Enhancement of corrosion protection ability of epoxy by inclusion of metakaolin clay

Fantaye Tasew

A Thesis Submitted to

The department of Material Science and Engineering

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Materials Science and Engineering

Office of Graduate Studies

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List of Acronyms and Abbreviations

ASTM: American Society for Testing and Materials

DSC: Differential scanning calorimetry

GZ: Galvanized steel

GDP: Gross domestic products

EIS: Electrochemical impedance spectroscopy

IR Spectroscopy: Infrared Spectroscopy

SEM: Scanning electron microscope

SPNNRS: Southern People Nations and Nationalities Regional State

TEA: TriethanolAmine

T_g: Glass transition temperature

TGA*:* Thermogravimetric analysis

PVC: Polyvinyl chloride

MK: Metakaolin

MT: Metric Tone

MMT: Montmorillonite clay

%wt.: Weight percent

XRD: X-Ray Diffraction

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Abstract

Epoxy resin are widely selected as corrosion protective coating, however, the formation of pore network limits its application. The aim of this thesis was enhancing the performance, thermal stability, water absorptions and sulfuric acid resistivity, of kadilux epoxy resin by inclusion of metakaolin fillers. The first step of this thesis focused on the study of kaolin and metakaolin clay property by using water absorption test. This part also includes surface modification of filler by using triethanolamine. Results showed that the metakaolin clay had low water absorption property and in case of surface modification triethanolamine modifier didnot show any significance change on interplanar spacing.

As a second step, samples was prepared by using 0,1,3,5, and 7wt% metakaolin and kadilux resin by direct mixing methods. The investigation was carried out by using optical microscopy, XRD analysis, thermogravimetric analysis, water absorption and acid immersion test. Acid immersion and water absorption was done according to ASTM G31 and ASTM D-570 standards respectively. The performance of the composite in acidic solution was evaluated by measuring the weight loss, thickness reduction and visual inspection of coated sample after immersed in acidic solution. According to optical microscope study there was the formation of pore network in cured epoxy. In case of acid immersion test analysis the weight loss, visual assessment and thickness reduction reveal that the inclusion of metakaolin in epoxy matrix had a positive effect on protection of substrate from sulfuric acid and further increment of metakaolin concentration and coating thickness gave better performance for polymer coating. Regarding to water absorption test the % weight gain of immersed sample were indirectly measured and composite samples showed low water absorption. According to the results epoxy composite shows better barrier and acid resistance properties among all samples epoxy with 7 wt% of metakaolin composite shows better barrier and acid resistance properties. The presence of metakaolin filler totally reduce the transparency of matrix. Thermal stability of composite also improved and 5wt% composite show better thermal performance.

Key words: Acid immersion, Barrier property, Corrosion, Kadilux epoxy resin, Metakaolin clay, Pore network, Water absorption

CHAPTER 1 INTRODUCTION

1.1. Description of the polymer

A polymer is a long molecule consisting of many identical or similar building blocks linked by covalent bonds. The repeating units that serve as the building blocks of a polymer are small molecules called monomers and these monomers put together by Polymerization process that is a process of connecting these monomers together and creating large macromolecules of different sizes and shapes. Polymers are a highly diverse class of materials which are available in all fields of engineering, from avionics through biomedical applications [1, 2], drug delivery system and tissue engineering [3, 4], biosensor devices [5], cosmetics [6] etc., due to their designable advantages such as specific strength properties with weight saving, potential for rapid process cycles, dimensional stability, and lower thermal expansion properties.

The corrosion resistant polymer coatings have attracted many attentions for many years due to its simplicity and efficiency [7, 8]. The numerous corrosion coatings have been developed and tested in an attempt to combat the harmful effects of corrosion on metal. Due to the variations in the physical and chemical properties of the different types of metals and alloys, the protection provided by each coating is dependent on the type of metal it is applied to and the environment in which it is exposed. The development of these coatings is focused on enhanced functionality comprising corrosion protection and adhesion, environmentally friendly materials, corrosion and mechanical damage detection, improved fatigue resistance, and water resistant.

Depending on how they are linked or joined (chemical bonds or intermolecular forces) and on the arrangement of the different chains that forms the polymer, the resulting polymeric materials can be classified as:

i. Thermoplastic polymer

Thermoplastic polymers are amorphous or semicrystalline polymers that soft or melt during heating and solidify during cooling. This type of polymers can be molded to shape by the application of heat and pressure in the molten shape and can be reshaped once formed. Some of the most commonly found thermoplastic polymers include polyethylene, polypropylene, polyvinyl chloride (PVC), polystyrene, polytetrafluoroethylene (PTFE, commonly known as Teflon), Acrylonitrile butadiene styrene (ABS plastic), and polyamide

ii. Thermosets polymer

Polymers which is irreversibly cured from a soft solid or viscous liquid, prepolymer or resin [9]. Thermoset polymers can be molded when they are first prepared. However, after being heated they "set" hardening irreversibly. If heated to a high temperature, thermosetting polymer decompose rather than melt. Include Polyester resin, Polyurea/polyurethane, Vulcanized rubber, Duroplast, Urea-formaldehyde, Melamine resin and Epoxy resin.

iii. Elastomers

Elastomers are loosely cross-linked polymers and they have the characteristics of rubber in terms of flexibility and elasticity [10]. In elastomer long coiled structure with loosely cross-linked structure is formed and can be stretched easily, but when the force or stress is removed it can return in to their original shapes. Examples of elastomers include natural rubbers, acrylonitrile butadiene rubber, butyl rubber, ethylene propylene diene rubber, silicone elastomers, fluoroelastomers, polyurethane elastomers, and nitrile rubbers.

1.2. Epoxy resin

Epoxy resins are one of the more commonly encountered families of commercial thermosetting polymers [11] and are widely used in a diverse range of industrial applications including coatings, adhesives, electronic devices, and as the matrix resin for advanced structural composites (e.g. aerospace automobiles, marine vessels and space vehicles)[11,12], due to their excellent mechanical properties, high adhesiveness to many substrates, and good heat and chemical resistances. Currently epoxy resins are intensively used across a wide range of fields, global production of epoxy resins in 2009 was about 1,800,000 MT; the largest markets are in coatings and electronics, which account for nearly 80% of all epoxy resin use [13, 14].

The term epoxy resin refers to both the polymer and its cured resin/hardener system. The polymer which is epoxy is a low molecular weight oligomer that contains one or more epoxy groups per molecule. The characteristic group, a three- member ring known as epoxy, epoxoid, oxirane, glycidyl or ethoxy line group is highly strained and therefore are highly reactive. They exist either as liquids with lower viscosity or as solids [15]. Through the ring opening reaction, the active epoxide groups in the uncured epoxy can react with epoxy group of their molecules themselves which is known as homopolymerization or with many curing agents or hardeners that contain hydroxyl, carboxyl, amine, and amino groups called an

addition or catalytic curing reaction [15]. The curing process of an epoxy resin proceeds as a function of time or temperature [12].

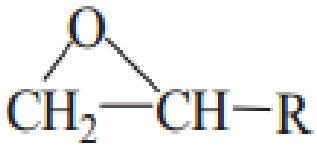


Figure 1.1. General Structure of epoxy resin [13]

The most commonly used epoxy resins are produced from diglycidylethers of bisphenol A (DGEBA) which is made by reacting epichlorohydrin with bisphenol-A in the presence of a basic catalyst [13,16]. Other types of epoxy resins are glycidyl ethers of novolac resins, phenoxy epoxy resins, and (cyclo) aliphatic epoxy resins. Glycidyl ethers of novolac resins, and phenoxy epoxy resins usually have high viscosity and better high temperatures properties while (cyclo) aliphatic epoxy resins have low viscosity and low glass transition temperatures [13,15].

1.2.1. Curing of epoxy resin

The curing or crosslinking of epoxide is the process by which one or more kinds of reactants, i.e., an epoxide and one or more curing agents, with or without the catalysts, are transformed from low-molecular-weight to a highly crosslinked structure or infinite network. Curing of polymers takes place under the action of special reagents (curing agents) or through the interaction of reactive oligomer groups upon exposure to heat, ultraviolet light, or high-energy radiation [12]. Different curing agents may be used to react with epoxides; but for different curing agents, there exist different mechanisms of the curing reaction with different final properties. High degree of cross-linking and the nature of the inter chain bonds give cured epoxies many desirable characteristics. These characteristics include excellent adhesion to many substrates, high strength, chemical resistance, fatigue resistance, corrosion resistance and electrical resistance [17]. Based on their curing kinetics epoxy resin are classified in to two which is one-part epoxy and two-part epoxy.

1.2.1.1. One-part epoxy

One-part epoxies also called single part epoxies, one component epoxies, no mixing required since in a one-part epoxy (assuming it isn't premixed and frozen or UV curable), the resin and curing agent are both present in the initial mixture. Typically, they polymerize when heat is added. (Robert M., Master Bond Inc., 2010). One-part epoxy have different

applications like bonding, sealing, coating, potting and encapsulation, and impregnation however it needs high temperature of curing and cold storage to provide sufficient shelf life.

1.2.1.2. Two-part epoxy

Two-component epoxy which consists of ‘base resin' and a ‘curing' agent. The two components are mixed in a certain ratio and chemical reaction occurs between the two parts generating heat (exotherm) and hardening the mixture into an inert, hard ‘plastic'. They are cured at room temperatures or elevated temperature; The curing is done with the help of catalysts, and the process can be accelerated by heat, in which high cross linking achieved by applying heat [11].

1.2.2. Curing agents

Curing agents are any type of additives or ingredients that are used to help harden or cure some type of substance. It is typically applied to polymer surfaces to facilitate the bonding of the molecular components of the material or transform the epoxy resins into a three-dimensional and infusible network [17]. The stronger the molecular bonds are, the harder the material surface is. Many curing agents may be used to react with epoxides; but for different curing agents, there exist different mechanisms of the curing reaction and different properties will resulted.

Curing agents used for room temperature cure usually alipahatic amines, whilst commonly used higher temperature, high performance hardener are aromatic amines and acid anhydrides [15]. However, an increase number of specialized curing agents, such as poly-functional amines, polybasic carboxylic acids, mercaptans and inorganic hardener are also used. All of these results in different, tailored properties of the final polymer. In general, the higher temperature cured, the high temperature curing system is generally divided into a pre-curing stage at low temperature and a post-curing stage at high temperature [13, 18] resin systems have improved properties, such as higher glass transition temperature, strength and stiffness, compared to those cured at room temperature [13]. Generally curing agents can be divided into amine-type curing agents, alkali curing agents, anhydrides, and catalytic curing agents according to their chemical compositions.

Amine type curing agents are one of the basic curing agents for epoxy resins in which its liquid, low viscosity and easy to miscible with epoxy resin at room temperature. They can be classified into three major categories: primary amines which may be aromatic, cycloaliphatic (cyclic), or aliphatic primary amines [13, 19]. A primary amine has two active

hydrogens that are each capable of reacting with an epoxy group. A secondary amine will react with only one epoxy group. The reaction rate of the secondary amine with an epoxy resin is much slower than that of a primary amine. In contrast, tertiary amines which have no active hydrogens, will not react with epoxy resins but can cure epoxy resins catalytically, resulting in homopolymerization. The major disadvantage of amine type curing agents are skin irritation and its toxicity.

Anhydrides curing agents are generally used for their long pot life and comparatively well-balanced properties [16]. They possess good mechanical, chemical, and electrical with a less amount of heat generation [13]. Anhydride curing agents have many advantage includes low shrinkage during curing, low internal stresses, reduced water absorption, high glass transition temperature and excellent electrical insulation [20,21]. However, most anhydride-epoxy systems are less reactive and require high temperature (> 120 °C) to initiate and propagate curing reaction [22, 23]. To increase the rate of curing reaction and lower the curing temperature sometimes accelerators are added to the formulation [23]. These accelerators are mainly Lewis bases such as tertiary amines [24, 25], imidazoles or quaternary ammonium salts etc. [19]. In general using of different curing agents on epoxy can give different properties due to this reason the selection of curing agents is based on final application we need.

Table 1.1. Summary of advantage, disadvantage and application of some common epoxy curing agents, E. Petrie (2005)

Curing agents	Advantage	Disadvantage	Application
Aliphatic Amine	• Low viscosity • Low cost • Fast cure	• Strong skin irritant • Poor bond strength above 80°C • High vapor pressure	• Adhesives and sealants • Casting and encapsulation
Polyamide	• Loose mix ratio • Room temperature cure • Good bond strength and flexibility	• High formulation cost • Low mechanical and chemical properties	• General-purpose adhesives • Casting and encapsulation
Aromatic Amine	• High T_g • High mechanical performance • Moderate thermal and chemical resistance	• Long elevated-temperature cures • Rigid	• Composites • Adhesives • Electrical encapsulation
Anhydride	• Good thermal and chemical resistance	• Long elevated-temperature cures • Insoluble in resin	• Composites • Adhesives • Electrical encapsulation

1.2.3 Epoxy curing systems

The curing systems of epoxy comprise the chemical reactions of the epoxide groups in the epoxy resins with a curing agent to form a highly cross-linked, three-dimensional network [13]. Epoxy resin curing that takes place at room temperature by using room-temperature curing agents, such as aliphatic polyamines, alicyclic polyamines, low molecular weight polyamide, and modified aromatic amines is called Room-temperature curing. Room temperature curing provides a lower T_g, higher flexibility, greater impact resistance, and greater electrical and thermal shock resistance. the other curing system is heat curing in which using of high temperature resins, chemicals, rods or other fluids to harden a polymer by facilitating the cross-linking of polymer chains. It is primarily performed on adhesives and coating materials that are exposed to harsh environmental conditions to increase their ability to withstand corrosion, erosion and degradation. The high temperature curing system is generally divided into a pre-curing stage at low temperature and a post-curing stage at

high temperature. Heating increases molecular mobility resulting in higher cross-link density which in turn results in higher T_g, greater tensile strength, higher heat resistance, and greater chemical resistance [11]. Epoxy also cured by using infrared, ultraviolet light, or electron beam irradiation in the presence of a photo initiator which is photo-curing system. Photo curing system can reduce the curing time from hours to minutes. In addition, it provides a more consistent and controlled process compared to the other curing processes. Electron beam curing method reduces the cure time and cure temperature and the cured resin attain good dimensional stability.

1.2.4. Application of epoxy resin

Epoxy resin is one of the most popular synthetic thermosetting polymers owing to its superior properties such as great chemical resistance, high adhesion strength to various substrates, low curing contraction, high moisture and solvent resistances, good thermal and dimensional stabilities and superior electrical properties [26, 27, 28]. Some of the applications are listed as follows:

i. Coatings

Epoxy resins provide durable coatings of high mechanical strength coupled with good adhesion to many substrates. Their main applications include Primers and paints for vehicles, chemical tank linings, and the inner coatings in beer cans [29].

ii. Adhesives

Upon curing epoxy resins possess excellent bonding characteristics. The reaction takes place without the evolution of volatiles and, often, without heat or pressure. They may be used to bond various metals, rubbers, wood, ceramics and glass with satisfactory results. Epoxy adhesives are better in heat and chemical resistance than other common adhesives. In general, epoxy adhesives cured with heat will be more heat- and chemical-resistant than those cured at room temperature. The strength of epoxy adhesives is degraded at temperatures above 350 °F (177 °C) [30].

iii. Laminates and composites

Epoxy resins are excellent matrix for composites material because they show good adhesion to reinforcement, cure with low shrinkage and provide mechanical, electrical, chemical, thermal and moisture resistance properties. As laminating resins, they are used with a variety of reinforcements such as glass fibers, asbestos and certain synthetic fibers. Glass cloth is usually the reinforcing material in electric laminates. Epoxies are also used in combination

with graphite, boron and Kevlar fibers. Typical applications of epoxy laminates include structural components for aircrafts and missiles, chemical resistant tanks.

iv. Casting and tooling

Casting techniques are widely used with epoxy resins in the field of electronics industry for potting, encapsulating transformers, valves, capacitors and many other electronic components [31]. Switch gear components, insulators and high voltage cable accessories are produced by epoxy casting techniques [29]. Epoxy foams are suitable for use in encapsulation of electronic compounds where strength to weight ratio is critical. Epoxy cast tools are used mainly for making dies, jigs, foundry patterns and plastic processing models. In the manufacture of tools, epoxy casting resins are used as prototype models for product design, drilling and welding jigs, checking fixtures, stretch blocks and injection molding. They are less expensive than metals and can be modified quickly and cheaply.

v. Construction

Epoxy resins are used to improve the performance of traditional materials in the construction industry and are incorporated in flooring, concrete, metal or wood. Epoxy terrazzo floors provide adhesion, impact resistance and strength. Epoxy formulations for roads and bridges are effective barriers to moisture. Epoxies are used to repair concrete cracks in adhesives and grouting systems. Concrete to concrete bonding can be done with epoxy-polysulphide formulations in conjunction with polyamine hardeners. Epoxies are used as binders for swimming-pool decks and walks and to consolidate the soil around oil-well drills.

1.2.5. Drawback of epoxy resin

Epoxy coatings protect against corrosion by forming a physical barrier and when integrated with corrosion inhibitors, resist attack of aggressive species [32]. The primary function of epoxy coatings in corrosion protection is to isolate the metal from the corrosive environment. In addition to forming a barrier layer to stifle corrosion, the epoxy coating can contain corrosion inhibitors. However, epoxy coatings are not perfect barriers as they can be penetrated by corrosive media, such as oxygen, water molecule, and ions [33, 34, 35], and also, they are only usable at narrow temperature range. Epoxy tends to absorb significant amounts of water when exposed to high humidity conditions [34]. Water can migrate through polymer coatings by a number of different means. For example, individual water molecules can take a random walk through holes in the polymer network, or through channels, capillaries, or pores in the coating [36]. The absorbed moisture has many detrimental effects on the composite performance. The water molecules are often assumed

to occur in two different environments in the polymer matrix: the water is either strongly interacting with specific (polar) groups of the epoxy matrix or clustered together in free volume micro-voids as ‘‘free water’’. The water absorption behavior is hence considered to depend on free volume properties which is formed during curing and type and concentration of polar groups in the epoxy system [32]. When this happens, metal corrosion can occur underneath the epoxy coating/metal interface. Thus, the corrosive media accumulated beneath the epoxy coating not only leads to metal corrosion but also decreases the adhesion of the coating to the metal [33].

1.2.6. Methods to improve the performance of coating

Generally, there are three methods often used to improve the protective performance of the organic coatings. First addition of fillers [37], such as graphene, nanoclay, ZnO, and MoS_2, are added into the coating to extend the diffusion path of corrosive media through the coating. Second, corrosion inhibitors are added to inhibit metal corrosion reaction underneath the coating. Third, high density, high cross-linked, thicker, and self-healing coating are needed to reduce the coating permeability [38]. Adding fillers to a polymer matrix has a great effect on improving the mechanical, chemical and thermal properties. The barrier performance of epoxy coatings can be enhanced by the incorporation of a second phase that is miscible with the epoxy polymer, by decreasing the porosity and zigzagging the diffusion path for deleterious species [32]. Barrier and corrosion protection properties of organic coating systems may be improved by addition of fillers, by using polymer composite [33].

1.3. Polymer composite

Polymer composite materials typically consist of two or more components that comprise significantly different physical and/or chemical properties, polymer as a matrix, [41]. They provide unique combination of mechanical and physical properties that cannot be found in any single material. They are light in weight, hard, ductile, high temperature resistant as well as shock-resistant materials [42]. Composite are now extensively used in various industries such as automotive, aerospace, coating, and construction applications [43, 44, 45]. Christina Konecki (2017) [46] applied hybrid polymer composites as ultrathin films to protect iron against corrosion. Ammar Patel (2018) [47] used Fiberglass as dispersed corrosion resistance filler to protect iron from corrosion.

The properties of polymer micro/nanocomposites are affected by the nature of polymer matrix and filler, their intrinsic properties, by the size and shape of the fillers, by the dispersion of the particles into the polymer matrix, by the surface functionalization and the thickness of the filler surface treatment and also, by the interactions and adhesion between the polymer matrix and the fillers [47]. The most common types of polymer/filler composite include silicate, carbon or metal oxide nanoparticles. Among the various available polymer fillers, clay and its derivatives are widely used, because of plate-like shape and aspect ratio, clay filler combine different valuable properties such as; excellent barrier to moisture and gases through filling of the micro voids and crevices [48], appropriate mechanical properties and thermal stability, improved flame retardancy and increased corrosion resistance.

1.4. Clay minerals

Clay minerals are the basic constituents of clay raw materials and platy structure is the dominant morphology. Depending on the clay type, the individual layers could be composed of two, three or four sheets of either $[SiO_4]^{4-}$ tetrahedra or $[AlO_3(OH)_3]_6$ octahedra. The physical characteristics of clays are more important in defining various clay groups. Therefore, the clay minerals are broadly classified on the basis of the number and arrangement of sheets in a clay layer. Depending on the number and the way that the tetrahedral and octahedral sheets are packed into layers, the clay minerals can be classified into three classes, i.e., two-sheet layer, three-sheet layer and four-sheet layer (Lee and Tiwari 2012). Tetrahedral sheets (T), made up of silicon (Si^{4+}) and oxygen (O_2^-), and octahedral sheets (O) built up of hydroxide (OH^-) and either aluminium (Al^{3+}) (named dioctahedral) or magnesium (Mg^{2+}) (named trioctahedral). Two or three such sheets form a TO or TOT layer. The tetrahedral within a T sheet are linked by sharing three of the four corners (O atoms) to form a hexagonal pattern. The oxygen at the fourth corner of the tetrahedrons forms part of an adjacent octahedral sheet, with octahedrons linked by sharing edges [49, 50].

1.4.1. General classification of clay minerals

Clay minerals are generally classified as Illite, Smectite, Vermiculite and Kaolinite group [50].

i. Illite group

A typical dioctahedral 2:1 phyllosilicate representing illite group. The unit cell structure of illite resembles very much that of muscovite, where a sheet of octahedrally coordinated

cations is sandwiched by two tetrahedral SiO_4 4-sheets to form a layer. Since such 2:1 layers in illite exhibit a net negative charge, planes of K^+ ions are present in between every two layers to keep the whole structure electrically neutral. A general chemical formula of illite can be written as $K_yAl_4(Si_{8-y},Al_y)O_{20}(OH)_4$, where y is typically around 1.5, and therefore it can be learned that illite contains more Si but less K than muscovite. This group of clay includes hydrous micas, phengite, brammalite, celadonite, and glauconite.

ii. Smectite group

These clay materials consist of TOT (2:1) layers in which there are three Sheets, two tetrahedral (T) sheets and one octahedral (O) sheet placed between the tetrahedral ones. It includes montmorillonite, bentonite, nontronite, hectorite, saponite and sauconite [51].

iii. Vermiculite group

A hydrous phyllosilicate mineral, the raw material for vermiculite is a natural clay mineral that has a layered structure with water in between the layers and it undergoes significant expansion when heated.

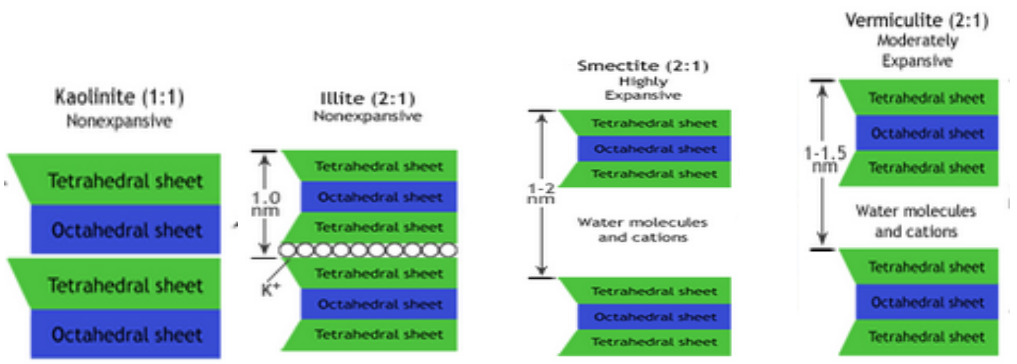
iv. Kaolinite group

This is the most common clay of the kaolinite group and it has a T-O dioctahedral structure (1:1 layer) with chemical formula of $Al_2Si_2O_5(OH)_4$. The primary constituent of kaolin (40-70%) other minerals comprising kaolin include quartz, muscovite-like micas, and rutile (Moulin, 2001). The kaolinite structure is based on a gibbsite-like sheet of octahedrally coordinated Al bound to a sheet of Si tetrahedra through shared oxygens (Bish, 1993). Since the layers are electronically neutral, the bonding between layers is by weak Vander Waals bonds. These weak bonds cause the cleavage and softness of this mineral. Also, kaolin is non-swelling clay because the layers are uncharged. The water in this structure is located in between the clay particles. Kaolin employs to improve color, opacity, and printability of paper. Kaolin is also used as filler extensively in the ceramic and rubber industries and has found minor applications in ink, organic plastics, and cosmetics. Kaolin clays including kaolinite, dickite, nacrite, and halloysite.

Kaolin clay was selected as a filler for making of polymer composite due to their low swelling capacity than the other as illustrated in Table 1.2. The Kaolinite contains little or no surface adsorbed water in its structural unit when compared with other clay types; therefore, most of the dehydration (loss of constitutional OH) takes place between 400℃ and 600℃, i.e. the energy used dehydration is lower than the other types of clay [52]. Despite its lower swelling capacity it's relatively inexpensive and also non-toxic. This work

focuses on optimization of epoxy properties by inclusion of MK clay which is formed by calcination of belesa kaolin (Ethiopian kaolin).

Table 1.2. Summary of Structural and physical properties of most common clay minerals, Black (2009) and Rodrigo, F. (2009)

Clay mineral group	Kaolin	Illite	Semectite	Vermiculite
Structure	1:1, non-expanding	2:1, non-expanding	2:1, high expansion	2:1:1, non-expanding
Swelling capacity	Almost none	Low	High	Very low
Layer thickness	0.7nm	1.0nm	1.0-2.0nm	1.4nm
Interlayer bonding	Strong	Strong	Very weak	Moderate to strong
CEC (meq/100g)	3-15	10-40	80-150	10-40
Surface area(m^2/g)	5-10	50-100	700-800	< 80
Chemical formula	$Al_2Si_2O_5(OH)_4$	$(K,H)Al_2(Si,Al)_4O_{10}(OH)_2$-$xH_2O$	$(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2$-$xH_2O$	$(Mg,Fe^{+2},Fe^{+3})_3[(Al,Si)_4O_{10}](OH)_2 \cdot 4H_2O$
Structural arrangement				

1.4.2. Kaolin deposits in Ethiopia

Exploration for kaolin in Ethiopia was carried out mainly at the granites and pegmatite. Intensive explorations have been carried out at Bombowha and Kombolcha areas and both of them are related to acidic intrusive rocks, Haile M., 1998. The main sources of kaolin for the ceramic industry in Ethiopia are the weathering products of granites and pegmatite. Acidic volcanic rocks (such as rhyolite or trachyte) in central and northern Ethiopia and the coal related clay sediments of northwest Ethiopia [53].

Table 1.3. Kaolin Occurrences in Ethiopia [53]

Occurrence name	Longitude	Latitude	Region
Belesa kaolin	37° 58'E	7° 35'N	SPNNRS
Awzet kaolin	38° 07' 48" E	11° 45' 00" N	Amhara
Debre Tabor kaolin	38° 00' 36" E	11° 50' 02" N	Amhara
GypsiteMariam kaolin	37° 35’ 24” E	11° 45’ 36” N	Amhara
Kerker kaolin	37° 24' 43" E	12° 42' 40"N	Amhara
Bombowha kaolin	38° 46' 30" E	06° 05' 20" N	Oromia
Kombelcha kaolin	42° 08' 50" E	09° 27' 58" N	Oromia
Ansho Kaolin	37° 38' 28" E	7° 20' 6" N	SPNNRS

1.4.3. Calcinations of kaolin

Calcinations of kaolin referee to firing of row kaolin to remove the structural water, and this process is known as dehydroxilation. Below 100 °C (212 °F), exposure to dry air will slowly remove liquid water from the kaolin. The end-state for this transformation is referred to as "leather dry". Between 100 °C and about 550 °C (1,022 °F), any remaining liquid water is expelled from kaolin. The end state for this transformation is referred to as "bone dry". Throughout this temperature range, the expulsion of water is reversible: if the kaolin is exposed to liquid water, it will be reabsorbed and disintegrate into its fine particulate form. Subsequent transformations are not reversible and represent permanent chemical changes.

Endothermic dehydration of kaolin begins at 550–800 °C producing disordered metakaolin [54].

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O\uparrow \text{ [54]}$$

When kaolin heated to temperatures of 600-900 °C, it loses 14% of its mass in bound hydroxyl ions. This heat treatment, or calcination, breaks down the structure of kaolin such that the alumina and silica layers become puckered and lose their long-range order [55]. The calcination temperature of raw kaolinitic clay impacts the degree of crystallinity of the metakaolin obtained as well as its reactivity. When a calcination temperature is above 850°C, it leads to the beginning of the metakaolin recrystallization and the decrease in its ability to react. Further heating (925°C to 950°C) converts the metakaolin ($Al_2O_3.2SiO_2$) to an aluminum-silicon spinel ($2Al_2O_3.3SiO_2$). After calcination at 1050°C, the spinel phase ($2Al_2O_3.3SiO_2$) becomes mullite ($3Al_2O_3.2SiO_2$) and crystalline cristobalite (SiO_2) [54]. Calcination at inappropriately high temperature (> 1000 °C) or long retention time may decrease the reactivity of clay particles due to possible recrystallization of the reactive phase into a stable crystalline phase [56].

Metakaolin is not a by-product [57]; it is obtained by the calcinations of pure or refined kaolinite clay at a temperature between 600^0 C and 850^0 C. As OH groups form part of the octahedral layer and link it to the tetrahedral layer, removal of these groups leads to a state of more structural disorder that is a metastable state as shown in Figure 1.3. (Rodrigo F., 2009) described that the term metakaolin refers to the mineral kaolin that has been heated to disorder the structure through heating. MK is a high quality pozzolonic material silicate-based material, which is blended with cement in order to improve the durability of concrete.

Metakaolin platelets resulting from the heat treatment of kaolin have similar but more disordered morphology and more individualized platelets [58]. These observations reveal that the heat treatment of the kaolin results in dehydroxylation and disorganization of the crystalline structure of the material without a significant change on the morphology of the kaolinite clay. Proper thermal treatment of kaolin clay leads to the dehydroxilation of the kaolinite's crystal structure and its transformation into metakaolin – MK [59]. MK used in concrete it will fill the void space between cement particles resulting in a more impermeable concrete [60]. Metakaolin can reduce the hardened cement permeability to liquids and gases. By partially replacing Portland cement with metakaolin not only reduces carbon dioxide

emissions but also increases the service life of buildings [61]. Metakaolin presents various advantages in concrete, such as increased strength, increased resistance to chemical attack, enhanced concrete finishes, reduced shrinkage, and reduced permeability due to these advantages, metakaolin is widely used in producing high performance and high strength concrete.

1.4.3.1. Advantages of metakoalin

- Increased compressive and flexural strengths
- Reduced permeability (including chloride permeability)
- Reduced potential for efflorescence, which occurs when calcium is transported by water to the surface where it combines with carbon dioxide from the atmosphere to make calcium carbonate, which precipitates on the surface as a white residue.
- Increased resistance to chemical attack
- Increased durability
- Reduced effects of alkali-silica reactivity (ASR)
- Enhanced workability and finishing of concrete
- Reduced shrinkage, due to "particle packing" making concrete dense

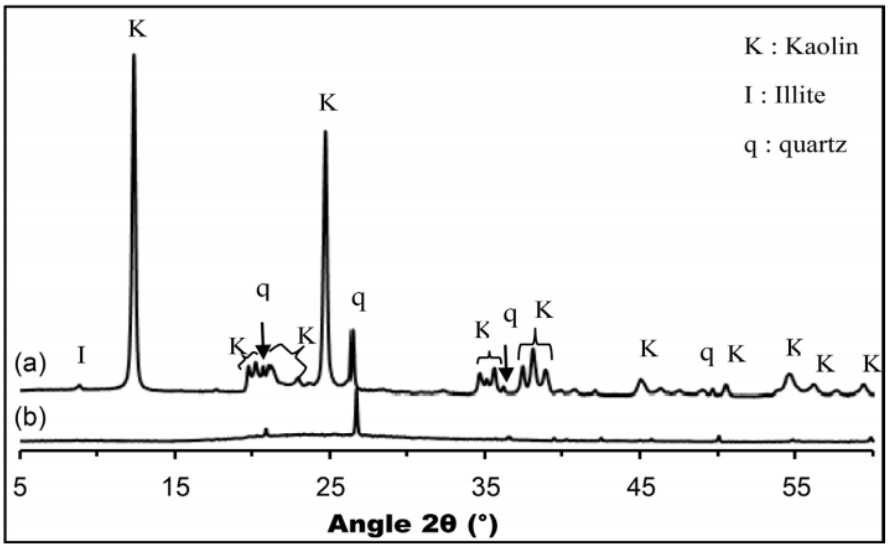


Figure 1.2. X-ray diffraction spectrum (a) kaolin and (b) metakaolin [48]

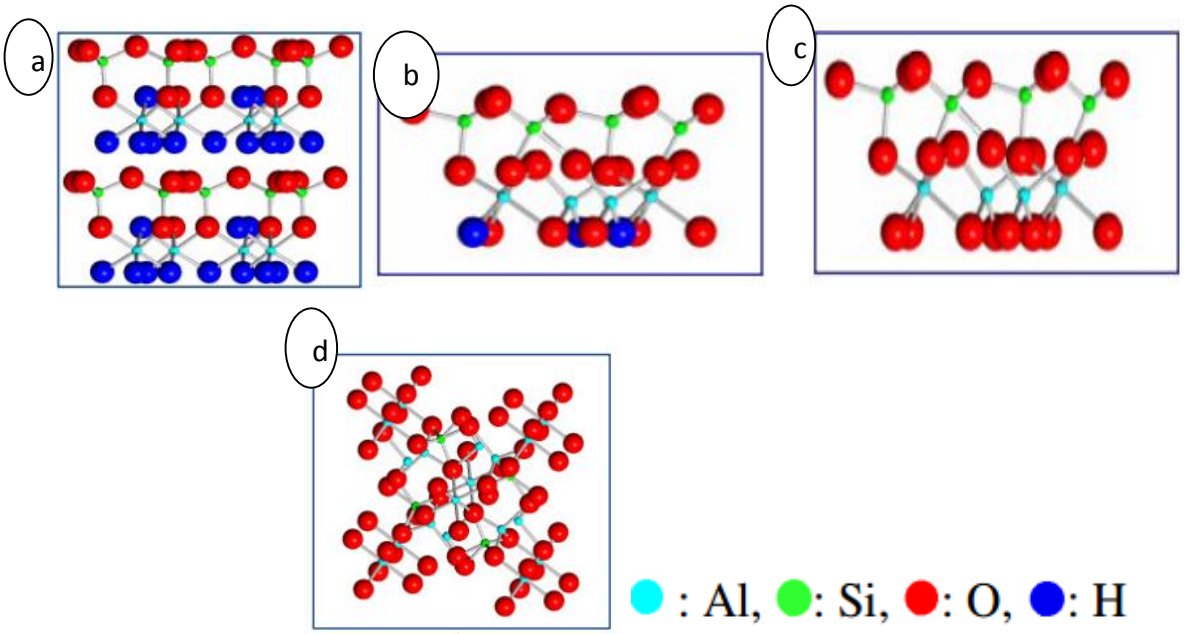


Figure 1.3. Schematic change of structure of kaolinite during calcinations a) Natural kaolinite b) Calcinated kaolinite during pre-dehydration c) calcinated kaolinite during dehydroxylation d) Calcinated kaolinite after de-hydroxylation (Thu-Ha P. Thi, 2013) [62]

1.5. Objective of the study

1.5.1. General objective

The objective of this research is enhancing the performance of kadilux epoxy resin by the addition of MK clay (epoxy- clay composite).

1.5.2. Specific objectives

- Investigate the difference in water absorption between kaolin and MK clay
- Investigate the effect of MK on pore refinement and the reduction on pore density of kadilux epoxy by using optical microscope
- Determine the influence of inclusion of MK clay on corrosion property (using water absorption and acid immersion test based on ASTM standards) and thermal stability of kadilux epoxy resin
- Investigate the effect of filler concentration on barrier properties of polymer matrix.

1.6. Significance of the study

Corrosion has been a serious problem around the world; Failures occurring as a result of corrosion attack is very expensive therefore preventing or reducing these attacks becomes very significant to the industry and households. Reducing corrosion attack of metal by using DUPLEX coating system has great advantage for extend service time of metals on the high performance applications (American Galvanizers Association, 2012). Duplex system is formed by painting or powder coating over hot-dip galvanized steel therefor the exterior

layer of paint or powder coating slows down the rate at which the zinc is consumed, which can greatly extending the life of the galvanized steel. Epoxy paint is the most widely applicable coating over galvanized steel due to its availability and excellent mechanical and thermal properties, but during crosslinking of epoxy resin pore network was formed which can act as the path for water and corrosive species. An effective means of improve the performance of an epoxy coating is by the introduction of inorganic fillers. This study showed the effectiveness of MK filler on performance improvement of epoxy and it also the relationship between filler concentration and properties of kadilux resin i.e., acid resistance and water absorption of neat epoxy in relative to epoxy composite. This study may give some knowledge about the kadilux resin and can initiate other researchers to find out its structure, properties and application by analyzing in different conditions.

1.7. Scope and limitation of the study

The general aim of this research was to improve the corrosion resistance of epoxy matrices through the incorporation of MK clay as filler. The study was narrowed down to investigate the water absorption, sulfuric acid resistivity and thermal stability of epoxy and epoxy/filler composite separately. Therefore, this study did not cover the full range of the corrosion characterization techniques due to lack of available or reliable data and prior research studies on kadilux epoxy resin and its property and also due to limitation of characterization equipment's. This work was done to indicate presence of porosity and its effect on water absorption, and point out performance enhancement of kadilux resin like barrier property, thermal stability and acid resistivity by adding MK filler.

CHAPTER 2 LITERATURE REVIEW

2.1. Corrosion

Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. Corrosion of materials usually takes place in the presence of oxygen and moisture and involves two electrochemical reactions, oxidation occurs at anodic site and reduction occurs at cathodic site [63]. Most metals, especially steels which are iron based, are very likely to suffer from corrosion. In general corrosion of a metal substrate does not occur without water, oxygen, and environmental electrolytes present to promote metal dissolution. For corrosion to occur four essential factors are required. The factors are; the anode, cathode, electrolyte and an electrical connection. The corrosion resistance of metals and alloys is a basic property related to the easiness with which these materials react with a given environment. The corrosion of steel can be delayed or slowed down by special measures (i.e. preventive/protective methods), it can never be "stopped" in a natural environment without any protection [64]. There are several stimulating factors that lead to the corrosion of steel in the environment. Moisture, temperature, pH values, mineral salt content, sulfides, organics, precipitates, and so on are major factors that contribute to corrosion of metal. Organic protective coating are widely applied for corrosion protection of metallic structures [65, 66]. These organic coatings provide a physical barrier between corrosive media and metal surface. However, they are not long lasting due to the penetration of corrosive agents i.e. oxygen, water and ions to the coating/metal interface. In order to improve the barrier properties of these coatings, various inorganic fillers have been used into the polymer matrix.

2.2. The Effects of Corrosion

Corrosion affects us in everyday life-in the manufacturing of products, the transportation of people and goods, the provision of energy, the protection of our health and safety. The effects of corrosion in our daily lives are both direct, in that corrosion affects the useful service lives of our possessions, and indirect, in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers [65]. Corrosion costs society in three ways; first, extremely expensive replacement is needed, second wastage of natural resources and leads over damage to the environment. The worldwide cost of corrosion is estimated to be over 3% of the world's GDP, which is large considering the impact of corrosion evades public awareness until catastrophic failure occurs at the expense of lives

[66]. In particular corrosion is a serious problem in automotive, maritime as well as aerospace industry. Many methods have been established to prevent or protect metals from corrosion, such as barrier protection [67-70], galvanization [71-73], and cathodic protection [74, 75]. The corrosion resistant coatings have attracted many attentions for many years due to its simplicity and efficiency. One of the most commonly used type of anticorrosive coatings are organic polymeric resin coating, because of their good barrier properties and excellent chemical resistance

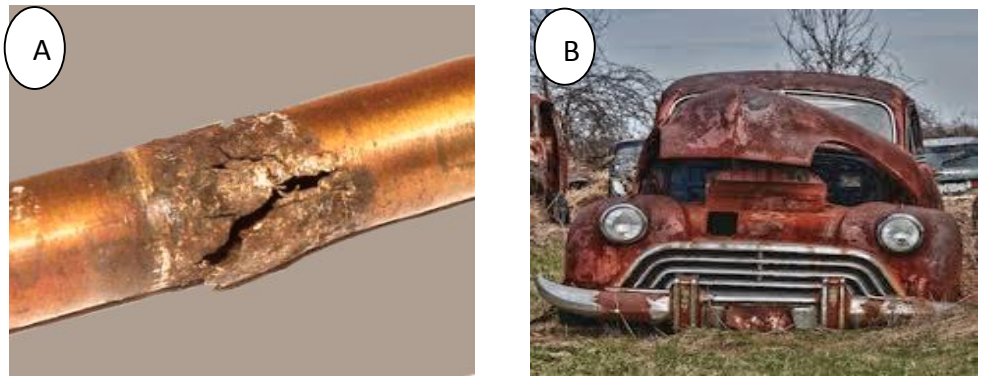


Figure 2.1. Corrosion and its impact on A) metal pipe and B) automobile car

2.3. Corrosion protection by polymer coating

When corrosive media have direct access to metal substrate, corrosion electrochemical reactions will take place at the metal surface. Corrosion cannot be fully prevented and is only retarded and minimized [76]. To have synergetic corrosion protection using both galvanization and painted or powder coated can be used. The duplex system provides a more sophisticated manner of corrosion protection used independently, both protective coating and galvanizing provide corrosion protection to steel; however, when utilized together, the two coatings work effective than use independently. Hence, the exterior layer of paint or powder coating slows down the rate at which the zinc is consumed, which can extending the life of the galvanized steel. In return, once the exterior layer has been weathered down or damaged, the zinc beneath is still available to provide cathodic and barrier protection. As a result, the substrate steel is afforded corrosion protection for 1.5 to 2.3 times the sum of the expected life of each system alone (American Galvanizers Association, 2012).

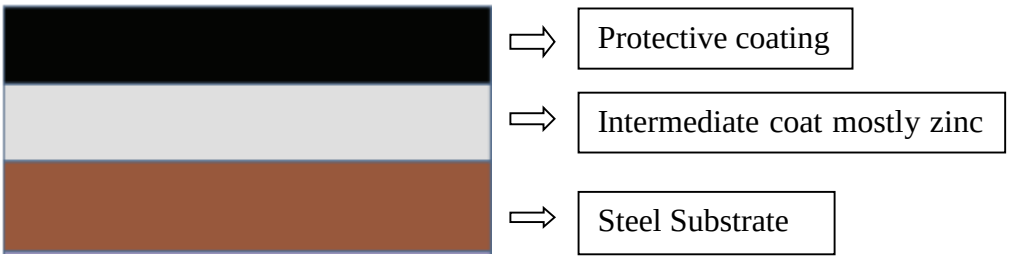


Figure 2.2. Different stages of corrosion protection coatings

Recently organic polymeric resins such as epoxies, polyurethanes, and polyesters have traditionally been used as protective (exterior) coatings. Such coatings act as a physical barrier against the diffusion of corrosive species that are present in the atmosphere. Polymeric coatings are not permanently impenetrable since the presence of small defects leads to ions (i.e., that are present in the atmosphere) diffusing through the coating and attacking the metal substrate [77]. A second line of defense can be implemented against this process by incorporating various inorganic filler materials that increase the anti-corrosion performance of the coating matrix.

Epoxy coatings are employed to prevent the corrosion of metal structures due to their ease of application and reasonable costs and used to protect metals against corrosion and harsh environments for many years. This coating is usually used to protect metals against corrosion and this is most likely achieved by means of barrier properties [16]. However, all polymeric materials absorb some amount of water when immersed in an aqueous solution or exposed to high humidity conditions [78]. Water can migrate through polymer coatings by a number of different means. For example, individual water molecules can take a random walk through holes in the polymer network, or through channels, capillaries, or pores in the coating. The diffusion of water and oxygen through this coating is several times greater than the minimum amount required to initiate the corrosion of metallic substrate.

Application of inorganic fillers is one method to enhance anti-corrosion property of organic coatings. There are various reports concerning improving corrosion resistance of coatings using nanoparticles such as; TiO_2 [79], ZnO [80], SiO_2 [81] and ZrO_2 [82].

i. Polymer-filler composites

Mineral fillers have made an important contribution to the spectacular growth of polymers composites. Domna M. et al. [71] worked on Corrosion Protection of Steel by Epoxy-Organoclay Nanocomposite Coatings; the investigation was carried out using salt spray exposures, optical and scanning electron microscopy examination, open circuit potential, and electrochemical impedance measurements. The mechanical, thermomechanical, and barrier properties of pristine glassy epoxy polymer and epoxy-clay nanocomposites were examined. The mechanical, thermomechanical, and barrier properties of all the epoxy-clay nanocomposites were improved compared to those of the pristine epoxy polymer. In addition, both the pristine epoxy and the epoxy nanocomposite coatings protected the steel from corrosion. Furthermore, the protective properties of the nanocomposite coatings were superior compared to those of the pristine epoxy polymer. The protective properties of the nanocomposite coatings varied with the modified clay used.

Lazbourne A. et al. [83] determine the corrosion protection, mechanical and thermal properties of nanoclay filled epoxy and poly (vinyl chloride-co-vinyl acetate) (VYHH) resins on their work of evaluation of nanosilicate filled poly (vinyl chloride-co-vinyl acetate) and epoxy coatings. Nanoclay was incorporated into VYHH at 0%, 0.5% and 1.5%wt loadings, and into epoxy at 0% and 1.5% loadings. Steel substrates were prepared and coated with each of the prepared coatings. Some of the samples were submerged in a tank containing 5% NaCl solution and tested periodically using EIS to study the effect of the nanoclay on the corrosion protection of the coatings. Films were cast from each system to be used to evaluate the mechanical performance of the coatings. Notched and unnotched samples were cut from the films and some were submerged in the 5% NaCl solution while some were left unsubmerged as controlled samples. EIS measurements showed that VYHH/0.5%nanoclay provided superior barrier protection. The nanoclay filled epoxy exhibited increased barrier properties after 21 days. The tearing energy of the neat VYHH coating decrease by 27% after submersion, while the nano-coatings showed a slight increase. The neat epoxy showed no change in the tearing energy after submersion, while that of the nano-coating was increased by 14% after submersion. DSC results showed that the nano coatings have improved the thermal barrier properties compared to the neat.

S. Radhakrishnan et al. [84] prepare coatings from polyaniline–nano-TiO_2 particles synthesized by in situ polymerization were found to exhibit excellent corrosion resistance much superior to polyaniline (PANI) in aggressive environments. The corrosion studies were carried out on steel plates coated with these formulations containing 10 wt. % polyaniline prepared with different concentrations of nano-TiO_2.The electrochemical impedance spectroscopy was studied at periodic intervals during exposure to hot saline (65^0C) conditions for prolonged durations over a period of 90 h. The open circuit potential (OCP) was found to shift with time from−0.38 V SCE to more anodic side (−0.2 V SCE) much above that of bare steel (−0.5 V SCE). The presence of nano-TiO_2 was found to be vital in the prevention of corrosion and the shift of OCP to anodic side. From these data, one could envisage more than 100 times improvement in the corrosion resistance especially for polyaniline prepared with 4.18wt% nano-TiO_2. The exceptional improvement of performance of these coatings has been associated with the increase in barrier to diffusion, prevention of charge transport by the nano-size TiO_2, redox properties of polyaniline as well as very large surface area available for the liberation of dopant due to nano-size additive.

Haque et al. [85] have manufactured S2-glass/epoxy-clay nanocomposites by the vacuum assisted resin infusion method and they reported an improvement of 44, 24, and 23% in interlaminar shear strength, flexural strength, and fracture toughness, respectively, in comparison to conventional S2-glass/epoxy composites. In addition, they found the thermal decomposition temperature of the nanocomposites to be approximately 26^0C higher than that of conventional composites.

N. Kouloumbi et al. [86] determine the effect of quartz (0 - 60wt.%) on the mechanical, anticorrosive, and dielectric properties of pretreated steel coatings in a 3.5wt.% NaCl solution was studied by abrasion and impact resistance, pencil and Shore D hardness measurements, visual observations after salt spray tests, as well as by electrochemical impedance spectroscopy and water permeability measurements. Results revealed that coatings with a quartz load up to 30% exhibit a noticeable improvement of their mechanical characteristics as well as better dielectric and anticorrosive behavior than that of pure epoxy coatings. Further increase of the quartz content results in a lower degree of their behavior improvement or even in their worsening, with the exception of the coatings' surface hardness that increases with the increase of the quartz content.

Xianming S. et al. [87] Homogeneous epoxy coatings containing nanoparticles of SiO_2, Zn, Fe_2O_3 and halloysite clay were successfully synthesized on steel substrates by room-temperature curing of a fully mixed epoxy slurry diluted by acetone. The surface morphology and mechanical properties of these coatings were characterized by scanning electron microscopy and atomic force microscopy, respectively. The effect of incorporating various nanoparticles on the corrosion resistance of epoxy-coated steel was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. The electrochemical monitoring of the coated steel over 28 days of immersion in both 0.3 wt.% and 3 wt.% NaCl solutions suggested the beneficial role of nanoparticles in significantly improving the corrosion resistance of the coated steel, with the Fe_2O_3 and halloysite clay nanoparticles being the best. The SiO_2 nanoparticles were found to significantly improve the microstructure of the coating matrix and thus enhanced both the anticorrosive performance and Young's modulus of the epoxy coating.

Corrosion performance of epoxy coatings containing silane treated ZrO_2 nanoparticles on mild steel in 3.5% NaCl solution by M. Behzadnasaba et al. [88] Clear epoxy coatings were modified by adding various levels of ZrO_2 nanoparticles. In order to achieve proper dispersion of nanoparticles in the epoxy-based coating and making possible chemical interactions between nanoparticles and polymeric coating, the surface of the nanoparticles was treated with amino propyl trimethoxy silane (APS). Corrosion performance of mild steel coated specimens was investigated employing EIS, electrochemical noise (ECN) techniques and salt spray test. Coatings with 2–3 wt. % ZrO_2 nanoparticles possessed the best corrosion performance among the coating specimens. Possible chemical interactions between polymeric matrix and treated nanoparticles in nanocomposites.

ii. Polymer-kaolinite composites

Zhang et al. (2011) prepared kaolin modified polyester fibers with different concentration of the filler. They reported that tensile strength, modulus, and boiling water shrinkage of the kaolin modified fiber were reduced with the increase of the kaolin content. However, moisture adsorption was increased with the increase of the kaolin content. They also investigated the non-isothermal crystallization of kaolin modified polyester and observed that the addition of kaolin increased both the melting and crystallization temperature

Lutfun N. Hilary et al. [89] determined the effect of kaolinite clay on polyester where the sample was fabricated by open molding method. Different percentage of kaolinite clay and polyester resin with a fixed percentage of styrene monomer (10 wt. % of polyester resin) was taken to prepare the polymer filler composites. Mechanical properties such as compressive, flexural and tensile strength, and rebound hardness of composites were investigated. Results indicated that the flexural and tensile strength of the composites decreased and E-modulus increased with the increase of clay content. Compressive strength and rebound hardness were increased with the increase of clay content in the composites.

Naveen A. N. et al. [90] worked on Rheological and Thermal Analysis of Polystyrene – Kaolin Nanocomposite Prepared by Solution Intercalation Technique, Polymer-clay nanocomposite of commercial polystyrene (PS) and kaolin were prepared via solution intercalation technique. Organically modified kaolin was used to render kaolin miscible with hydrophobic PS. Vinyl modified kaolin was used for the study. The kaolin was well dispersed in PS solution. Different amounts of nanoclay were added to polystyrene, to analyse the effect of nanoclay concentration in nanocomposite prepared. SEM analysis provides information of the morphology of the polystyrene-clay nanocomposite. Intercalation occurs at low modified clay content, whereas aggregation and agglomeration. SEM analysis was performed and it revealed that the clay was of nano size. Also, nanoclay was well dispersed in the polymer matrix. The thermal behavior of the Polystyrene nanocomposite was studied for various concentration of added modified kaolin nanoclay. The sample added with 5% wt. of nanoclay showed more thermal stability than other samples, also the degradation happens at a higher temperature when compared with other samples. The addition of modified kaolin nanoclay has shown an improvement in the rheological and thermal properties of the polymer nanocomposite occurs at high filler content.

Namory M. [58] used cassava starch for their work in the production of plastic films; Metakaolin was used as filler obtained after heat treatment at 700˚C of kaolin for one hour. A sample starch (2.5 g) is mixed with 2 ml of glycerol (50% volume) in the presence of 3 ml of 0.1 M hydrochloric acid. The mineral filler (0.5 g) is added to the mixture. This is homogenized and then heated to 100˚C on a heating plate equipped with a magnetic stirrer for 10 min. The suspension is then neutralized by the addition of 2 ml of 0.1 M sodium hydroxide solution. Finally, the resulting viscous suspension is poured into Petri dishes and

then dried at room temperature in 72 hours. The samples had studied by various techniques (X-ray diffraction, IR-TF spectroscopy, scanning electron microscopy, tensile tests, and thermal resistance). The result revealed that metakaolin, an amorphous material of disordered structure, is more favorable to surface dissolution and to a good dispersion of the layers in the matrix of the polymer. This contributes to strengthening the mechanical and thermal properties of plastic films based on metakaolin-reinforced cassava starch. The Young's modulus increases to 25 MPa and the thermal resistance to above 120˚C against 90˚C for the non-reinforced bioplastic. Therefore, cassava starch reinforced with metakaolin, seems to be a very attractive alternative to replace plastics made from petroleum products.

iii. Epoxy-kaolin/metakaolin composites

Dalila L. et al. [91] worker on elaboration and characterization of composite material based on epoxy resin and clay fillers, the untreated kaolin and kaolin physically treated (metakaolin) were used as fillers for their study. The study is divided into two parts: The first one is devoted to the study of the composite material based on epoxy resin with kaolin, using different size fractions at rates ranging from 2% to 20%. The second part examines epoxy resin-based composite with calcined kaolin (metakaolin) with regard to the influence of the structure, the particle size and the charge rate on the properties of the material. It is shown that the clay fillers give the epoxy resin different properties compared to the epoxy resin alone and, additionally, reduce the cost of materials. It was also observed that the fillers enhance the mechanical properties by increasing the rigidity of the material. There is a maximum value of 2.4 GPa to 18% kaolin, or more than 325% increase in the modulus of elasticity with respect to unfilled resin for the finer particle size.

Jabbar Hussein M. [92] on his study of Tensile and Compressive Properties of Kaolin Rienforced Epoxy, by using epoxy (type: CY233) and hardener (HY956) as a matrix and Kaolin clay with a density of 2.64 g/cm³ as a filler. Kaolin powder was washed thoroughly with water then dried in an oven at 110˚C for 2 h to remove any moisture. Epoxy-kaolin composite with different weight percent (0, 10, 20, 30, 40 %wt.) of kaolin were prepared by hand lay method. Different measurements were taken like Compressive Strengths, Modulus of Elasticity, Tensile Strength and Yield Strength. The result showed that as the concentration of kaolin increase (40%wt) has higher compressive strength than other i.e.,

82.3, 88.67, 105.22, 111.15 and 123.3 MPa for 0, 10, 20, 30, 40 %wt. in case of yield strength and tensile strength the increase in concentration of kaolin showed the reduction of those values.

2.3. Gaps in literature

In general using different filler in organic matrix will result unpredicted physical/mechanical properties. According to different scholars point of view the presence of those filler in a polymer matrix can make corrosive species to travel along path until it reaches to surface of substrate. MK is one of effective filler and if MK used in polymer matrix as a filler it will give good protective coating, but according to most available journals MK clay is used as a replacement of cement (cement concrete for construction material). They mainly investigated the mechanical, chloride penetration and water absorption of concrete which is fabricated by combination of cement and MK, while the effectiveness of MK filler on different properties of kadilux resin had not been discussed. For this work MK was selected as a filler due to its different significant property and availability.

2.4. Statement of the problem

Metals such as steel and rebar are usually exposed to humid and severe environments, and the absorbed water as well as acidity of environment leads the metal to corrode and reduce its performance. The most popular and simplest protection method of steel such corrosive environment is coating which is called duplex coating system, galvanization and organic coating or paint together. One of the most applicable and low volatile organic coating is epoxy resin however, epoxy is high water absorbant which can cause numerous unwanted effects such as swelling, plasticization and in certain cases degradation of substrate as well as coating. These may significantly affect main properties and application of the polymer matrix. The recent and effective way of reduction of those effect was adding of inorganic fillers. The study aims to examine the water absorption and acid resistance of epoxy composite coating containing different amounts of MK microfiller by analyzing the %weight gain and acid resistance tests of composite and neat epoxy.

CHAPTER 3 MATERIALS, METHODS AND CHARACTERIZATION

3.1. Material selection

Epoxy, kadilux epoxy paint which is a two part epoxy resin and prime hardener as curing agents which is manufactured by kadisco paints and adhesive industry, purchased from salah mohammmed building materials and kadisco paint shop, the kaolin clay was received from Jimma science and technology university, MK- clay was prepared by heating the kaolin clay at temperature of 600^0C for 3 hours in high temperature box furnace, Galvanized steel sheet which was manufactured by Adama sheet and steel factory, purchased from building material supplier then cut in to pieces with a dimension of 8x3 cm by using steel cutter as Figure 3.1 b. For making molds liquid silicone rubber was used which is purchased from TSENAT car decoration shop. Thinner also used for cleaning purpose

a)  b) 

Figure 3.1.a) Image of prime hardener (left) and kadilux epoxy prime (right) b) pieces of galvanized steel

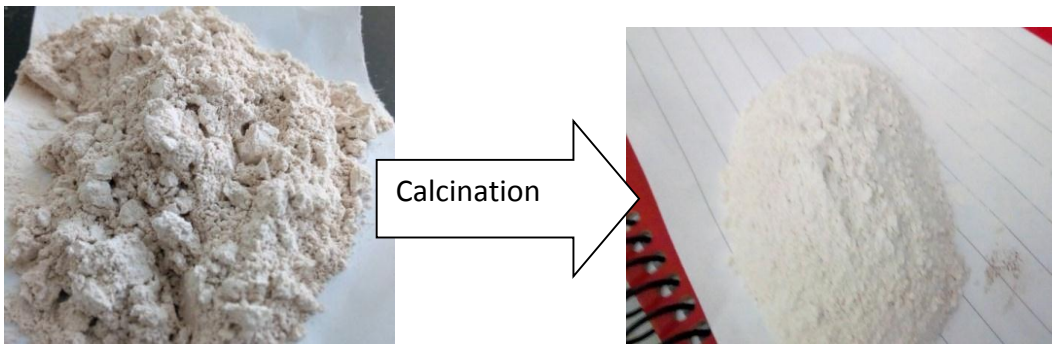


Figure 3.2. Raw kaoline and calcinated kaolin at 600℃ (MK)

Table 3.1. General properties of kadilux resin

Optical property	Transparent
5% weight loss temperature	~130^{0}C
50 % weight loss temperature	200^{0}C
100 % weight loss temperature	453^{0}C
Curing state	Depend on thickness, for full curing 7days
Curing agents	Different curing agents can be used

3.2. Sample preparation and characterization

3.2.1. Sample preparation for reducing impurities of kaolin clay

The received kaolin clay was grinded by RRH-A350 high speed multi-function comminutor with speed of 28000r/min. After grinding the powder was sieved by 45μm sieves to get kaolin clay with a particle size ≤ 45 μm. Two types of treatment were taken for selecting the better purification of clay, the one was water (for removal of impurities) and heat treatment (600℃ for 3 h), by using high temperature furnace, together and the other was only heat treatment for removing moisture present in kaolin clay. In the former case kaolin was first purified by distilled water by dispersed 5g of clay in to 100ml of water followed by magnetic stirring for 1 h then Leave the solution for 2 h for sedimentation of heavy components and impurities like quartz and iron. Purification was followed by decantation of solution by using filter papers and then dried in an oven. After preparation of powder samples X-ray characterization was done.

Kaolin clay powder which prepare by two different treatment showed the kaolin clay with different quartz content and other impurities, and low amount of quartz found in water and heat treated kaolin compared to only heat treated kaolin, since some amount of impurities (include quartz, iron and other) were washed during water treatment as shown in Figure 3.3.

3.2.2. Sample preparation for surface modification of clay

A common problem encountered when incorporating fillers in to composite is poor adhesion of filler to polymer matrix causing low mechanical and other properties. This problem can be overcome by treating the surface of fillers with surface modifiers. In this research TEA

is used as a surface modifier due to its availability. Triethanolamine (TEA) is a viscous organic compound that is both a tertiary amine and a triol. Triethanolamine is a strong base it used as organic additive in the grinding of cement clinker for preventing agglomeration and coating of the powder at the surface of balls and mill wall. For determining the effect of TEA the first step was mixing TEA with different concentration (2.5 g, 3.75 and 5g) and 50ml of distilled water separately. Mixing was done by using magnetic stirrer for 1 h and then dispersed a constant of 5g of MK powder in each water/modifier solution and mix for 90 min. After mixing the solution was distilled and put in to oven for removing residual water and then the powder was characterized by XRD.

Figure 3.3. Iron (impurities) during water treatment of kaolin clay

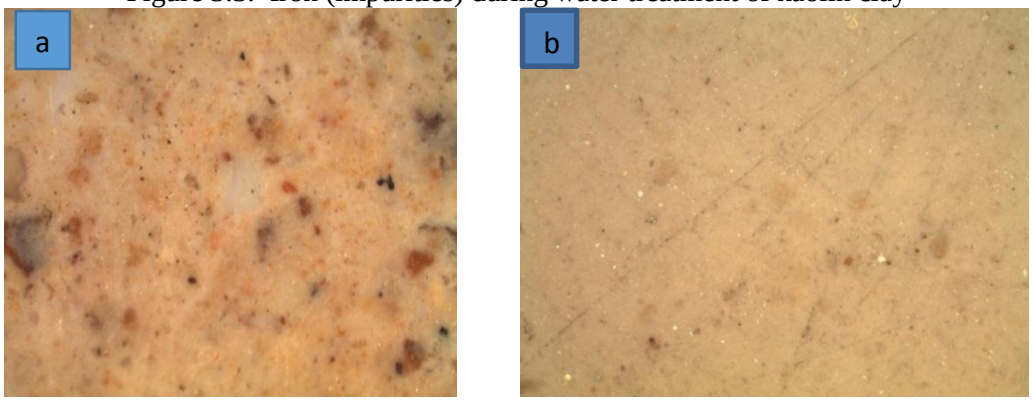


Figure 3.4. Optical image of a) Row kaolin and b) MK clay

3.2.3. The difference in Water absorption between kaolin and metakaolin

Kaolin is a phyllosilicate, consisting of alternate layers of silica and alumina in tetrahedral and octahedral coordination, respectively. This electrically neutral crystalline layer structure, which is a common characteristic of clay minerals, leads to a fine particle size and plate like morphology and allows the particles to move readily over one another, giving rise to physical properties such as softness, soapy feel and easy cleavage. Kaolinite is the mineralogical term for hydrated aluminium disilicate, $Al_2SiO_5(OH)_4$[36]. Under normal environmental conditions, kaolin is quite stable. However, when kaolin heated to

temperature of 600 – 900℃ it loses 14% of its mass in bound hydroxylions. This heat treatment, or calcination, breaks down the structure of kaolin such that the alumina and silica layers become puckered and lose their long-range order. Result of this de hydroxylation and disorder are metakaolin, a highly reactive transition phase, amorphous material with pozzolanic and latent hydraulic reactivity, suitable for use in cementing applications.

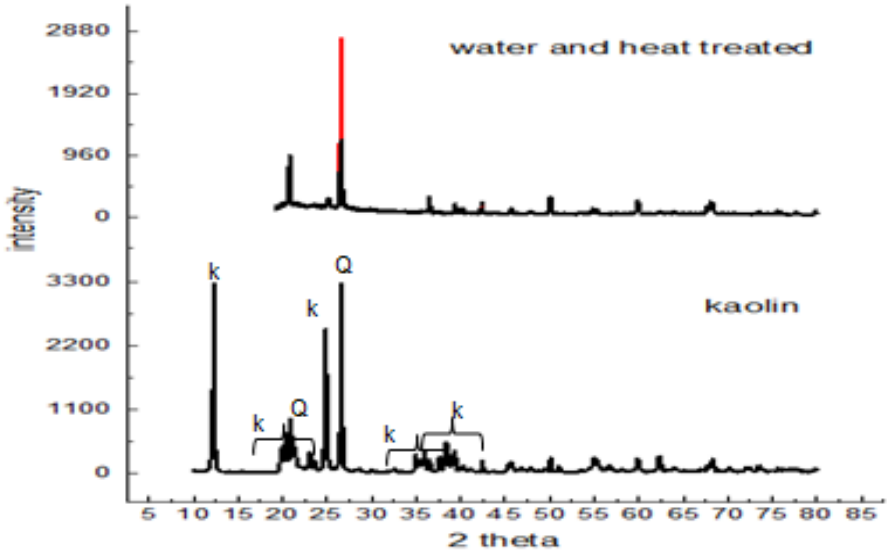


Figure 3.5. XRD analysis of belesa kaolin and metakaolin clay

To determine the water absorption capacity of both clay epoxy/kaolin and epoxy/MK kaolin clay was prepared and immersed in distilled water for 3 days. The conversion of kaolin into metakaolin was carried out by heating the kaolin clay at 600°C for 3 h. Preparation of the epoxy composite started by weighing 50 g of resin and heated at 60 °C for 10min to reduce the viscosity of resin. The water absorption test was carried out based on ASTM D-570. The samples were cut, cleaned and weighed before immersion in distilled water at room temperature. The specimens were removed from the water after some time and the surface was wiped off and weighed immediately. Weight measured was carried out before and after (1, 2, 3, 4, 12, 16, 24, 48 and 72h) immersion and weight gain was calculated according to equation 1.

$$\text{Percent Water Absorption} = \frac{wet\ weight - dry\ weight}{dry\ weight} \times 100 \quad \ldots\ldots\ldots\ldots \text{ equation 1}$$

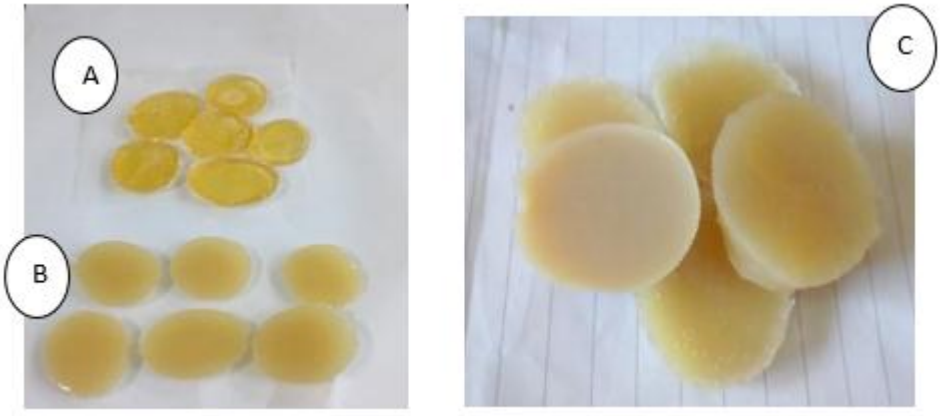


Figure 3.6. Sample prepared for water absorption test A) Neat epoxy B) Epoxy/kaolin and C) Epoxy/MK composite

3.2.4. Sample preparation for studying exfoliation and corrosion property of epoxy/MK composite

Epoxy resin was preheated at 60ºC to lower the viscosity so that it was easier for the added MK clay to disperse and this step was conducted by using magnetic stirrer. 0,1,3,5,7 wt. % filler was added into 50 parts of epoxy resin separately in different container and mixed by magnetic stirrer with speed of 40 x10 rpm for 20min. This speed assisted the clay to break into small particles and helped to increase the clay/epoxy interfaces, then to increase homogeneity of the composite ultrasonication for 10min. The mixture was then added with 25 g of prime resin curing agents (2:1 ratio of resin to hardener based on factory specification data sheet) and mixed for 10min by using magnetic stirrer. The obtained Polymer composite was then poured into a silicon mold, pristine epoxy polymer, without the addition of filler, was also prepared as reference sample. For acid corrosion testing purpose sample was prepared by immersed the galvanized steel sheet in the prepared composite. The immersed steel specimen was prepared according to Yuanwei, L. et al (2017) in which samples were washed with acetone and double distilled water, they were immersed into ethanol solution for 1 hr. for hydrolysis. Finally, sample was dried at 100 °C for 20min. then immerse in to Epoxy/filler composition for 5 sec. All samples were cured at room temperature for 7 days. The epoxy curing procedure was done according to kadisco paint factory specification data sheet. The sample thickness before coating was 0.28mm and after coating the total thickness become 0.46 ± 0.03mm.

Table 3.2. Sample specifications

Symbol	Name
GZ/GS	Bare steel (galvanized steel)
EP0	Epoxy without addition of filler
EP1	Epoxy with addition of 1wt% filler
EP3	Epoxy with addition of 3wt% filler
EP5	Epoxy with addition of 5wt% filler
EP7	Epoxy with addition of 7wt% filler
EP9	Epoxy with addition of 9wt% filler

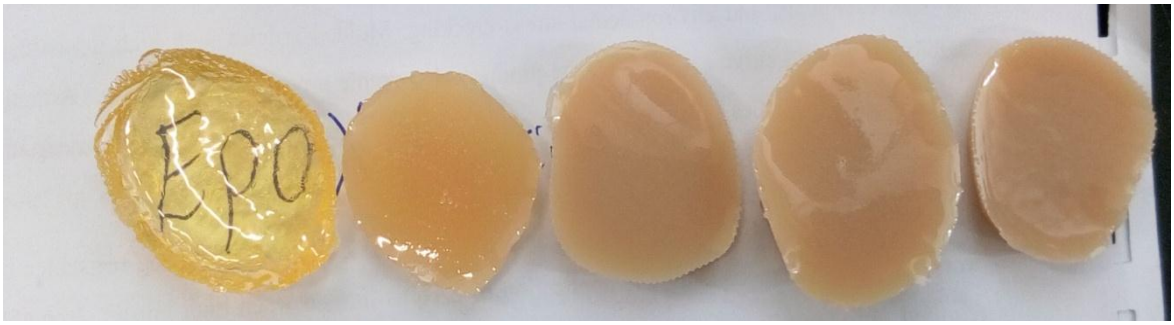


Figure 3.7. The reduction in transparency due to the addition of MK filler

After the addition of kaolin filler transparency is totally reduced as illustrated in Figure 3.7. Optical transparency in polymer composite is limited by the particle size of filler since if the fillers are large enough to scatter the incident light the composite become translucent or opaque depending on the amount of scattered light. According to this research the composite sample was opaque since there was total scattering of incident light due to the presence of microsized MK filler.

CHAPTER 4 RESULTS AND DISCUSSION

4.1. Surface modification of clay by using triethanolamine

To estimate the optimum amount of TEA for grafting of MK, the various percentage of TEA was used and analyzed by XRD technique. Figure 4.1 shows the XRD result of untreated MK and treated MK microsized particle with different gram of TEA (2.5, 3.75 and 5 g). For untreated MK (Figure 4.1a), the interplanar spacing of strongest peaks are 7.133, 4.251, 3.574 and 3.343 Å. It can be seen from Figure.4.1 (b-d), the various peak of TEA modified kaolin particles also shows nearly similar d-spacing values as illustrated in Table 4.1 and Figure 4.1. The insignificance modification of TEA is due to high basic nature of TEA, which is a fairly strong base, and the negative surface charge of kaolin clay. This also confirmed by M. S. NASSER et al. (2009) [93] who worked on kaolin clay surface charge, from their data the faces or surfaces of kaolinite carry a permanent negative charge and depending on the pH, there is positive or negative charge. Under alkaline conditions, the charge is either absent (neutral charge) or negative which implies that instead of grafted it tends to repeal by the surface charge of clay. This TEA modifier can be used for positive surface charge fillers as surfactant or modifier agent.

Table 4.1. Result of TEA on interplaner (d) spacing of kaolin clay

Angle of peak reflection (2θ)	Kaolin as received, d-spacing (Å)	Kaolin modified by 2.5g TEA, d-spacing (Å)	Kaolin modified by 3.75g TEA, d-spacing (Å)	Kaolin modified by 5g TEA, d-spacing (Å)
26.60	3.343	3.344	3.347	3.347
12.36	7.133	7.145	7.155	7.155
24.84	3.574	3.577	3.580	3.580

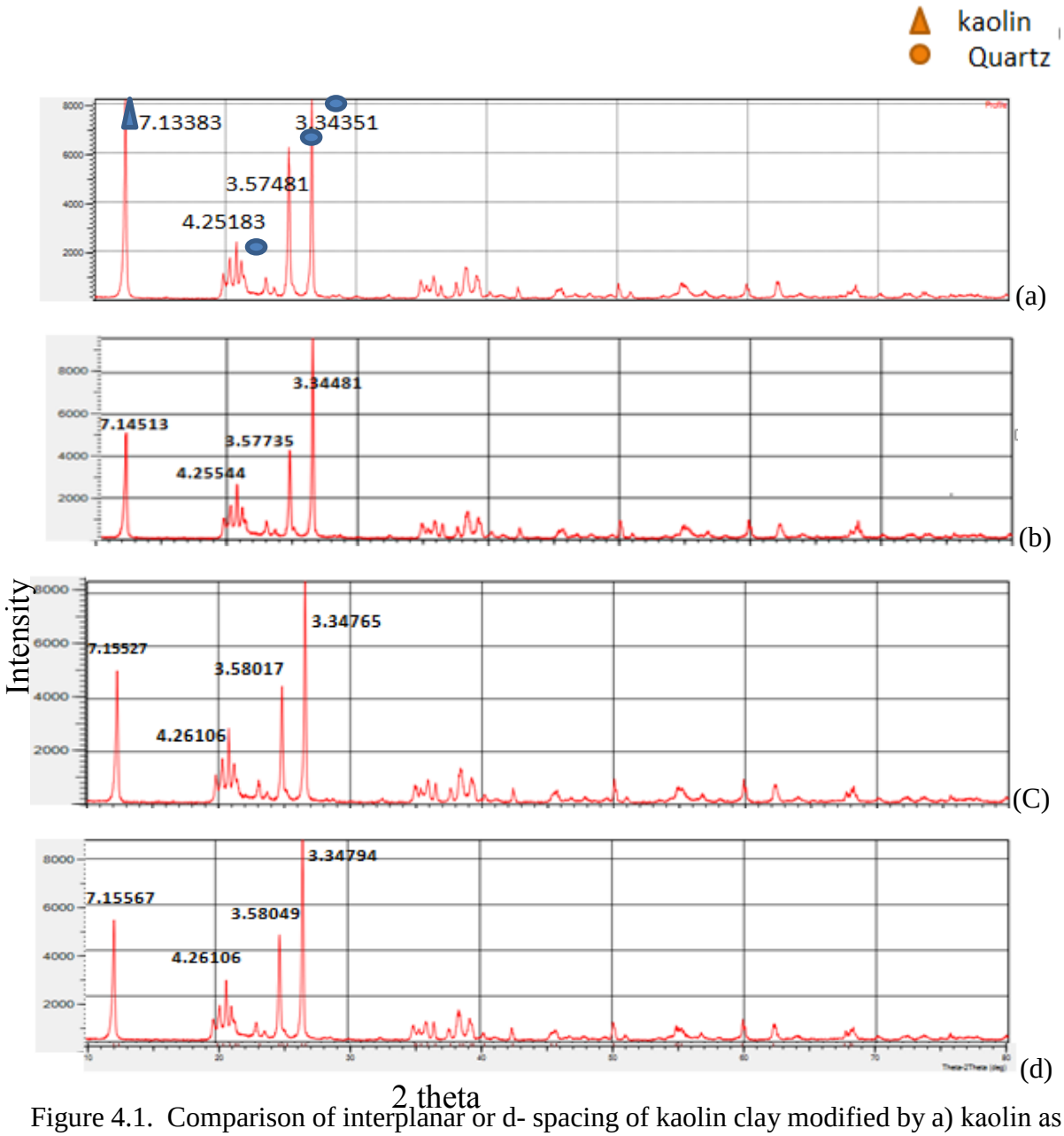


Figure 4.1. Comparison of interplanar or d- spacing of kaolin clay modified by a) kaolin as received, b) 2.5g c) 3.75g and d) for 5g of TEA modifiemr based on XRD analysis.

4.2. The difference in Water absorption between kaolin and metakaolin

The result of water absorption test for different h (1, 2, 3, 4, 16, 24, 48, 72 h) of immersions are given in Figure 4.2. Kaolin and MK shows different water absorption properties in epoxy matrix. Epoxy/MK composite shows lower water absorption property than epoxy/kaolin and neat epoxy samples. This makes MK clay become preferable filler for corrosion protection coatings. The increase of water absorption in kaolin than MK is due to the available

hydroxyl groups which can form hydrogen bonds in the composite, and this lead to the increase in water uptake [94].

Table 4.2. Weight gain of EP0, EP/MK and EP/kaolin after different hours of immersion

Immersion time (h)	1	2	3	4	16	24	48	72
weight gain (Neat/EP) (g)	0.073	0.0921	0.1331	0.1021	0.4444	0.6316	0.7344	1.3665
weight gain (EP/MK) (g)	0.0173	0.0284	0.0450	0.0523	0.1706	0.2439	0.2878	0.2805
Weight gain (EP/kaolin) (g)	0.0373	0.0581	0.1417	0.1630	0.2505	0.2825	1.2852	1.4352

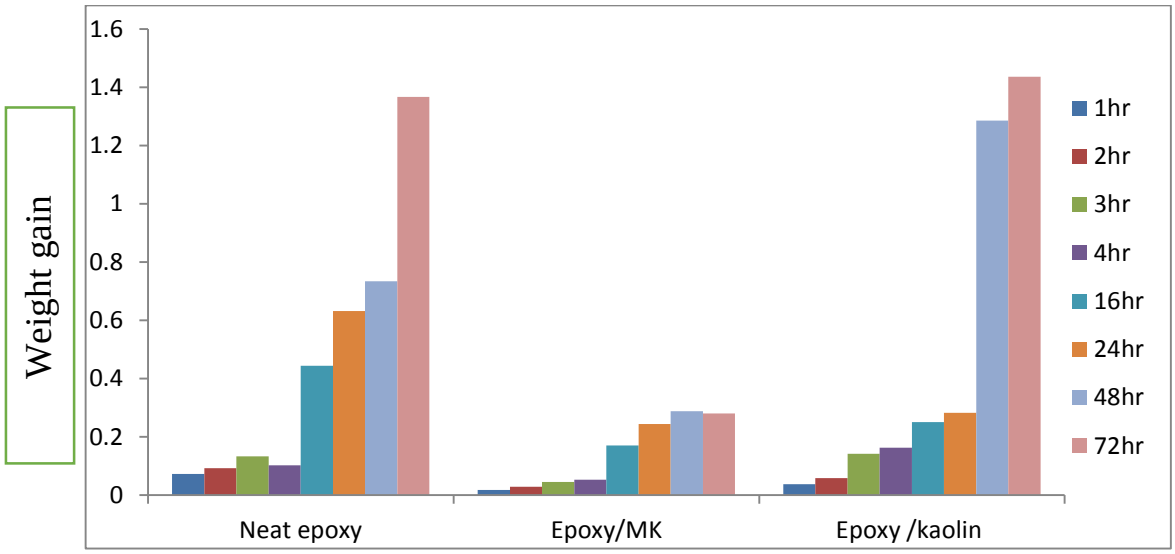


Figure 4.2.Weight gain of neat epoxy, epoxy/MK and epoxy kaolin composite after different days of water immersion

There is general increase in absorption rate with increase in time of immersion in polymer /kaolinite composites [95, 96]. Amit M. et al., 2015 [42] shows the difference in water absorption between calcinated kaolin and row kaolin on their study of physico-mechanical properties of composite materials of low density polyethylene and raw/calcined kaolin. According to their work calcinated kaolin showed low water absorption than kaolin the same situation was observed in this research as illustrated in Figure 4.2 and Table 4.2.

4.3. Optical microscope observation

During polymerization of epoxy, the hardener opens the C—O—C rings, and the bonds are rearranged to join the monomers into a three-dimensional network of crosslinked chain-like molecules this curing (shrinkage) leads to the formation of pore network in epoxy. Hana Ali Alharari Omar (2015) [97] suggest the presence of porosity and free volume on polymer network on her study of water sorption and solubility of resin filled composites. Similar concept also observed on this study. Based on optical microscope study the formation of pore network after curing of kadilux resin was illustrated in Figure 4.3a. The neat epoxy has high porosity than composites and as concentration of MK increase the reduction of pore density also increases as given in Figure 4.3 (b-e). The pore size distribution and the reduction in pore density indicated the marked influence of MK additions when compared with the samples without MK. Even though the pore refinement was not 100%, high pore reduction performance was showed by composite with 7wt% MK**.**

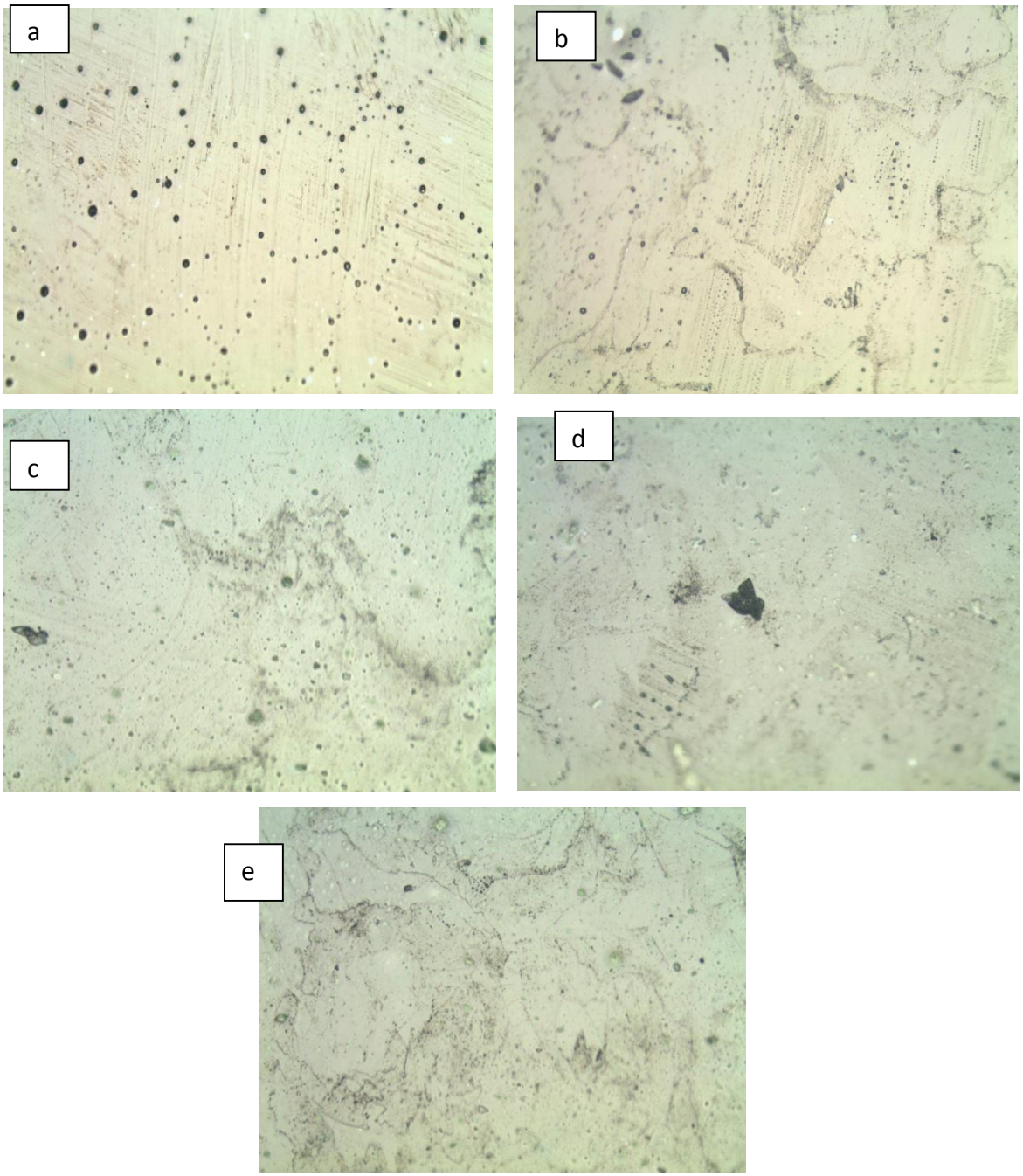


Figure 4.3. Optical image of a) Neat epoxy b) EP1 c) EP3 d) EP5 and e) EP7 composite

4.4. XRD analysis

Depending on the nature of the clay, polymer matrix and level of interaction between them, different type of polymer composite morphology are observed, mainly intercalated and exfoliated composite structure. In intercalated structure matrix polymer resin is inserted into the gallery between the ordered layer of clay resulting in the increase in the interlayer spacing, but still maintaining the order. In case of exfoliated the individual clay disperse in a continuous polymer matrix without forming ordered structure. According to this research peak was appeared around 2θ of about 20^0 as given in Figure 4.4 this also showed by Jan, I. N., 2005 and Malucelli, G., 2007 and based on their point the peak appears at 2θ of about 20^0 for all epoxy composite as well as for the neat epoxy resin is usually associated with the amorphous structure of epoxy resin. But the increase in intensity of the peak was due to the presence of MK fillers.

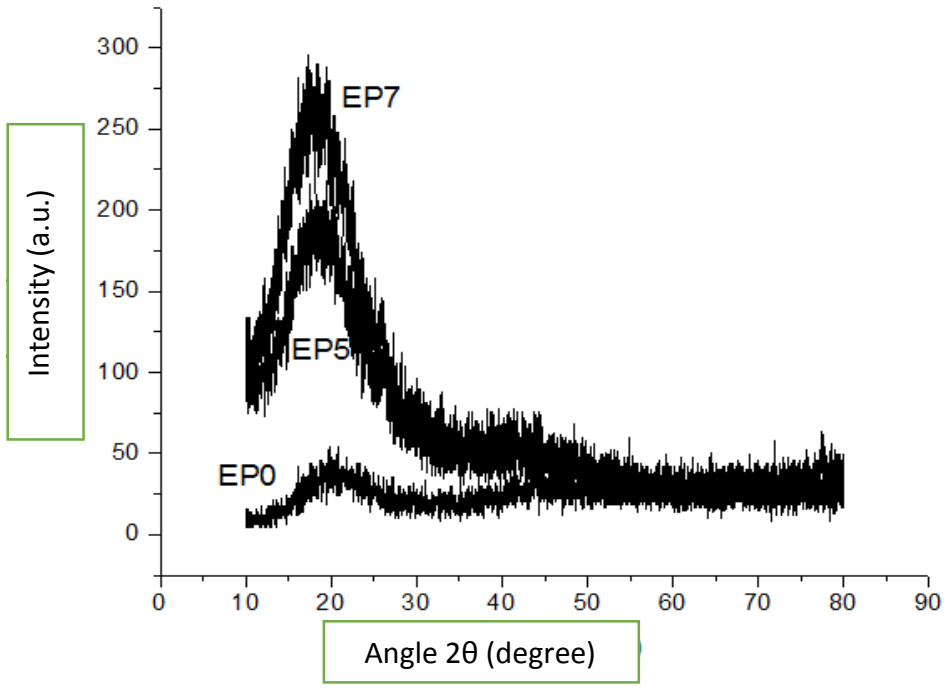


Figure 4.4. XRD analysis of epoxy composite

4.5. Corrosion study

Sulfuric acid is one of the most destructive acids to metal and depending on its concentration and formation manner, can cause severe degradation and damage to metal structures which come into contact with it. Galvanized steel is most commonly used in applications such as building roofing, automotive parts and water pipeline systems owing to its good resistance to corrosion. Corrosion resistance of galvanized sheet is largely dependent on the protection obtained from the zinc coating technique. A galvanized coating provides steel parts with

reliable and long-term protection from corrosion if they are exposed in a suitable environment. Galvanized parts perform best when exposed to climatic influences in locations with low air pollution and where wetting of their surface is only temporary. If the corrosion conditions are unsuitable for hot-dip galvanized coating the service life of the coating may be very short under certain conditions.

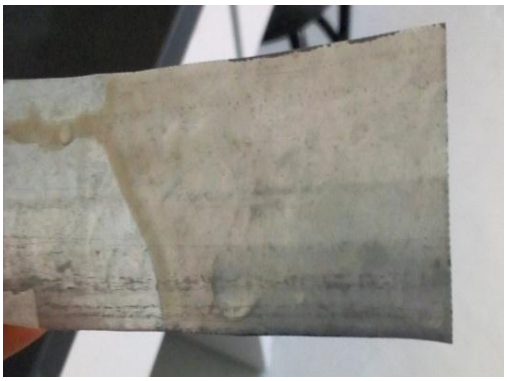
4.5.1. Acid immersion test

Galvanized steel performs best in solutions with a pH in the range of 5.5 to 12, pH between 3 and 5.5 (acidic) or 12 and 13.5 (basic) are corrosive to galvanized steel, but the galvanized coating will still give corrosion protection to bare steel, although the protection will only last for a few years. For determine the effect of sulfuric acid (pH) on corrosion, prepared sample was immersed for 2 and 24 h separately in different container. It should be noted that sulfuric acid migrates from the outside to the interior. Therefore, the outer surface which exposed to the acid must play an important role in neutralizing and preventing the solution from penetrating the inside or substrate.

According to the visual inspection result given in Figure 4.5b the uncoated GZ sample immersed in a 2wt% sulfuric acid solution were loss some of its zinc and the color become black. Figure 4.5e shows the performances of coating against the acidic solution after 24 h immersion. According to visual inspection analysis the specimens which consisted 7wt% MK had better resistance against a highly aggressive sulfuric acid solution than the reference (GZ) and the coated specimens. The rate of this action is dependent on factors such as number of pore and the pore structure of coating, and most importantly the pH and concentration of the sulfuric acid. Acid immersion test also study by calculating weight reduction and thickness reduction of the samples which is given in Table 4.3 and Figure 4.6. From the result of both analysis epoxy with 7wt% MK coating shows lower weight and thickness reduction.

a)

b)

c)

d)

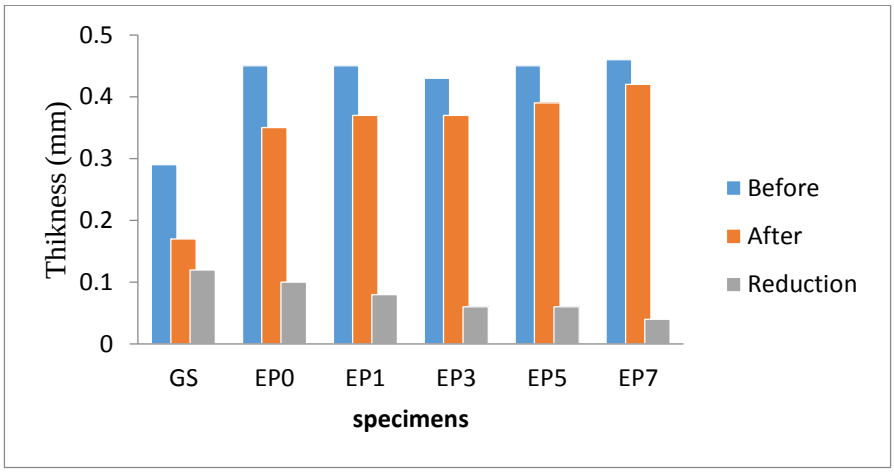

e)

Figure 4.5. The effect of strong acid on galvanized steel a) Before immersion b), c) and d) GZ, EP5 and EP7 after 2 h immersions, respectively e) After 24 h immersions in 2wt% H_2SO_4

Table 4.3. Thickness reduction and weight reduction of samples after 24h immersion H_2SO_4

Sample name	Thickness before immersion (mm)	Thickness after immersion (mm)	Reduction in thickness (mm)	Wight before immersion (g)	Weight after immersion (g)	Reduction in weight (g)
GS	0.29	0.17	0.12	4.2368	3.9838	0.258
EP0	0.45	0.35	0.10	4.2278	4.0358	0.192
EP1	0.45	0.37	0.08	4.2154	4.0364	0.179
EP3	0.43	0.37	0.06	4.1921	4.0391	0.153
EP5	0.45	0.39	0.06	4.1925	4.0445	0.148
EP7	0.46	0.42	0.04	4.2775	4.1695	0.128

a)



b)

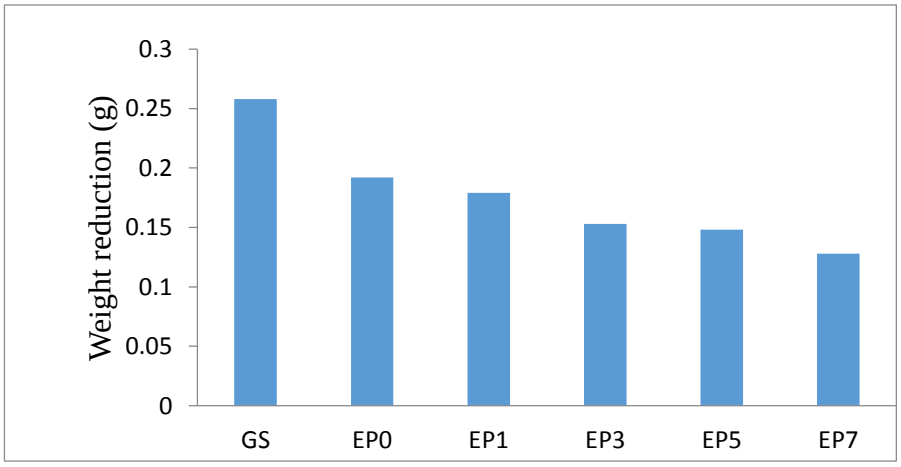


Figure 4.6.a) The reduction in thickness and b) Weight befor and after immertion for 24h in 2wt%of H_2SO_4

From the Figure 4.5e sample EP0 and EP1 shows high blister of the coated and in sample EP3 and EP5 there is high amount of local corrosion under the coated substrate this is due the presence of voids but EP7 shows better acid resistance properties. In general, to enhance the coating performance some suggestions are increasing coating thickness. According to Petr P. (2017) for sufficient lifetime extension, coatings of a uniform thickness of at least 200 - 300μm are recommended. But according to this experiment the coating thickness was average of 125 μm. Increase filler concentration, further refinement of porosity will occur if concentration of MK clay is greater than 7wt%.

To investigate the effect of coating thickness and MK concentration on acid resistance sample were prepared by using 9wt. % MK with an average coating thickness of 160μm and for determined the effect of coating thickness sample were prepared by double and triple dipping of the galvanized steel specimen. For double and triple coated specimen the coating thickness was approximately 262μm and 300 μm respectively. All prepared sample were immersed in 2wt% of H_2SO_4 solution for 24 and 360h002E Sample EP3 and EP7 shows high acid resisttance property inregardless of concntration increaments and the better corrosion resistance showed by EP7 coated substrate. According to acid immertion results increasing coating thickness showes better protection than increasing concentration of MK filler, as given in Figure 4.7 c and Figure 4.8.

a) 

b) 

c) 

Figure 4.7. Corrosion property of coated and uncoated GZ a) before immersion b) after 24h immersions and c) after 360 h immersions

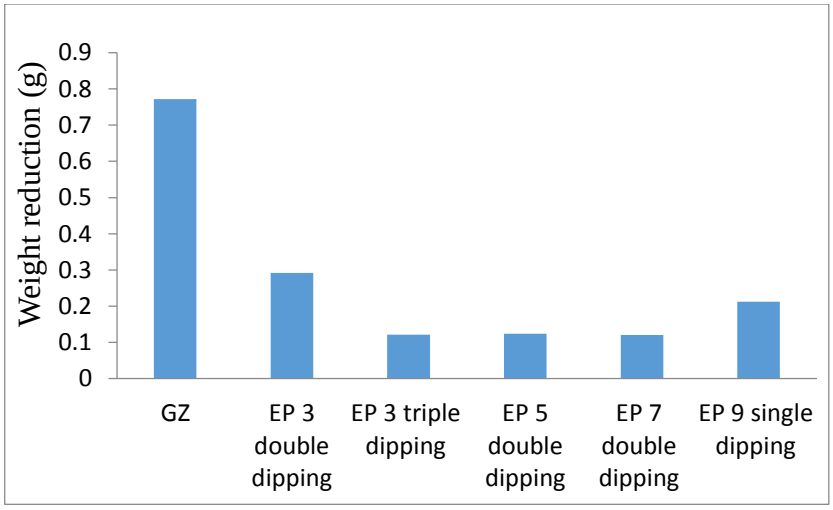


Figure 4.8. Weight loss of coated samples after 360h immersion in 2wt% of H_2SO_4

4.5.2. Water absorption test

It was clearly evident from the results given in Figure 4.9 and Table 4.4 the addition of metakaolin with different replacement ratios were found to eliminate the water absorption of composite when compared with neat epoxy. It was observed that the absorption increases as immersion time increases and maximum water uptake was seen in the neat epoxy than composites specimen. Dana A. Powers (2009) [98] also showed water in an epoxy resin increased with both the time and temperature of resin immersion. Water absorbed into epoxy resin associates with voids and polar centers in the polymer. As water accumulates onto the surfaces of the accessible void structure of the epoxy, water begins to diffuse into the polymer network and results in disruption of polymer network which leads to swell and plasticize the polymer and further opens the polymeric network and makes more water absorption centers accessible which leads to the increase in water absorption. The absorption indirectly represents the porosity, through an understanding of the permeable voids and its inter-connectivity which also shown by an optical microscope characterization was given in Figure 4.3a. The interactions of water along these pores include the disruption of hydrogen bonds among segments of the polymer networks. Polymeric chains will relax and this can create more pore volume accessible for water. In case of composite the presence of MK clay reduces the number of free volume which reduces the amount of water absorbed by the composite. The obtained results indicated that the water absorption was decreasing with increasing percentage replacement of MK. This was because the pore sizes decreased with time either by refining the voids and/or by segmenting the interconnected voids with MK particles. In the present study, it was observed that 7wt% replacement level exhibited the lowest water absorption values than other composite samples since the increase in concentration of MK leads to a reduction of pore spaces and permeable voids which presented in epoxy matrix. Joy M. Justice (2005) [99] said MK concretes had a lower porosity and finer pore structure, which encourages loss of water by self-desiccation rather than by diffusion to the surrounding environment.

Siddique R and Kadri E. (2011) [100] explained in their work that the reduction in water absorption was due to the beneficial effect of the filling effect of MK. According to the result of present work the water absorption decreased as time of immersion increased for high concentration of MK, this result also pointed out by Joy M. Justice (2005) he said there was a reduction in total porosity observed up to 28 days, after which it remained fairly

constant. In general, the water uptake is influenced by: (i) the hydrophilic character of the matrix and the filler (ii) the adhesion between the filler and the matrix, and (iii) the presence of voids in the material. Therefore, the addition of filler had a positive effect on reducing water absorbed by polymer matrix. Hana A. Alharari Omar (2015)[97] Water Sorption would result in elution of unreacted monomers and/or unreacted fillers, which in turn will result in loss of weight this is why negative weight reduction showed in EP 5 and EP7 composite.

Table 4.4. Weight difference and %Weight gain of different epoxy composites

Time (h)		EP0	EP1	EP3	EP5	EP7
1	Weight difference(Wt.)(g)	0.0031	0.0027	0.0021	0.0015	0.004
	%Weight gain (%Wt.)(g)	0.05	0.043	0.033	0.023	0.0063
	% Wt. (percent)	___	86%	66%	46%	12.6%
2	Wt.(g)	0.0041	0.0039	0.0034	0.0017	0.0009
	%Wt.(g)	0.066	0.062	0.053	0.026	0.014
	% Wt.(percent)	___	93.3%	80.3%	39.3%	21.2%
3	Wt.(g)	0.0077	0.0053	0.0041	0.0020	0.0010
	%Wt.(g)	0.125	0.085	0.064	0.031	0.015
	% Wt. (percent)	___	68%	51.5%	24.8%	12%
24	Wt.(g)	0.0134	0.0096	0.0059	0.0033	0.0006
	%Wt.(g)	0.218	0.154	0.093	0.052	0.0095
	% Wt. (percent)	___	70.04%	42.66%	23.8%	4.31%
48	Wt.(g)	0.0155	0.0099	0.0073	0.0030	0.0002
	%Wt.(g)	0.252	0.159	0.115	0.047	0.0031
	% Wt. (percent)	___	63.09%	45.63%	18.65%	1.25%
72	Wt.(g)	0.0166	0.0102	0.0085	0.0027	(-)0.0006
	%Wt.(g)	0.2609	0.163	0.132	0.0428	(-)0.0095
	% Wt. (percent)	___	62.47%	50.59%	16.4%	-3.64%
96	Wt.(g)	0.0169	0.0109	0.0092	0.0015	(-)0.0014
	%Wt.(g)	0.275	0.175	0.1477	0.023	(-)0.0222
	% Wt. (percent)	___	63.6%	53.7%	8.36%	-8.07%

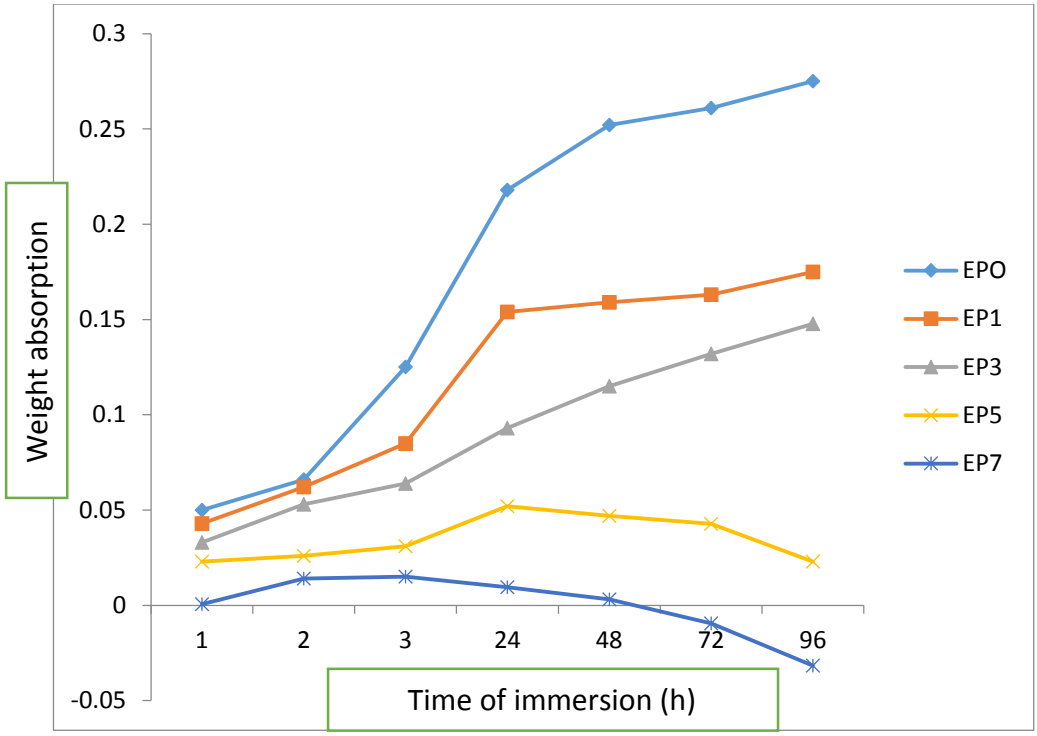


Figure 4.9. %weight gain of epoxy and epoxy composite after 96h immersion in distilled water

4.5.3. Thermogravimetric analysis

Thermogravimetric analysis was conducted on an instrument referred to as a thermogravimetric analyzer. A thermogravimetric analyzer continuously measures mass while the temperature of a sample is changed over time. Advantages of the method are high sensitivity for detection of low decomposition rates, speed of the temperature adjustment, simplicity of the apparatus, and small sample requirement. The experiment consisted in registering the weight loss of the sample as a function of temperature. Thermogravimetric analysis results are given in Figure 4.10 below. An improvement in the initial decomposition temperature of the nanocomposites was showed after introducing MK. Adding of 5wt% MK gave considerable retardation in the thermal properties of epoxy. The onset decomposition temperature, T_{onset}, and the maximum weight loss temperature, T_{peak}, are higher in the nanocomposites than reference sample (neat epoxy). There by revealing the presence of MK make a stable cross-linking network by hindering segmental motion of the polymers. This property attribute to the enhancement of thermal stability of kadilux resin this also confirmed by M. Dehghan et al (2014)[101] suggested that the enhancement in thermal stability of polymer filler composite is due to the formation of stronger interaction between the filler and matrix molecules which led to a highly rigid network. O. Meziane et al (2016) [102] also proved that the presence of clay can enhance thermal stability of polymer matrix.

The T_{peak} of EP7 was lower than EP0 as illustrated Table 4.5 this is due to the presence of agglomeration in EP7 than the others. The agglomeration of fillers negatively affected the thermal properties of composite [103]. This phenomenon usually occurs when there is a large increase in the filler percentage. From the data given in Table 4.5 and Figure 4.10 EP5 gave better thermal properties than EP0 and EP7.

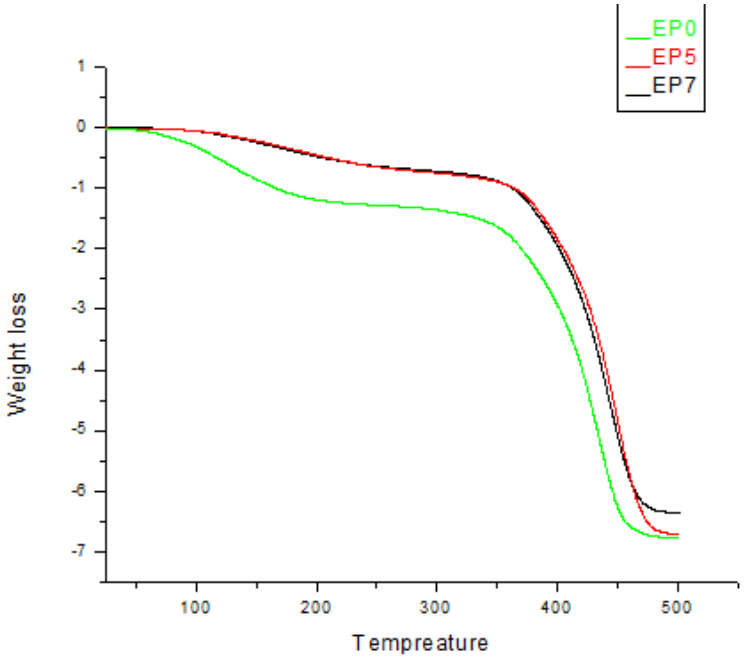


Figure 4.10. TGA analysis of EP0, EP5 and EP7

Table 4.5. TGA analysis of neat epoxy and composite samples

Sample name	5% weight loss	Maximum loss
EP0	130℃	453℃
EP5	190℃	455℃
EP7	165℃	448℃

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

In this study, epoxy was reinforced with MK (with different concentration) in order to observe the effect of those MK reinforcements on the pore refinement and corrosion property (the water absorption and acid resistance property) of the composite. From the result obtained an improvement of thermal property, acid resistance and reduction of water absorption and also reduction of pore density were observed after the addition of MK. The better acid resistance, lower water absorption and pore density were obtained by using 7wt% of MK. According to TGA analysis EP/5wt% MK have high thermal stability. The effects of coating thickness and filler concentration on corrosion performance of coating were investigated. Increasing coating thickness could help for reduction of corrosion rate.

The author recommended that for further enhancement of corrosion protection property with kadilux resin:

- Using nanosized particle instead of microsized filler
- Apply temperature during crosslinking of epoxy
- Using silane coupling agents for surface modification of filler to have better polymer –filler interaction

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