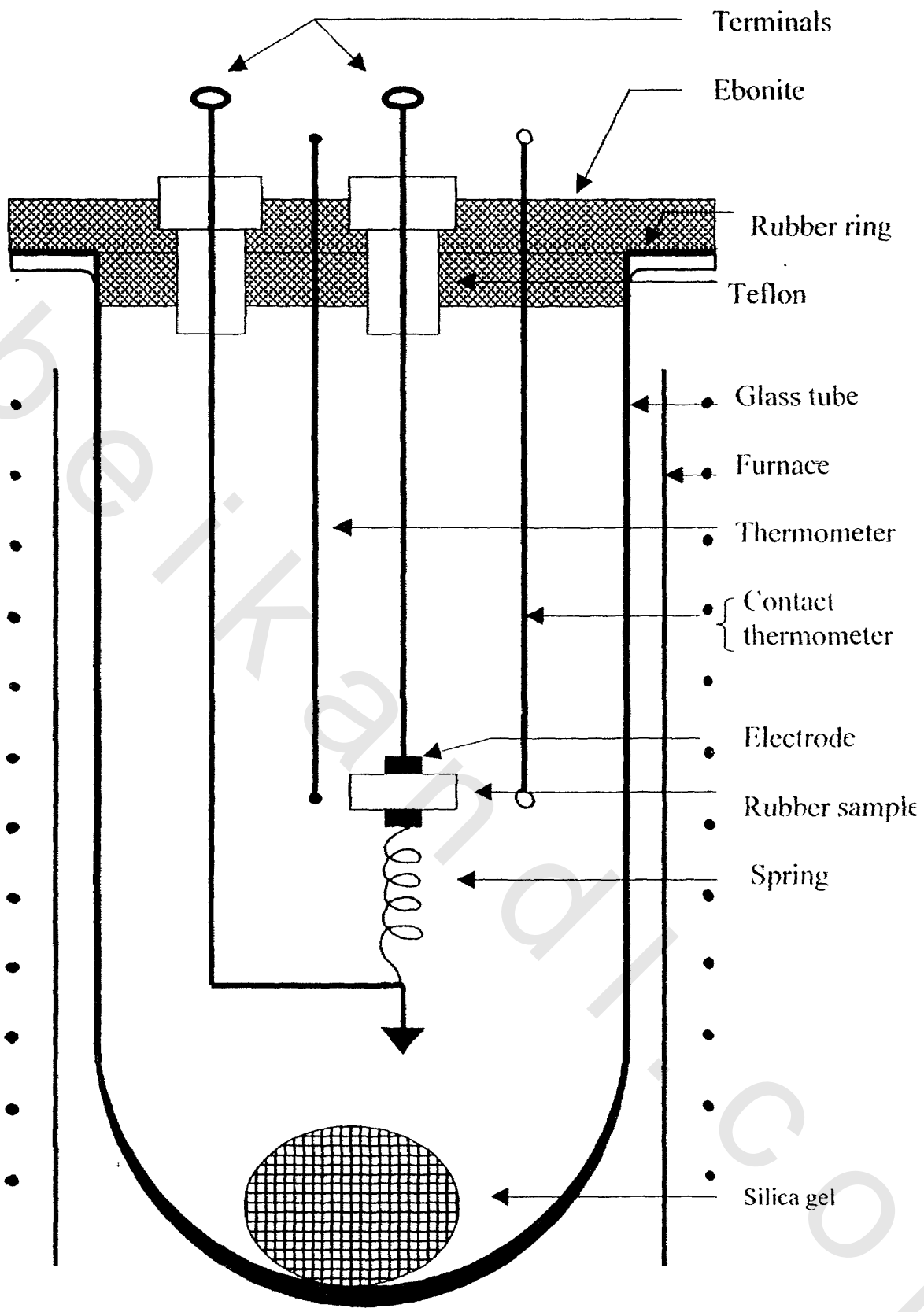
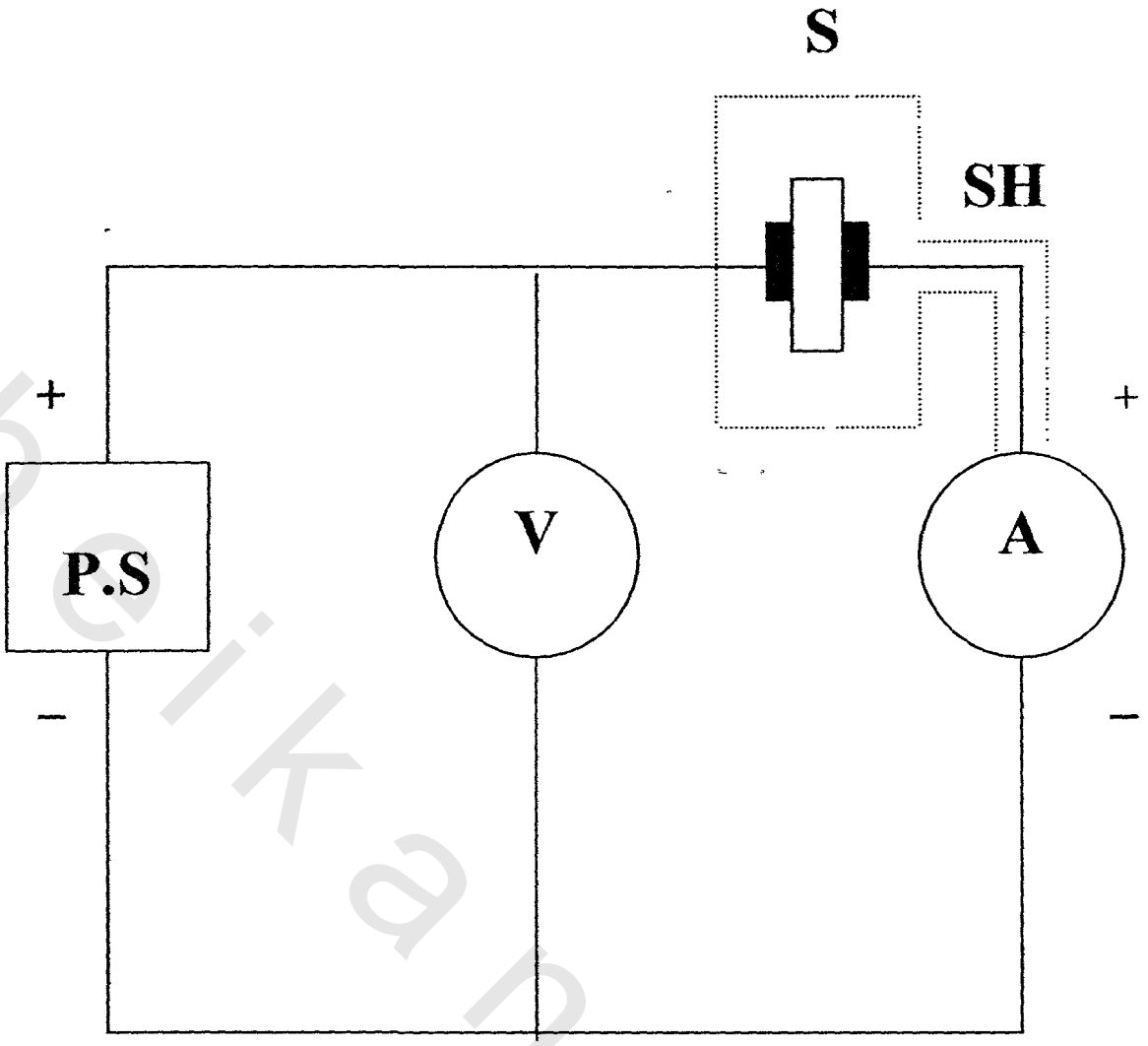


Fig. (3.3) – The cell used for the measurement of the electrical conductivity



A : DC currentmeter

V : DC voltmeter

P.S : Regulator power supply

S : Sample

Sh : Metallic shield

Fig. (3.4) - The circuit used for the measurement of the electrical conductivity.

media on the morphology of carbon steel substrate. Also, polymer blends test samples were examined by SEM to study the morphology of the blends. The coatings were peeled after 24 months of ageing in natural sea water, then both carbon steel substrate and polymer coating were examined by SEM to detect the morphology changes during exposure time. The surfaces of all the polymer test samples were coated with gold before examining. SEM micrographs were conducted or taken at various locations on the specimens.

(b) X – ray diffraction analysis :

Carbon steel samples along with the dried spilled corrosion products were subjected to X - ray diffraction analysis using X-ray (Philips) diffractometer, at 3, 6, 9 and 12 months of ageing in sea water. The test was performed, also, on the substrate when the coating was peeled (after 24 months of immersion in test media) to detect the presence of any corrosion products on the surface in order to evaluate the efficiency of EPDM / PE blend in protecting carbon steel against corrosion.

(c) UV exposure :

As a result of the increased use of rubber and polymeric coatings for out door applications, an adequate knowledge of the long - term performance of the UV exposed products is essential. This knowledge, allows one to evaluate the product performance and predict its lifetime [131]. The UV exposure was based on the standard method ASTM G53. To simulate the deterioration of the coating caused by sunlight, we exposed our samples to two 20 - watt fluorescent lamps of UV – β radiation (in wavelength between 280 and 315 nm) which was the most photochemical aggressive UV region. The samples were exposed to UV for 16 days at distance of 10 cm from the lamps, which is equivalent to eight years of sun exposure in Montreal according to the surface power of the UV lamps and the formation given by Environment Canada [132].

(d) Fourier transform infrared spectroscopy (FTIR) :

Vibrational spectroscopy is being used extensively to characterize polymers, changes in polymer structure, and chemical modification of polymers. The UV exposed and non-exposed polymer samples were analyzed by FTIR to identify the effect of UV exposure on polymer structure. The FTIR spectra over the range 650 – 3800 cm^{-1} were recorded with the use of FTIR Spectrophotometer Perkin Elmer – Spectrum one (CSI Beam splitter), using HATR (Horizontal Attenuated Total Reflectance) Zn. Se 45° C plate.

3.4.6 Analytical method (ICP) :

The presence of corrosion products in immersion test media was investigated using Spectro Flame Modula, optical emission spectrometer with inductive coupled plasma (ICP). This test was carried out to evaluate the efficiency of coatings in corrosion prevention. The test was carried out periodically at 3, 6, 9, 12, 18 and 24 months of ageing.