
إهداء إلى.................

أهدي نتاجي هذا إلى وطني العزيز، وطن الأحرار والصمود، وطني

يا جمالاً" يكتب الشعر فيه، و يا جنة يطيب بها العيش ويغنيه. إلى

الفؤاد النابض بالحنان، إلى هبة الرحمـــن أمي، التي سهرت

الليالي لراحتي. إلى أعظم رجل وقف بجانبي، إلى أبي الذي تحمل

مشاق السفر والتنقل معي. إلى المعطاء أستاذي الفاضل شادي

صوالحة الذي أمدني بالمعلومات والارشادات البناءة. إلى كل من

الأستاذ يوسف رطروط و الأستاذ عميد عميرة والأستاذ سمير على

جهودهم البناءة لإنجاح هذا العمل. وإلى زملائي فكري طوباسي

ومحمد كلبونة و رشيد رشيد أشكرهم كل الشكر على مساعدتهم لي.

إلى أختي وصديقتي ربا طعمة التي وضعت اللمسة الأخيرة بكتابتها

الإهداء. وإلى كل من ساعدني وساهم في إنجاز هذا العمل وبذل

جهداً" لإتمامه بكفاءة ونجاح شكراً" جزيلاً" لكم.

Abstract:-

Marble glue is an adhesive compound used to join parts of marble, granite and other stones in addition to fill holes and cavities that might exist.

The objective of this project is to produce local marble glue according to local and international specifications and with competitive cost. This aim was blossomed from the non-existence of a local product to improve the Palestinian economy.

The First step was started with execution a lot of trials to produce the local marble glue, followed by doing tests to determine the suitable sample. A layout for the plant was done; finally the cost of the plant was analyzed.

The optimum sample which gives the best performance was composed from (38.835 % Polyester, 24.272% Pure $CaCO_3$, 24.272% Cutting stone, and 12.6213% Talc); with 9.3015 (Mpa) average stress. The selling price of one kilogram of local marble glue is 19.998 NIS. The payback period of the project is 4 years with 12 years as project life.

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Introduction:-

The history of adhesives tells that adhesives have been used since the 4000 B.C [1] the time of Egyptians and Assyrians. The Egyptians used adhesives to bond papyrus, and pieces of veneered furniture have been found in the tombs of some of the pharaohs, these adhesives were from animal origin [2]. In the year 200 B.C, simple procedures for making and using animal glue were developed and a concern about glue and glue art began [1]. The Assyrian were bonded the brick together with a cementations mortar based on clay. Later, near the Euphrates River Assyrians discovered bitumen springs and used this pitch as a cementing material. The next period of activity is from 1-500 A.D. when the Romans and Greeks developed the art of veneering and marquetry, which is the bonding of thin sections or layers of wood [1], then the Greeks were built structure of limestone that was veneered with a fine grained marble. The Chinese used mortars in there structural work, and animal glues in there decorative building work [2]. The first glue patent was issued in Britain for fish glue in about 1750. Patents were then rapidly issued for adhesives using natural rubber, animal bones, fish, starch, and milk protein (casein). By 1900, the United States had a number of factories producing glue from these bases [1]. After that, an explosion has taken place in the number and types of materials available for adhesive bonding, epoxies, polyester; the list seems almost endless. Most of the technology of adhesives has been developed during the last 100 years [2].

In order to meet the high criteria of manufacturing process which lead to high performance and low cost the industry of adhesives had been developed to reach the product which is available for many applications nowadays. Firstly, structural engineering applications are these days considered a very important field in using adhesives, structural adhesives have the ability to reduce weight, improve fatigue performance together with reduce production and cycle cost[3]. Adhesives can be used in construction and it started with finishing trades, flooring materials, wallpaper, and roofing cements and then developed to wall covering like tiles, paneling, and after that ceiling panels [2]. Adhesives also used in wood for composite panel like fiberboard based on petrochemicals [4]. For electrical field isotropic conductive adhesive (ICA) is recently achieved a lot of attention as potential substitute to led bearing solders [5].

This project aims to study the production of marble glue from different available imported raw materials and abundant materials which available in Palestinian market, and because of the non-existence of similar industry. Besides the production of glue from its raw materials with different formulas will be prepared and characterized to select the optimum recipe of marble glue, with acceptable cost compared with imported ones.

Chapter One

Adhesives

1.1 Definition:-

Adhesive or glue is a substance used to bond two or more solids so that they act or can be used as a single piece; the raw materials for adhesives are mainly polymeric materials, either naturally or synthetic occurring. An adhesive must wet the surfaces, adhere to the surfaces, develop strength after it has been applied, and remain stable. For examples are resins, glue, paste, cement [6, 7].

1.2 The nature of adhesion:-

Most experts agree that the strength of an adhesive joint is determined by a mechanical and chemical interaction between the adhesive and adherent [8], these two factors are response of the force holding two materials together [2].

A mechanical interaction is the bonding force provided by interlocking action, this force appears in bonding porous materials like limestone and most marbles as a prime factor. The surface of most materials especially stone consists of a microscopic peaks and valleys. If the adhesive is able to penetrate the open spaces of the substrate and displace the air that is present, known as wetting, a mechanical bond is formed. Mechanical adhesion is most effective under shear-type loading and contributes little to the tensile strength of a joint [2,8].

A chemical interaction (namely specific adhesion) is the molecular attraction between two materials, so it becomes much more important than the mechanical interaction in joining extremely dense or non-porous materials like granite. The chemical interactions that dominate when bonding natural stone are based upon the adsorption theory and can be attributed to Van der Waals bonds. Van der Waals bonds are secondary bonds (ionic, covalent, and metallic bond being considered primary bonds) that cause otherwise neutral molecules to be attracted to one another. Chemical adhesion is effective under tensile, shear, and peel-type loadings [2,8].

For a material to perform as an adhesive it must have four main requirements:-

- Wet the surfaces: - the roughened surface is more difficult to wet with the adhesive, and this may result in discontinuous in the adhesive film, so the surface must be smooth but not polished. And the surface of the substrate must be clean, because the water, oils, dust, and dirt make wetting of the stone by the adhesive much more difficult and therefore greatly reduce the ability of the adhesive to mechanically and chemically bond to the stone [2,7,8].
- Adhere to the surfaces: - after the adhesive material flowing over the whole surface area, it must be adhere and stay in position and become tacky.
- Develop strength: - the adhesive material must change its structure to become strong.
- Remain stable: - the adhesive material must remain unaffected by environmental conditions and age [7].

1.3 Adhesion theory:-

Adhesion is a specific interfacial phenomenon, so there are a number of theories on how adhesives work in order to know the mechanism of bonding because this has related to the surface preparation of the adherent surface, and the materials being attached [7, 9].

1.3.1 Adsorption theory:-

Adsorption theory is based on the assumption that the adhesive 'wets' the surfaces of the adherent surface and adhesive molecules are attracted to specific sites on the adherent [9,10].
In this theory the attractive force between materials is interpreted in terms of the chemisorbed and physisorbed atomic and molecular species that are exist at an interface. According to this theory, the adhesive strength arise as a result of a secondary intermolecular forces at the interface include Vander Waals forces [7, 10].
Essentially this theory regards adhesion as one particular property of phase interface where polar molecules or grouping will be oriented in an ordered way [7].
This theory has resulted lower surface tension than the adherent surface which the adhesive

materials being developed. Example supporting this theory is Epoxy which wet the steel and results in a good bond [9].

1.3.2 Electrical theory:-

Electrostatic forces occur between charged atoms or molecules, so this theory explains adhesive attraction force in terms of electrostatic effect at an interface [7, 10].

This theory is based on the electrical double layer where developed at the bond interface as a result of the interaction of the adhesive and adherent which referred to the bond strength, whereas at any boundary an electrical double layer is formed to produce attraction for the adhesion and resistance to separation [7, 9].

Electrostatic adhesion is used in coating industry where polymer particle are negatively charged, whereas the piece to be coated in positively charged. Therefore adhesion strength improved with lowering of temperature [9, 10].

1.3.3 Diffusion theory:-

Diffusion theory based on the solubility of one material into another, so it is attributed to intermolecular entanglements at the interface [7, 10].

This theory applies to the union of high polymers for cases of self-adhesion or auto-adhesion where a movement and entanglement of long molecules of polymer can occur, but it doesn’t fit well in providing an explanation for polymer-polymer adhesion. Therefor high molecular of thermoplastic polymer often has high melt viscosity and will not diffuse within the time rang of bonding operation [7, 9].

The fundamental concept of diffusion theory is that adhesive can diffuse into adherent surface with an interchange of molecules, based on the nature of chain that is flexibility and the ability of chain to movement on a sub-molecular scale [7, 9].

This theory used cohesive energy density to interpret diffusion bonding. A major difference in this theory is that it implies a three dimensional volume process rather than a two dimensional surface process [7, 10].

The effect of this theory in contact time is appeared in plastics, where influence time and temperature on bonding rate and influence of polymer molecular weight and polymer structure [9]

1.4 Adhesive Types:-

1.4.1 Adhesives types based on raw materials:-

Adhesives can be classified according to the principle of raw materials they are made from as shown in figure (1), and more details about each type are mentioned below:-

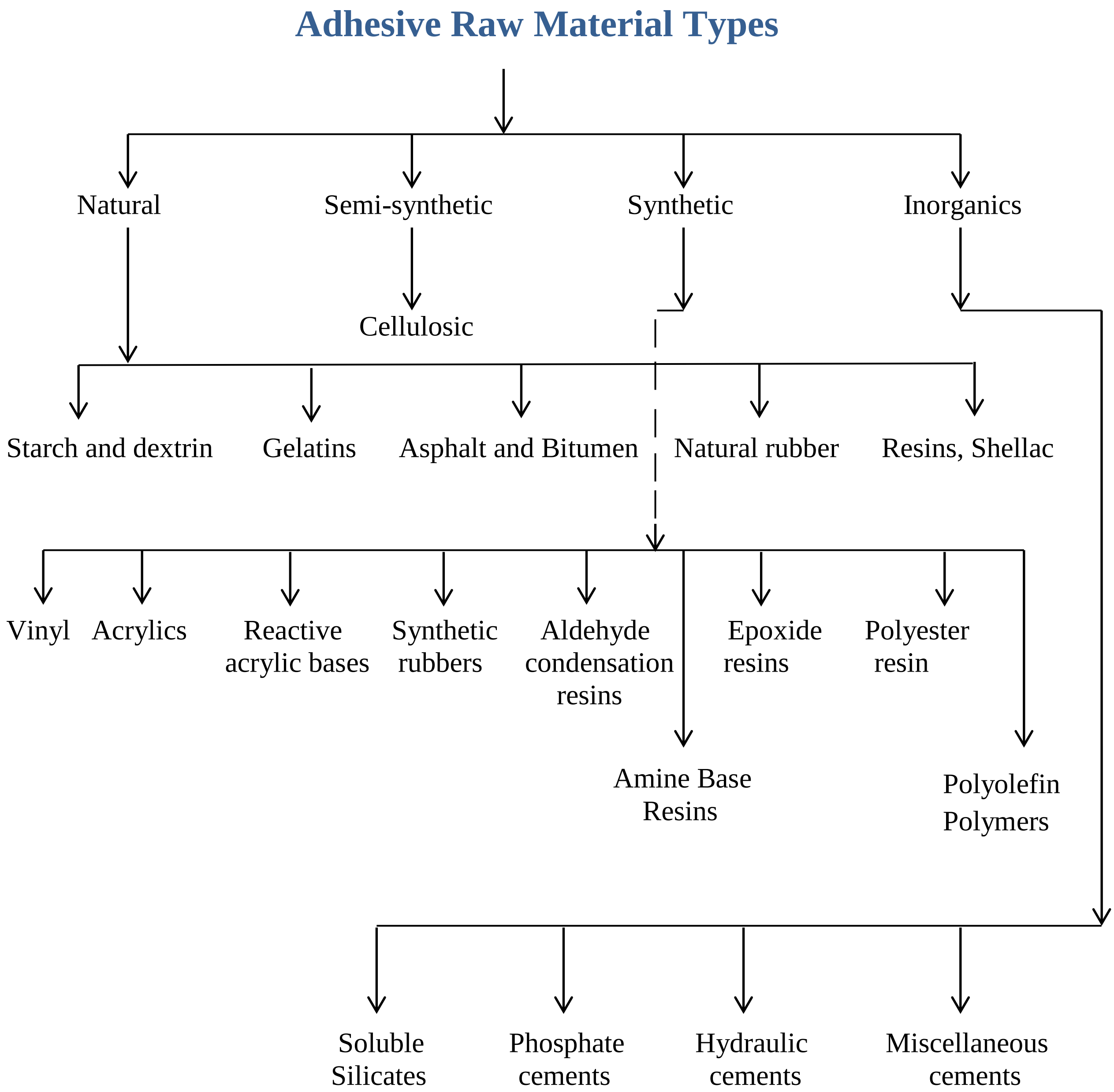

Figure 1: Adhesive Raw material Types.

Natural:-

Starch and dextrin:-

They are made from corn, wheat, tapioca, potatoes and other starch product. The basic constituent is polysaccharide. They are used in paper industry, corrugated board, and multiwall bags. They are also used for textile to improve their resistance to abrasion during the weaving process [2, 7].

Gelatins (animal, fish, vegetable glues):-

- Animal glues are made from bones and hides that supply the collagen that is the base component in the glue. They are used in gummed tape, textiles, and coated abrasive.
- Fish glues are manufactured from skins that also supply collagen. The glues are used in adhesive for glass, metal, wood, paper, and ceramic.
- Cassein glues are made from skim milk. These glues are used in wood to wood bonds, composite wood beams, and in paper bonding.
- Soybean glues are derived from soybean, and they are used in paper backs.
- Blood glues are made from dried blood of hog and beef, they are mainly used in veneering and plywood [2, 7].

Asphalt and Bitumen: -

These high fractions of crude oil, and they are more used as sealers rather than adhesives except in the bonding of coarse grade papers to produce waterproof building papers [7].

Natural rubber: -

Rubber is derived as latex from the rubber tree, this latex allowed to dry to form the self-adhesive envelop and other touch-adhesive applications. They are used in pressure sensitive applications or where long bond times and tack are required such as tapes, ceramic tile adhesives, flooring adhesives [2, 7].

Resins, Shellac:-

They are natural resins have been used as adhesives. Shellac is used in bonding mica splitting's to form mica board and used to be used in abrasives [2, 7].

Semi-synthetic:-

Cellulosic:-

They are derived from cotton fibers and wood pulp. They have many organic derivatives such as:-

- Cellulose nitrate: - is used in small area but mostly used for wood, metal, paper, lather, and glass.
- Cellulose acetate butyrate: - is used in paper to paper and plastic adhesives.
- Methyl cellulose: -is used in leather paste to prevent shrinkage as drying, wallpaper pastes, paper making, and textiles.
- Ethyl cellulose: - is used in low temperature adhesives [2, 7].

Synthetic:-

Vinyl:-

They are produced either as emulsion or as solvent soluble type such as:-

- Polyvinyl acetate and polyvinyl alcohol: - they are used to make 'white glue' for home use. paper converting, book binding, wood, leather binding, tile cement and textiles.
- Polyvinyl acetal: - is used to make safety glass, metal foil, and plastic film.
- Polyvinyl chloride: - is used to make pipe adhesives.
- Polyvinyl ether: - is used in pressure sensitive tapes [2, 7].

Acrylics:-

Structurally similar to the vinyl's but have very different properties. They are used as pressure sensitive adhesive. Also they are used as binders for making paper coating, paints; pigment finishes for leather, flocking adhesives, wall paper, and ceramic tiles [2, 7].

Reactive acrylic bases:-

These types of adhesives are different from the standard acrylics, because the final polymer from it is mixture from acrylic monomer with a synthetic rubber. The advantages of these adhesives are very fast bond time, and their ability to bond a wide variety of substance.

They are used for metal to metal and metal to plastic bond, also used in thread locking applications which is called anaerobic adhesive.

Other type from these adhesives is cyanoacrylate glue, which is used to stick any two surfaces together [2, 7].

Synthetic rubbers:-

Natural rubber is polyisoprene and has good tack properties but normally not very high strength; so it is needed to add various resins and other compounding ingredients to give specific properties. These include:-

- Styrene-butadiene: - are used for pressure sensitive tapes, tile adhesives, and floor adhesives.
- Polyisobutylene: - are used for electrical tapes, and sealing tapes.
- Polyurethane: - often cross linked with an isocyanate, they are used in many applications where outstanding performance is required such as; automobile, shoes, magnetic tapes, and garments.
- Polysulfide: - mainly as sealants but also used with epoxy resins for concrete adhesives.
- Silicone adhesives: - are used for ceramics, glass, fabrics, wood, leather, metal, paper and plastics [2, 7].

Aldehyde condensation resins:-

These resins are condensation polymers of aldehydes with amino compounds and phenolic forming methyl derivatives including:-

- Phenolic: - is used for abrasive discs, foundry industry, fiber bonding, and plywood.
- Urea: - is used in particleboard, and plywood
- Melamine: - is used in particle board.
- Resorcinol: - is used in making water resistance adhesives, and widely employed to make exterior-grade plywood [2, 7].

Epoxide Resins:-

- Epoxy: - This is the main group and is characterized by having the epoxide group ideally at each end of the molecule. The adhesive is used in bonding metal, glass, ceramics, and widely used for concrete and masonry repair on highways and bridge.

- Phenoxy: - This is high molecular polyether, and differs from epoxy resins in that they are deficient in epoxide groups. They are used in ceramic and metal bonding [2,7].

Amine Base Resins:-

There are many amine derived polymers that show good adhesive properties.

- Polyamide: - these resins similar to nylon, and are used as the thermoplastic adhesives in shoe and electronic industries. Also are used in hot-melt and thermosetting applications for aircraft, automobile, woodworking, and in product assembly.
- Polyimide: - is used for aluminum to aluminum adhesive at elevated temperatures.
- Polybenzimidazol: - is used for stainless steel bonding.
- Polyquinoxaline: - Also is used for stainless steel bonding at high temperatures.
- Polyethylenimine: - is a highly branched polyamine, and used for priming cellophane aluminum foil [2, 7].

Polyester resin:-

The polyester resins are produced by the reaction between terephethalic acid and ethylene glycol to form the ester group which is the repeating unit to form the polyester. The most important properties of the unsaturated polyester are ease of handling, rapid curing with no volatiles evolved, light color, dimensional stability, and good physical and electrical properties [12].

Polyolefin Polymers:-

Olefins can be used in adhesives especially as the base for thermoplastic types. Some examples about olefin are:-

- Polyethylene & Polypropylene: - is used as the base for hot melt adhesives in packaging.
- Ethylene-vinyl acetate: - is used in hot melt adhesives for packaging, labeling, and bookbinding.
- Ethylene-ethyl acrylate: - Has better adhesion to polyolefin.
- Ionomers: - These polymers contain carboxyl groups on the polyethylene chain, and they are used for bonding polyolefin [7].

Inorganics:-

Soluble silicates:-

They are manufactured by melting silica sand with sodium carbonate and then dissolving in water, and they are used as adhesives for metal, wood, paper wallboard, and fiber drums. Some examples about these types are:-

- Silicate cements are used for mortar.
- Lime mortars are used for plaster and setting tiles.
- Calcium silicates are used to make the various cements such as plaster cement and lime cement when combination with other silicates [2, 7].

Phosphate cements:-

They are used as dental cements [7].

Hydraulic cements:-

These adhesives included calcium silicate, lime cements and others. They are used for bonding stone chips as concrete [7].

Miscellaneous cements:-

Glycerin, liquid sulfur, and nitrides are examples about these types of adhesives and used in special aspects [7].

1.4.2 Adhesives types based on their bonding the natural stone:-

a- Polyesters.

b- Acrylics

c- Epoxies [8].

1.4.3 Adhesives types based on their formation:-

Adhesives can be classified into three main types:-

a- Chemical reactive types.

b- Thermoplastic type.

c- Evaporation or diffusion types.

a- Chemical reactive types:-

Adhesives of this type can be supplied in a low molecular weight form and after a polymerization reaction is allowed to take place. This polymerization can be achieved by:-

Two component pack:-

This type can be Supplied as a two component; base plus hardener such as:-

- Epoxy adhesives.
- Unsaturated polyesters.

Moisture:-

Polymerization by moisture can be achieved either on the surface of the adherent or in the atmosphere to affect a cross-linking mechanism, this type is supplied as a single component. For example; Silicones containing an acetyl group.

Heat:-

This type is by using heat to polymerize the adhesive components. For example; Urethanes [7].

b- Thermoplastic type:-

Basically the adhesives in this type are thermoplastic in nature, such as:-

- Phenoxies
- Polyamides
- Polyesters (saturated).

c- Evaporation or diffusion types:-

The polymer for adhesive in this type is in its final form, wetting of the adherent is achieved by dissolving or dispersing the polymers in a suitable solvent:-

- **Solvent Based Systems:-**

For examples: - Vinyl resins such as polyvinyl acetate, polyvinyl chloride, acrylic resins and rubber adhesives.

- **Water Based Systems:-**

For examples: - Acrylic resins, rubber lattices, and vinyl resins.

Chapter Two

Main constituents of Marble Glue.

Marble glue consists of risen and fillers in addition to some kind of additives to improve many properties of marble glue. More details about these materials were explained below.

2.1 Polyester:-

Polyester resins are used to produce bonding pastes which are viscous, filled compounds designed for the assembly and bonding mouldings. They are used in mainly non-structural or semi-structural applications such as internal frames, ribs, hull to deck assemblies and car components, to give moderately high shear strengths without the need for mechanical fixings [11].

A typical polyester system consists of polyester resin and styrene. The ingredients of an unsaturated polyester resin are [Phthalic anhydride, Malic anhydride, Propylene glycol, Ethylene glycol, Styrene, and Hydroquinone].

The polyester resins are produced by the reaction between terephethalic acid and ethylene glycol to form the ester group which is the repeating unit to form the polyester as shown in figure (2).

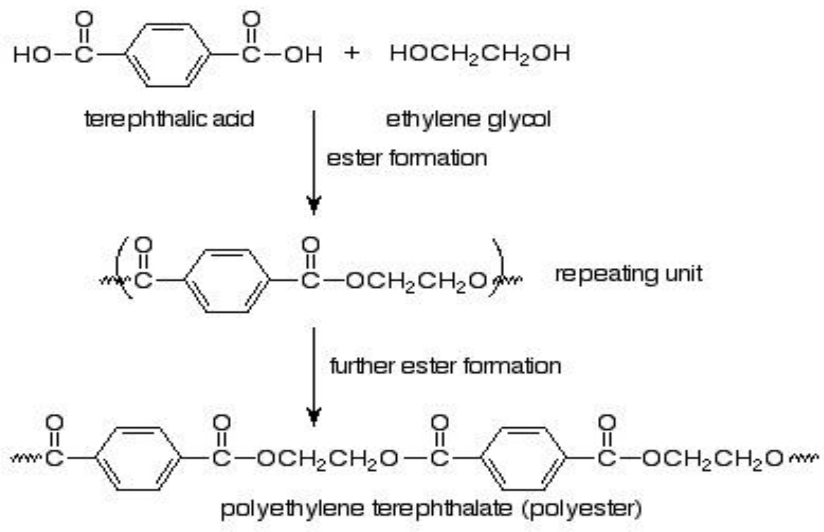

Figure 2: Mechanism of preparation of Polyester.

The unsaturation in the polyester is by inclusion of maleic anhydride or fumaric acid as one component, also a saturated acid or anhydride is often used such as phthalic acid, and these are the dibasic acids as shown in figure (3). A higher proportion of unsaturated acid gives amore reactive resin with improves stiffness at high temperature, and will increase the density of the cross linking but the use of saturation acid as phthalic acid will decrease the density of cross linking and increase the flexural strength [12].

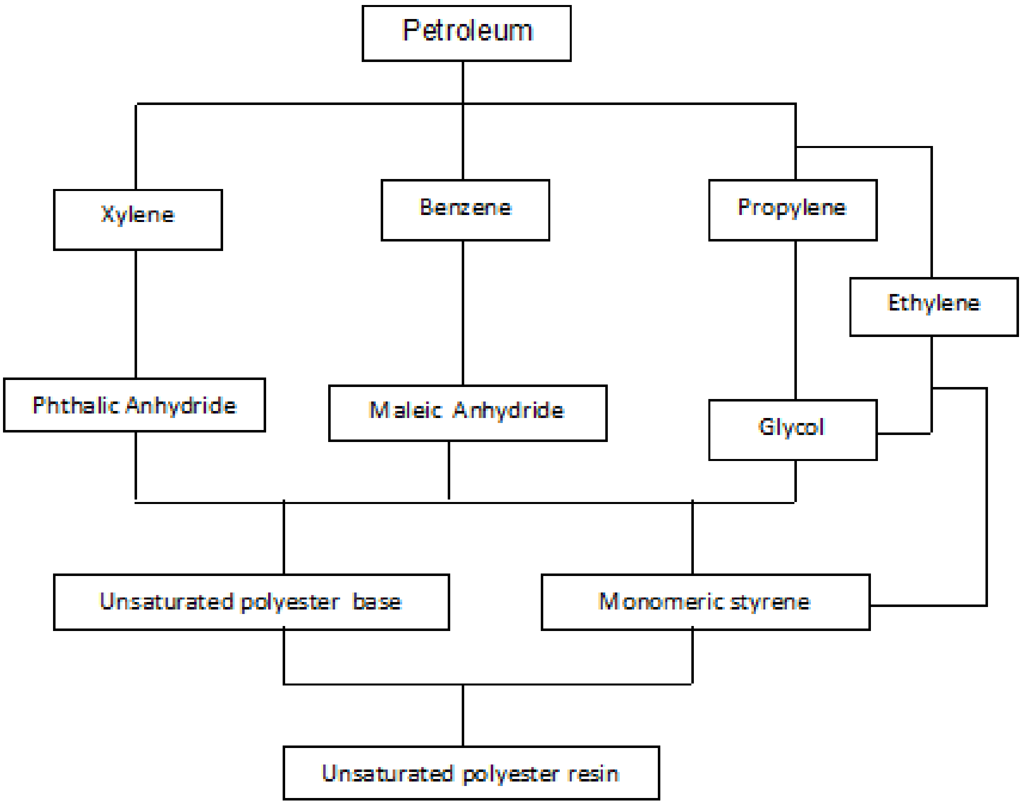

Figure 3: Derivation of compound used in the manufacturing of typical polyester resin [11].

The ester groups provide the basis for a chemical interaction with stone, but these groups are fairly shielded and in small concentration, therefore the polyester will not exhibit strong chemical interaction and work mostly by establishing a mechanical interaction. The ethylene and propylene are the most popular used as the dihydric alcohol [13]. The styrene is the most widely used as monomer in this system. The monomer is used as a solvent of the un-saturated polyester when it is formed and still hot after the combination of the saturated, un- saturated acids and the dihydric alcohol; decrease the viscosity within manageable limits. The type and concentration of the monomer affect the length of cross likening. The monomer allow the resin to cure from a liquid to solid by cross likening of the polyester. No need to use pressure because no by product is produced during the process, so polyester called low pressure molding resins [11].

These ingredients are mixed in a resin kittle and polymerized by a step reaction which is in the viscous liquid range. After cooling, the mixture is thinned down to a pourable liquid by addition of the monomer. The hydroquinone is an inhibitor and added to prevent premature polymerization.

Cure is begun by adding an initiator, commonly organic peroxide is used such as hydroperoxid or benzoyl peroxide, and cure take place in two stages; the initial formation of a soft gel followed by rapid polymerization. To promote the decomposition of initiator at room temperature, and thus rapid low temperature curing, the promoter are used such as cobalt naphthenate or alkyl mercaptans [11].

Properties:-

Polyester resin properties are function of its condensation, viscosity and molecular weight distribution, also Polyester resin properties are from the structural features of the three dimensional network which obtained from free radical copolymerization. Hardness, tensile and flexural strength and heat distortion temperature (HDT) all of these properties increase with the increasing in the molecular weight of the polyester [12].

All of the ratio and type and diol component and copolymerization monomer can affect both physical and chemical properties of polyester. Greater hardness and heat resistance of the cured resin can be achieved by higher proportion of maleic acid [12].

Polyester doesn’t exhibit a strong chemical reaction with the stone, and it works by establishing a mechanical bond with the stone. Since polyester subjected to a high shrinkage, stress will built up in the bond resulting with weakening the mechanical bond, therefore, polyester should be restricted to use with pours material like limestone, where a fairly mechanical bond will be formed between the adhesives and the stone [8].

The most important properties of the unsaturated polyester are ease of handling, rapid curing with no volatiles evolved, light color, dimensional stability, and good physical and electrical properties [12].

2.2 Epoxy:-

Epoxy resins have been commercially available since 1950's, and now used in a wide range of industries and applications [11]. They are used to produce structural adhesives suitable for many applications. Epoxy based adhesives will bond a wide range of substrates including composites, metals, ceramics and rubber. Epoxy system has the best overall bonding characteristic with natural stone, also used in automotive, and electronics industries. [8, 11, 14].

Epoxies are classified into two basic types of resins, these are:-

- Bisphenol A; this type has low molecular weight and low viscosity, the most ones widely used in the composites industry [11, 14].
- Epoxy Phenol Novalic; this type has higher cross-linked density and used in high performance applications, such as pre-pregs for the electrical industry [11, 14].

Epoxy used with stone are based upon a reaction between an epoxy resin and a modified a mine hardener, it is provide the strongest bonds to natural stone due to very high concentration of hydroxyl groups are response to establish a strong chemical interaction [8, 14].

2.2.1 Chemistry:-

The epoxy group is a three-membered ring consisting of an oxygen atom attached to two connected carbon atoms as shows in figure (4) [15].

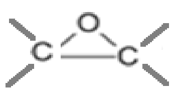

Figure 4: The Epoxy Group.

The epoxy resins are referred to an intermediate molecule which contains at least two reactive epoxy groups, these resins are categorized as thermosetting and they are capable of curing to produce cross-linked networks. The reactive ring can be opened by either acidic or basic materials; these materials can be affected by catalyst for homo-polymerization or by reactive hardeners [15].

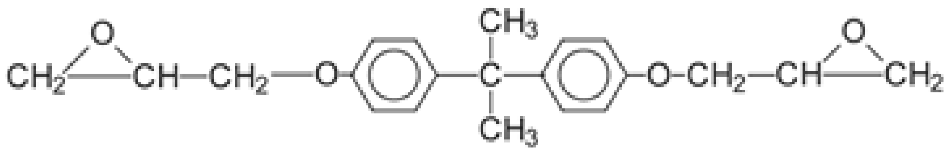

Figure 5: Epoxy resin

The epoxy resins are produced by the reaction between Epichlorhydrin and Bisphenol A as shown in figure (5), and are cured rapidly at room temperature with a reactive hardeners containing a mine groups either primary a mine such as polyamide or secondary a mine such as anhydride [11, 14, 15].

Epoxy resins can also be homo-polymerization by catalysts Lewis acid such as boron trifluoride, or Lewis base such as tertiary amines to form polyethers [14, 15].

The epoxy novolac resins combine the reactivity of the epoxy group and thermal resistance of the phenolic backbone. They are synthesized by reacting epichlorohydrin with novolac resin. The novolac resins can also be prepared from substituted phenols such as cresol, or polyhydroxy phenol such as resorcinol [14, 15].

Epoxy also is produced by oxidation of olefinic unsaturation within animal and vegetable oil [14].

2.2.2 Properties:-

- Epoxy offer excellent adhesion to a wide variety of substrates including concret, glass, wood, ceramics and many plastics [11].

- Epoxy resins offer a unique combination of properties for adhesive application includes:-
  - The ability to formulate liquid system without solvent or carriers.
  - The ability to convert this system to cured products without the production of low molecular weight by product.
  - The ability to bond dissimilar or non-porous surfaces.
  - And ability to produce thick sections without subsequent stress cracking due to shrinking [14].

- The most important properties of epoxy are provide good weather-ability, for construction works in winter epoxy resin usually kept above the lower useable temperature limit by covering with polyethylene sheets and by heating or preheating of liquid resin, hardeners and aggregates [8, 13].

- Because epoxy resins combine toughness, flexibility, adhesion, and highly chemical and corrosion resistance to a nearly unparalleled degree it's used as surface coating materials [11, 13].

- Epoxy has very little shrinkage during cure and therefor maintains a very good mechanical bond, and has high concentration of hydroxyl groups are response to establish a strong chemical interaction, means that they can be used where dimensional accuracy is if prime importance [8, 14].

- The epoxy resins with hardener may be used as unmodified form in adhesives system, but various additives are used to achieve specific effects such as:-
- Catalyst or blend hardeners are added to obtain a specific usable life of the mix and control the curing temperature.
- Reactive diluents are added to modify viscosity or flexibility.
- Fillers are added to improve compression strength and reduce shrinkage and cost.
- Solvent is added to reduce viscosity or improve adhesion.

These additives are added in low percent to reduce aeration and improve adhesion to difficult surface. In addition, they are used to minimize settlement of fillers, and also improve particularly properties such as; flam retardency, electrical insulation or conductivity and chemical resistance [14].

- These combinations of properties make epoxy resins suitable for use in many applications with composites industry include adhesives, construction or repair, casting, laminating and flooring [11].

The Disadvantages of epoxy adhesives:-

- Unlike polyester, the reactive ingredients of an epoxy are kept in a separate container until they are mixed for use.
- Discolor when exposed to sunlight.
- Long curing time (3-8 hour), so it less use in fabrication applications [8].

2.3 Fillers:-

When mineral fillers were first introduced to the composites industry it was as a means of reducing cost. At that time, excessively high loadings were used and this resulted in a serious deterioration in the mechanical strength and chemical resistance [11].

Today, the effects of fillers are better understood and they are used to enhance and improve certain properties of a resin, whereas the level of cost reduction achievable by the use of fillers is no longer a significant factor. Filled resins exhibit lower exothermic and shrinkage characteristic and make a resin more chemical and corrosion resistant, act as a fire retardant, and capable of withstanding weather conditions than unfilled systems [11, 15, 16].

Table 1: Types of filler and there functions.

Types of filler	Properties improved
Calcium carbonate.	Used where Lower exothermic temperatures, and lower shrinkage are desirable. Cheap filler Comes in various sizes, ability to improve impact strength, and used in role processing [2, 11, 15, 16].
Talc.	Used to increase 'bulk' and reduce exothermic temperature, usually in casting applications. Used to stiffen thermoplastics [11, 16].

Silica.	Used to impart thixotropy, improve mechanical strength, and reduce shrinkage and coefficient of thermal expansion, increase heat resistance and dielectric strength [11, 16].
Metal powders (Aluminum, brass, bronze, silver and copper powders).	Used to produce realistic metallic castings, increase thermal and electrical conductivity, and increase mechanical strength [11, 16].
Silane coupling agent.	For adhesion [15].
Fibrous filler.	Used in anywhere an economical fibrous filler is needed, increase viscosity and to improve slump and crack resistance in oil and water based systems, excellent resistance to acids, alkalis, bleaches, solvents, mildew and sunlight, uniform product which will not separate during mixing and is formulated for ease of dispersion, very low shrinkage upon drying, and airless spraying [16].
Cutting stone waste	Wide available, Used to improve impact strength, and very cheap filler.

- Depending on addition level, fillers will increase the usable life and extend the cure time of the mix, and usually reduced shrinkage, but chemical resistance will vary from filler to filler. In addition, tensile and compression strength increase maximally then decrease on further addition [12].

- Settlement of fillers during storage of product depends on the particle size and density of filler, and the viscosity of the formulated product. In fine particle with low specific gravity and high viscosity product will settle much less. To eliminate or reduce settlement by incorporation of fine fillers by use of a pigment-dispersing aid and use a thixotroping agent [12].

2.4 Additives:-

Different additives are using to improve many properties in marble glue as shown in table (2).

Table 2: Different types of additive.

Type	Function
Reactive diluent	- Modify viscosity and flexibility
Solvent	- Reduce viscosity or impeller adhesion
Plasticizer	- Degrade most physical properties - Increase impact resistance - Decrease tensile strength and chemical resistance
Deformers	- Reduce aeration
Thixotrops	- Reduce flow in product - Improve gap filling - Reduce settlement of fillers
Adhesion promoter	- Improve adhesion to certain non-porous substances like metal and certain plastic.
Elastomer	- Improve adhesion and flexibility
Anti-shrinking	- Prevent the shrinkage of the material when using to joint parts of stones.
Castor oil	- Lubricants - Tends to form gums in a short time

Chapter Three

Results

&

Discussion.

3.1 Methodology:-

The work started with execution a lot of trials to produce the local marble glue, followed by doing tests to determine the suitable sample. A layout for the plant was done; finally the cost of the plant was analyzed.

3.1.1 Experimental work:-

1- The first step in this semester was brought the raw materials.
2- The cutting stone filler was dried at 80° C furnace temperature to remove the moisture.
3- Primary samples were tried to determine the exact percent of both resin and filler.
4- Firstly, 40% of resin and 60% of different fillers were weighted.
5- The second step was mixing by adding the fillers to the resin until the desired texture was reached.
6- During the mixing, anti-shrinking material and lubricant oil were added.
7- The strength of product was tested by joining two pieces of stone with suitable amount of marble glue and hardener; and after the material was dried, the stone was tested by the flexural test as shown in part (3.1.B).
8- The results from the test were analyzed to get the optimum sample.
9- Other test like service life test was applied by soaking joining stones in (water, Citric acid and HCl) for 72 hour, to test the durability of the material.

3.1. 2 Tests:-

3.1.2.1 Flexure Test:-

The flexural strength of a material is defined as its ability to resist deformation under load, the use of flexural tests to determine the mechanical properties of resins and to determine the interlaminar shear strength using a short beam. It is frequently found that flexure tests give results which are very similar to those from other tests (tension and compression. A flexure test produces tensile stress in the convex side of the specimen and compression stress in the concave side. This creates an area of shear stress along the midline [17, 18. 19].

Flexure testing is often done on relatively flexible materials such as polymers, wood and composites. There are two test types; 3-point flexure and 4-point flexure as shown in figures (6 and 7). In a 3-point test the area of uniform stress is quite small and concentrated under the center loading point. In a 4-point test, the area of uniform stress exists between the inner span loading points (typically half the outer span length) [19].

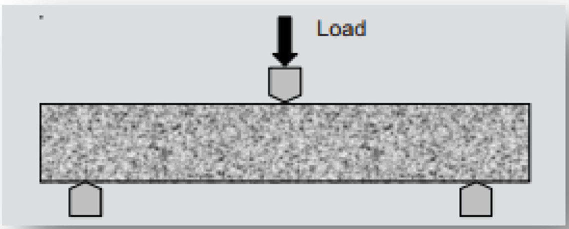

Figure 6: 3-point flexure test.

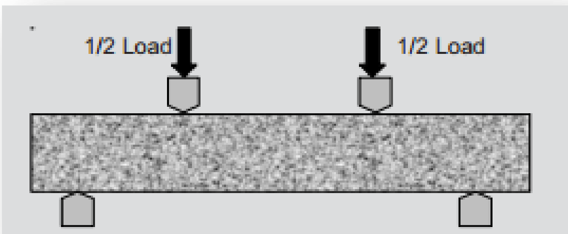

Figure 7: 4-point flexure test.

Flexure unit:-

This test performed by using flexural machine as shown in figure (8).

Figure 8: Flexural machine.

Procedure:-

1- Dimensions of the samples were measured by using caliper before testing as shown in figure (9).

Figure 9: Measuring dimension of the sample.

2- The samples were fixed on the lower two beams with a distance of (1 cm) between each beam and the end of sample (Focal distance). The above beam was located at the center of the sample (at the joining pint) as shown in figure (10).

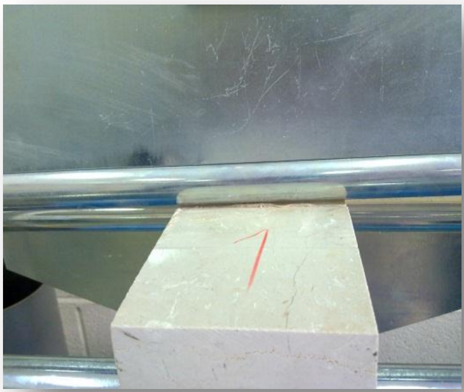

Figure 10: Fixing the sample on the machine.

3- The hand of the machine was rotating manually to concentrate the load on the joining point until the breaking of the sample as shown in figure (11, 12).

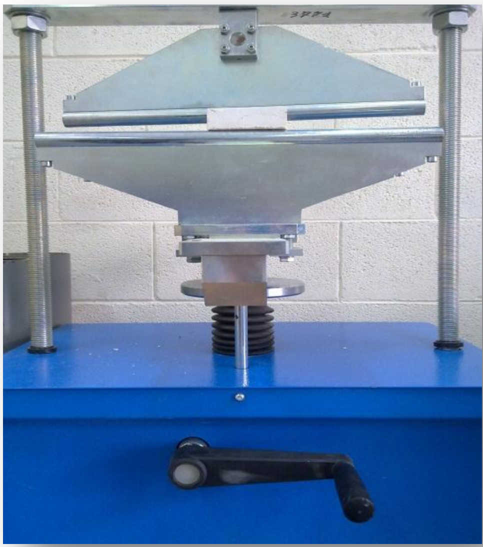

Figure 11: The hand of the machine

Figure 12: The sample after broken.

4- At the moment of the breaking of the sample the value of the load was read as shown in figure (13).

Figure 13: The gauge of the machine.

5- The value of load was converted to stress by using equation (1):-

Stress (σ) = $\frac{3*22.25*P*L}{2*B*(D^2)}$ ………………………………………………………..(1)

Where:-

- σ : - The maximum stress at the outer surface of the beam in three-point bending (MPa).
- P: - The value of the load from the machine (%).
- L: - Focal distance (approximately 20 mm).
- B:- The width of the sample (mm)
- D:- The thickness of the sample (mm)
- 22.25:- The correction factor for the machine.

3.1. 2 .2 Service life Test:-

Service life test was applied by soaking joining stones in (water, Citric acid and HCl) for 72 hour, to test the durability of the material as shown in figures (14, 15 & 16).

The concentration of the Citric acid and HCl were 5%.

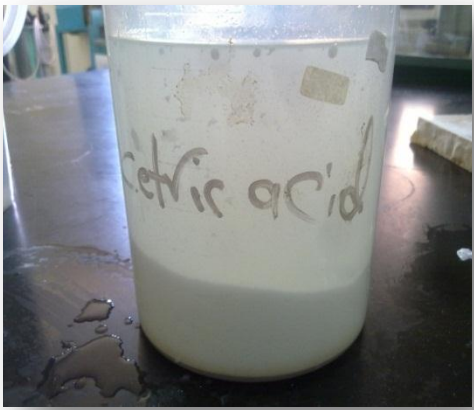

Figure 14: The sample after soaking in Citric acid.

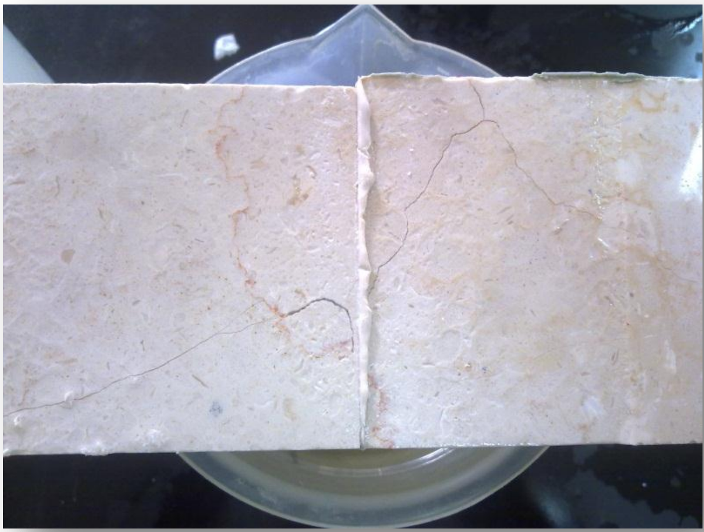

Figure 15: The sample after soaking in HCl.

Figure 16: The sample after soaking in Water.

3.2 Results and Discussion:-

Initially, the percentage of resin was chosen to be 40% and the rest for filler; based on the texture and strong of final product. Because as the percentage of resin decrease the strong of joining between two parts of stone will decrease.

Table (3) shows seven experimental samples composed of 40% resin as fixed percentage for all samples and the rest percentage include three different types of filler; to test and determine the suitable filler for the final product which has the acceptable texture compared with imported product in the market. The percent of the resin was in the rang (32% - 48%); this difference from the fixed amount (40%) refers to use different types of filler and some of them are lighter than others so that the amount of one part weight of some filler is larger than one part weight on other fillers.

Table 3: The first samples were prepared.

Sample number	Resin percent %	Type of filler			Texture
		Pure $CaCO_3$	Cutting stone	Talc	
1	36	64	-	-	Non acceptable
2	32	-	68	-	Non acceptable
3	58.82	-	-	41.18	Non acceptable
4	32	34	34	-	Non acceptable
5	46	27	-	27	Non acceptable
6	48	-	26	26	Non acceptable
7	41	19.6	19.6	19.6	acceptable

Samples from (1-6) were non viscose and not strong in joining two parts of stone than the imported product; this make these samples undesired to produce our product. Whereas sample (7) had desired properties to produce product that his ability to compete imported product.

Sample (7) in the above table contain three types of filler and the it's the only one which had the acceptable texture, so more experiments were done to determine the exact percentage of each filler as shown in table (4).

Sample (3) in the above table contained 41.18 % talc for 58.82 % polyester, and this sample is very expensive because the percentage of polyester is higher than talc. The usage of talc alone in the sample will make the product brittle.

Table 4: The trials which prepared by using three different types of filler.

Sample number	Resin %	Pure $CaCO_3$	Cutting stone	Talc
		Ratio/ Grams / Percentage%		
1	40.486	1	1	1
		19.6 g 19.8 %	19.6 g 19.8 %	19.6 g 19.8 %
2	38.835	1.5	1.5	1
		23.5 g 22.8155 %	23.5 g 22.8155 %	16 g 15.534 %
3	38.835	2	2	1
		25 g 24.272 %	25 g 24.272 %	13 g 12.6213 %
4	38.873	2.5	2.5	1
		26.2 g 25.462 %	26.2 g 25.462 %	10.5 g 10.204 %
5	42.554	9.63	9.63	1
		25.666 g 27.305 %	25.666 g 27.305 %	2.666 g 2.84 %

The sudden drop in the percentage of talc in sample (5) from other samples was for check the effect of addition of talc as an additive rather than filler.

The results from the flexure test for both reference and all the accepted samples are shown in table (5).

Table 5: Results from the flexure test.

Samples number	Average (MPa)	Standard Deviation
Reference	7.283 ±	0.505581±
1	7.4825 ±	0.091217 ±
2	8.2125 ±	0.234052 ±
3	9.3015 ±	0.25668 ±
4	8.621 ±	0.514774 ±
5	6.7955 ±	0.697914±

Because of not existence of Palestinian specification the natural marble stone was adopted as our reference to test the strong of our product. From the figure (17) it is cleared that samples (1, 2, 3, 4) have higher stress than the reference, but sample (5) has lower stress than the reference because the Talc was added as additive rather than its nature as filler and the function of talc is penetrating in gapes of stone resulting a strong joining.

As shown in the figure (17), sample (3) has the highest stress than other samples so it is considered as the optimum one.

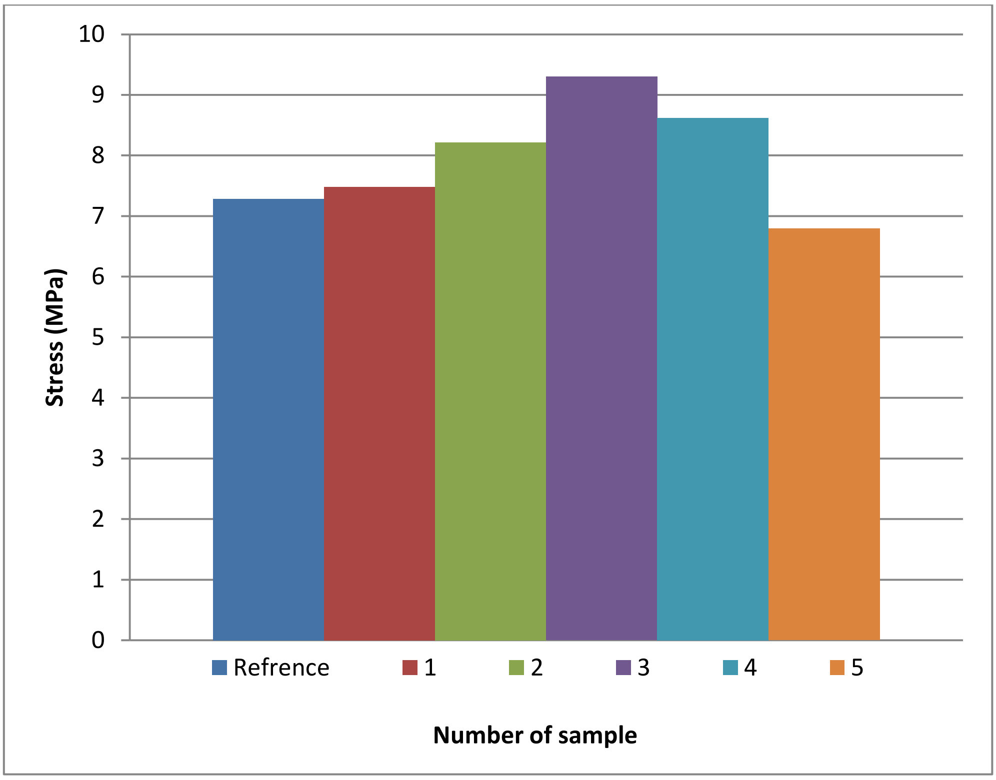

Figure 17: Results from the flexure test

Figure (18) shows the trend of decreasing Talc to Pure $CaCO_3$ and cutting stone, as the percent of talc decrease the stress increase until reach the maximum point, after that the stress decrease with increasing talc percent, this is attributable the properties of thermoset polymer.

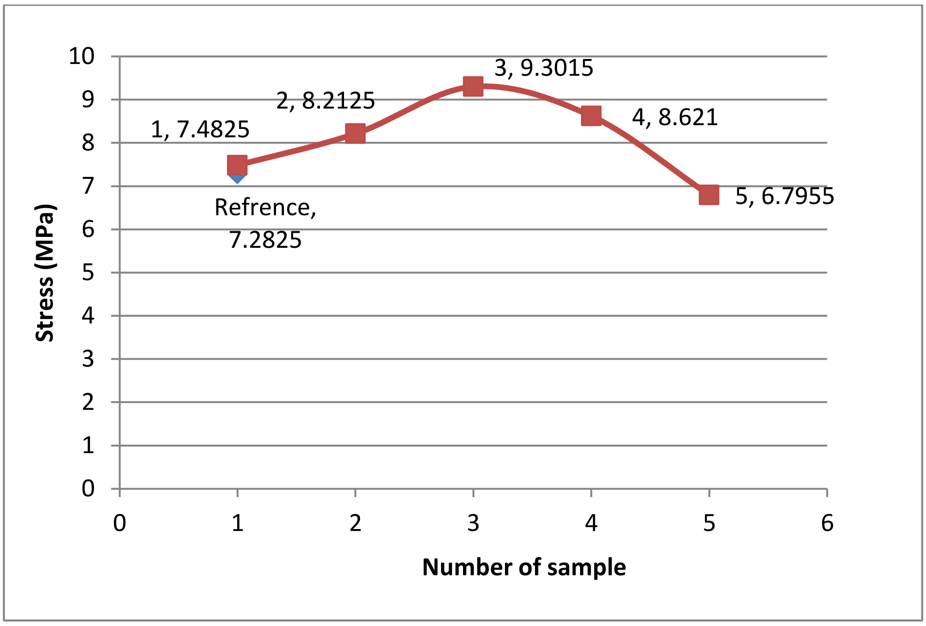

Figure 18: The trend of decreasing Talc to Pure $CaCO_3$ and cutting stone.

- (1, 7.4825):- where;

  1:- Sample number.

  7.4825:- Stress value.

Figure (19) include both the stress and the percentage of talc added to the samples, as shown sample (3) has the highest stress than other samples so it is considered as the optimum one, and it has around 12.62% talc.

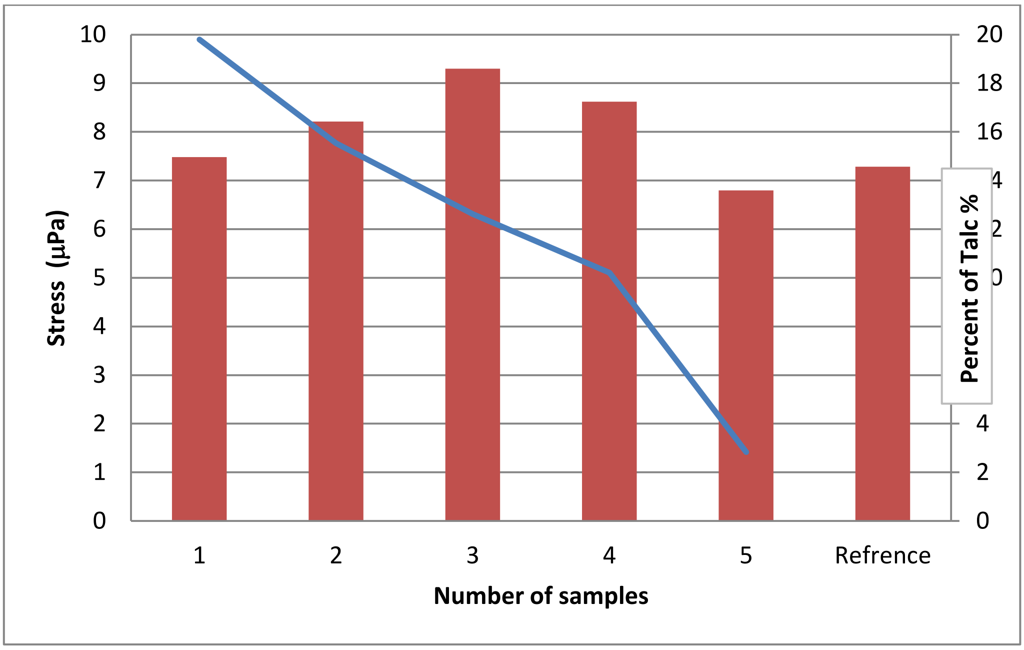

Figure 19: The stress and the percentage of talc added to the samples.

- For service life test the sample doesn't affected from (water, Citric acid and HCl), whereas the stone itself affected deeply from the cetric acid and moderately from the HCl, but doesn't affected from the water.

Hardener:-

To achieve the function of the marble glue of joining two parts it's very essential to use the hardener in a suitable percent because without hardener the material will not be dried at all.

Each type of resin has its suitable hardener, for polyester the suitable hardener is Cycloheaxanone Peroxide. The usage of hardener will achieve the drying of the material, but it's important to accelerate drying, so an initiator like Zinc Octate was used, as a result the drying time was reduced to 5 minute.

3.3 Cost analysis:-

Cost analysis will include the initial investment of the plant and the cost of raw materials, workers, equipment and operating cost, where the local product will obtain high performance and it will be able to compete the foreign product in the market.

The initial investment of the plant includes the cost of equipment (the cost of equipment includes purchase cost and its installation) and the infrastructure (Land and Building), and transportation are described in tables (6 & 7).

Table 6: Equipment cost.

Equipment	Cost (NIS)
Sieve trays (Mish)	19500
Mixer	585000
Filling machine	273000
Total	877500

Table 7: Infrastructure cost.

Infrastructure		cost (NIS)
Land	500 m^2= 10000 JD	50000
Building		75000
Transportation	Cars	40000
Total		165000

➢ Operating cost:-

The analysis of operating cost of the plant is shown below:-

Table 8: Raw materials cost.

Raw materials	Cost (NIS/Kg)
Polyester	30
Pure $CaCO_3$	2
Cutting stone	0.2
Talc	5
Additives:- **Anti-shrinking** **Castor oil**	 100 5

The amounts of raw materials needed to produce (1 Kg) of marble glue shown in figure ().

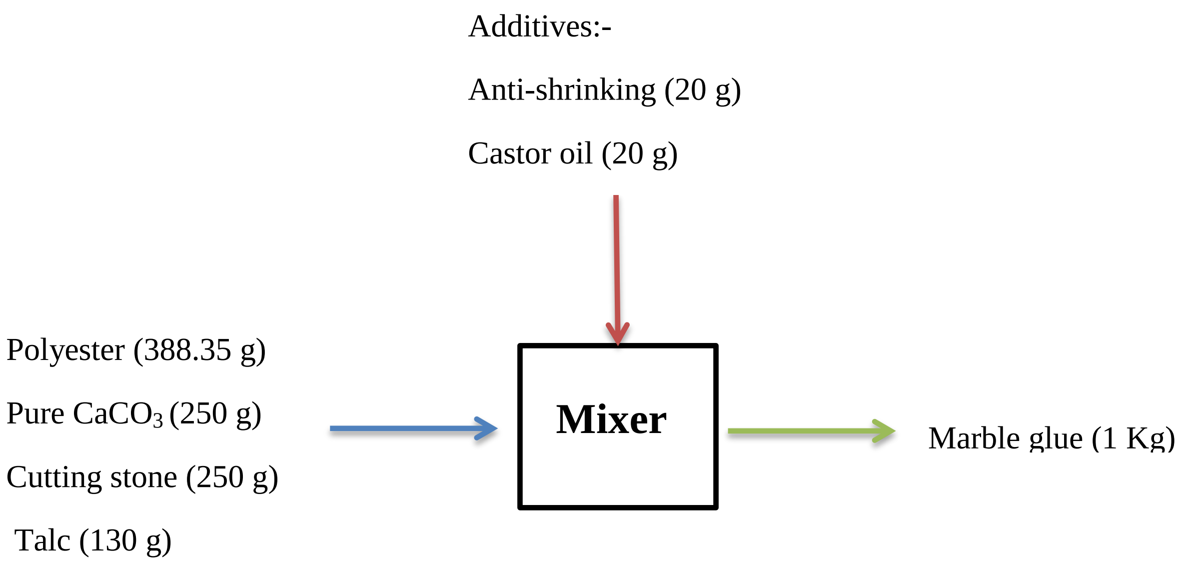

Figure 20: Flow diagram of raw material.

Table 9: The raw materials cost to produce (1 Kg) of marble glue.

Raw materials		NIS/Kg
Polyester	$0.38835\ Kg * 30\ \frac{NIS}{Kg}$	11.7
Pure $CaCO_3$	$0.255\ Kg * 2\ \frac{NIS}{Kg}$	0.51
Calculation **Cutting stone**	$0.25\ Kg * 0.2\ \frac{NIS}{Kg}$	0.05
Talc	$0.13\ Kg * 5\ \frac{NIS}{Kg}$	0.65
Additives	$0.02\ Kg * 100\ \frac{NIS}{Kg}$ $0.02\ Kg * 5\ \frac{NIS}{Kg}$	2 0.1
Total	-	15.01

Table 10: The raw materials cost to produce (1 Kg) of hardener.

Raw materials for hardener	Calculation	Cost (NIS/Kg)
Liquid hardener	-	500 g for each kg of polyester
Pure CaCO3	$0.125\ \text{Kg} * 2\ \frac{NIS}{Kg}$	0.25
Cutting stone	$0.125\ \text{Kg} * 0.2\ \frac{NIS}{Kg}$	0.025
Talc	$0.075\ \text{Kg} * 5\ \frac{NIS}{Kg}$	0.375
Total	-	0.65

- **Electricity:-**

Assume impeller power equals 50 Kw/hr, production rate of 60 Kg/hr, and $0.6\ \frac{NIS}{Kw}$.

Assume 216 working days in the year.

$$\text{Electricity cost} = 50\ \frac{Kw}{hr} * \frac{1}{60}\ \frac{hr}{Kg} * 0.6\ \frac{NIS}{Kw}$$

$$= 0.3\ \frac{NIS}{Kg}.$$

➢ Labor cost :-

Assume the plant needs 4 labors for 10 $\frac{NIS}{hr}$.

Labor cost = $\frac{4*10\frac{NIS}{hr}}{60\frac{hr}{Kg}}$

= 1 $\frac{NIS}{Kg}$.

➢ Maintenance:-

Assume 2% of investment.

Maintenance = 10.42 * 10^5 NIS * 0.02 = 20850 $\frac{NIS}{year}$.

= 20850 $\frac{NIS}{year} * \frac{1\ year}{216\ day} * \frac{1\ day}{8\ hr} * \frac{1\ hr}{60\ Kg}$

= 0.2 $\frac{NIS}{Kg}$.

➢ Depreciation:-

Depreciation = $\frac{Investment}{5\ year}$

= $\frac{10.42 * 10^5 5\ \text{NIS}}{5\ year}$

= 208.400 $\frac{NIS}{year}$.

= 208.400 $\frac{NIS}{year} * \frac{1\ year}{216\ day} * \frac{1\ day}{8\ hr} * \frac{1\ hr}{60\ Kg}$

= 2.01 $\frac{NIS}{Kg}$.

- General and administration expenses (G & A expenses):-

Annual Sales = $60\,\frac{hr}{Kg} * 8\,\frac{hr}{day} * 216\,\frac{day}{year}$

$= 103680\,\frac{kg}{year}$.

G & A expenses are in the range (5 – 10 %) of the annual sales.

Assume its 7.5% of annual sales.

G & A expenses = $0.75 * 103680\,\frac{kg}{year}$

$= 77760\,\frac{NIS}{year}$.

Cost of 1 Kg of product:-

The operating cost to produce (1 kg) of local marble glue is shown in table (12).

Table 11: Price of (1 Kg) of local marble glue.

Factor	Cost (NIS/Kg)
Raw materials	15.01
Electricity	0.3
Labor	0.66
Maintenance	0.2
Depreciation	2.01
Total	18.18

❖ Assume 10% profit for each (Kg) of product:-

Profit = 18.18 + (18.18*0.1)

$= 19.998\ \frac{NIS}{Kg}.$

❖ **Revenue = Sales * cost of 1 kg**

$= 103680\ \frac{kg}{year} * 19.998\ \frac{NIS}{Kg}$

$= 2.07 * 10^{6}\ \frac{NIS}{year}.$

❖ **Profit = Revenue – Expenses (cost of production + G & A expenses)**

$= 2.07 * 10^{6}\ \frac{NIS}{year} - [(103680\ \frac{kg}{year} * 18.18\ \frac{NIS}{Kg}) + 77760\ \frac{NIS}{year}]$

$= 107337.6\ \frac{NIS}{year}.$

➢ Cash flow:-

A cash flow is the movement of money into or out of a business, project, or financial product and its indicator of earning or losses of the project. It is calculated from the difference between the profit and expenses. The annual cash flow of the plant is shown in table (12) and figure (21).

Table 12: The annual cash flow of the plant.

Months	**1**	**2**	**3**	**4**	**5**	**6**
profit	38333	38333	230000	230000	230000	230000
Expenses	-36346	-36346	-218074	-218074	-218074	-218074
Net	1987	1987	11926	11926	11926	11926

Continue………

7	**8**	**9**	**10**	**11**	**12**
230000	230000	230000	51111	51111	51111
-218074	-218074	-218074	-48460	-48460	-48460
11926	11926	11926	2651	2651	2651

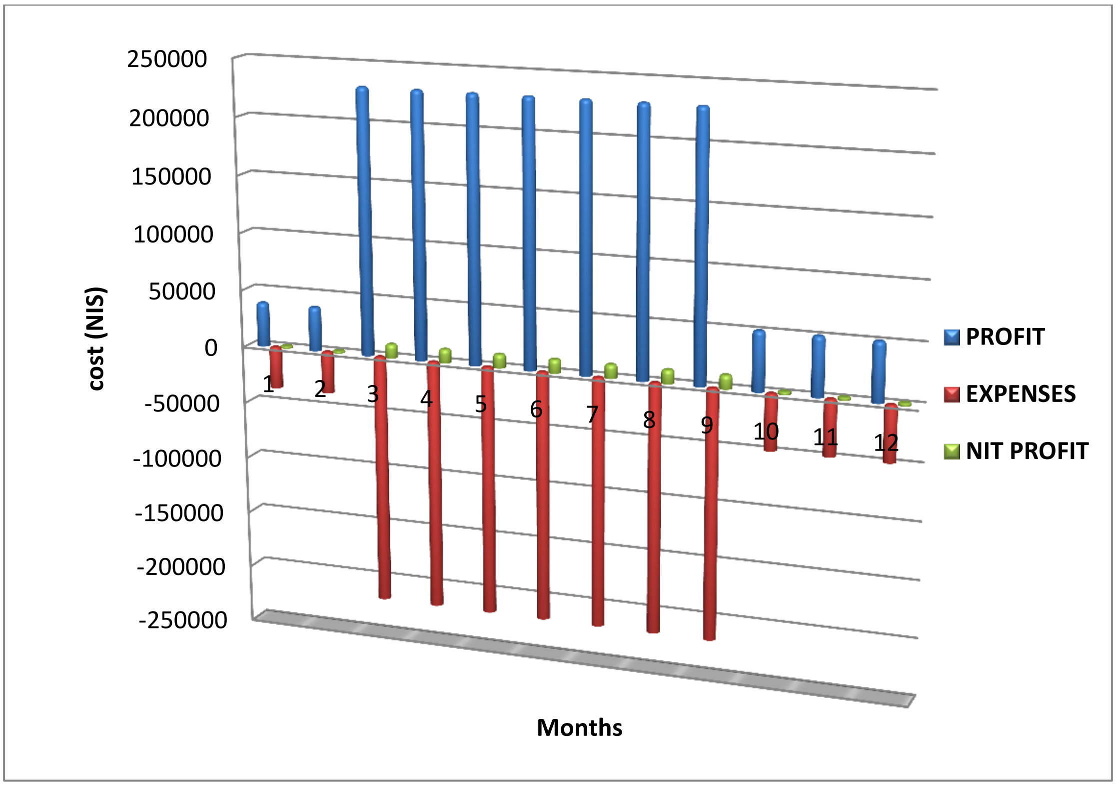

Figure 21: The annual cash flow of the plant

Payback period:-

The payback period is the period in which the all investment of plant is restore, and as shown in figure (22) the payback period for the local marble glue plant is 4 years and the life of the project is 12 years.

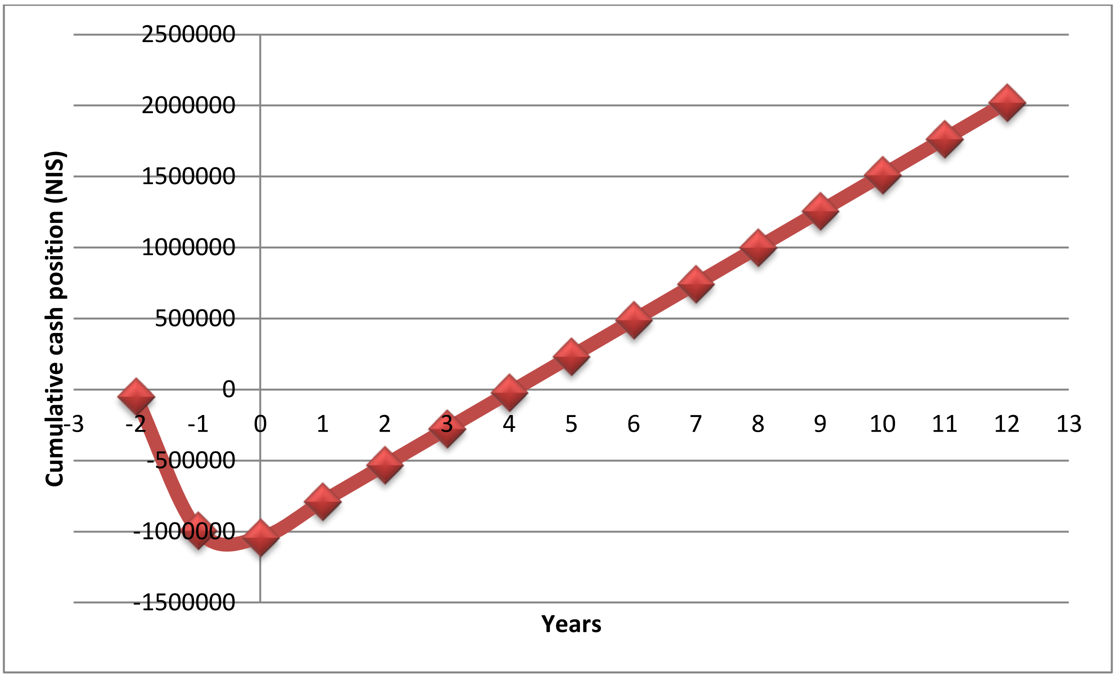

Figure 22: The payback period of the project.

3.4 Facility layout:-

Facility layout will include layout of equipment in the plant to achieve the performance of the process, and to find easier way to flow the input inside the plant, where the layout will achieve the safety for workers and reduce the cost. The layout of marble glue plant is shown in figure (22).

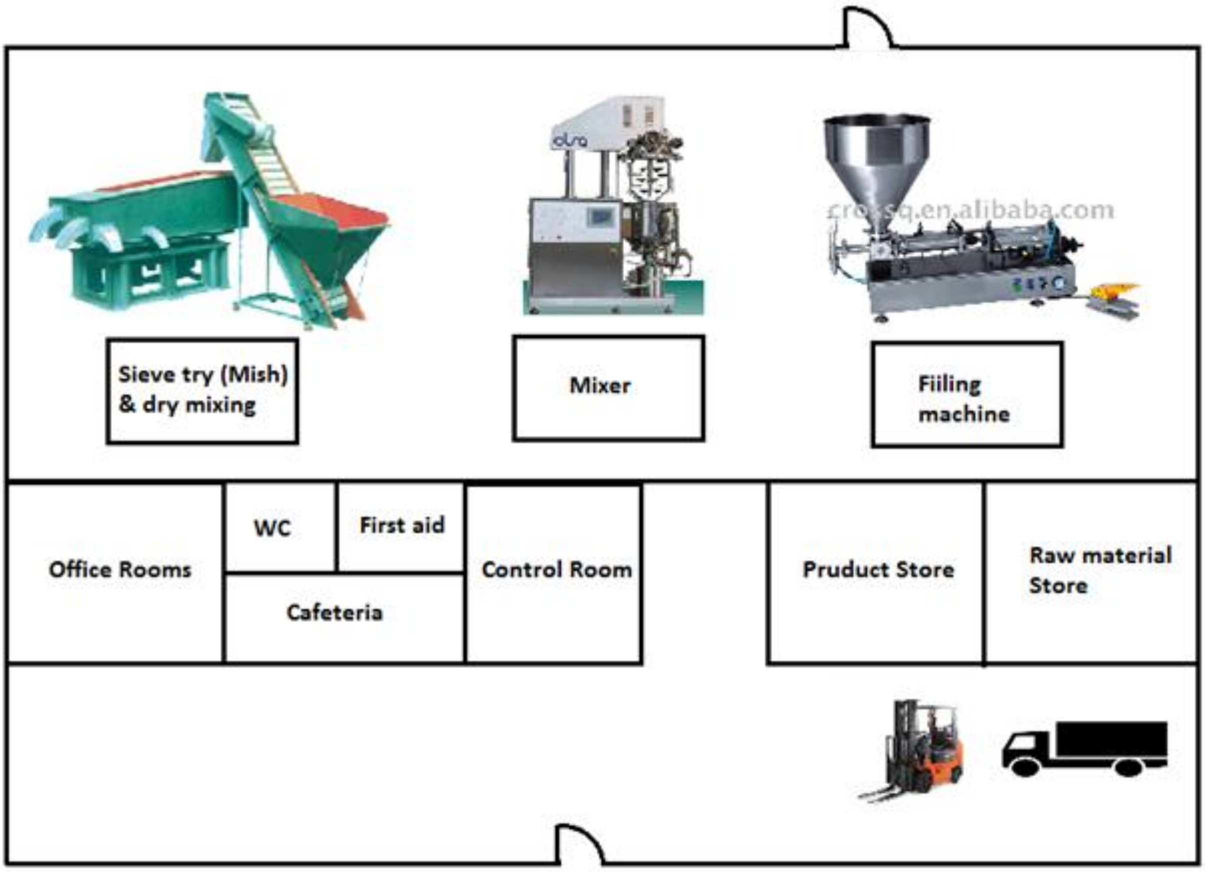

Figure 23: The lay out of the plant.

3.4.1 Impeller type:-

Speedy mix Vacuum mixer homogenizer is used for semi-solid products is shown in figure (23).

The designs of this mixer including three types of impeller and are:-

1- Two slow agitators: coaxial execution with outer anchor equipped with Teflon hinged scrapers and contra-rotating inner blades.
2- Fast agitator: rotor and stator type installed in a mixing chamber, installed on the truncated cone bottom of the vessel, with internal and/or external product recirculation [20].

Figure 24: Speedy mix Vacuum mixer homogenizer [20].

The inner foil-type agitator, which is contra-rotating to the anchor type agitator, is equipped with 3-axial flow blades, arranged at 120° to one another. The chord of each blade varies from the root to the tip, in order to compensate for the difference in peripheral tip speeds. Each blade is staggered, in relation to the blades above and below, and their rotating motion intersects with the rotating motion of the anchor pumping blades. This allows for a very efficient bulk agitation, while minimizing dead zones.

The angle of the contra-rotating blades provides an effective pumping action downwards to the central zone of the mixing zone, feeding the high speed agitator. The resulting mixing actions of the two low-speed agitators and the high speed homogenizing turbine are an overall reduction in mixing and homogenization time.

In this unit, both the dispersing and the homogenizing of particles are enhanced by the special truncated-cone bottom vessel execution. Inside the high-swirling homogenizing chamber, installed externally under the vessel bottom, strong mechanical and hydraulic forces occur, resulting in superior dispersion, homogenization and emulsification. The homogenizing turbine speed is variable, controlled by means of an AC variable frequency inverter drive. The product return through a recirculating pipe, tangent to the upper side of the vessel, increases both the mixing action of the two slow agitators and the rate of product deaeration [20].

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Conclusion:-

- The optimum sample which gives the best performance was composed from (38.835 % Polyester, 24.272% Pure $CaCO_3$, 24.272% Cutting stone, and 12.6213% Talc).
- The average stress of the optimum sample was 9.3015 (MPa).
- The price of 1 Kg of local marble glue was 19.998 NIS with expenses cost of 18.18 NIS, the profit percentage was 10%.
- The payback period of the project was 4 years with 12 years project life.

References:-

[1]: William Botterill and his colleges. History of Adhesives, ESC Report (1), 1991.

[2]: Julian R. Panek, John Philip Cook. Construction Sealants and Adhesives. Second edition, published in Canada (1984).

[3]: Shaw S. J. Adhesives in Demanding Applications, Polymer International 41 (1996) 193-207.

[4]: GUO Meng-lin(Monlin Kuo). Protein-based Wood Adhesives. (Department of Natural Resource Ecology & Management,Iowa State University,Ames,Iowa,USA)

[5]: D. Irfan Mir. Kumar. Recent advances in isotropic conductive adhesives for electronics packaging applications, International Journal of Adhesion & Adhesives 28 (2008) 362–371.

[6]: www.encyclopedia2.thefreedictionary.com/adhesive. Accessed on February 15,2012.

[7]: Glen A Rowland, Adhesives and Adhesion, CHEM NZ, 1998, No.71, 17-27.

[8]: www.superiorstoneproducts.com/ Adhesive Bonding of Natural Stone. Accessed on February 18, 2012.

[9]: www.roymech.co.uk/Useful_Tables/Adhesives/Adhesive_Bond.html. Accessed on February 18, 2012.

[10]: www.unaime.edu/adhesion/gardner/450lecture/adhesion%20lecture9.pdf. Accessed on March 18, 2012.

[11]: Scott Bader Company Limited Wollaston, Wellingborough, Northamptonshire NN29 7RL. [www.scottbader.com].

[12]:Pizzi. A. Hand book of adhesive technology, Second edition, Unsaturated Polyester Adhesives, Chapter 36.

[13]: Fked W. Billmeyer, JR. Text book of polymer, Second edition.

[14]: Goulding T. M. Hand book of adhesive technology, Second edition, Epoxy Resin Adhesives, Chapter 43.

[15]: Irving Skeist. Hand book of adhesives. Second edition, Litton Educational publishing, 1977.

[16]: www.plasticmaterials.net/fillers/fillers.html. Accessed on February 22, 2012.

[17]: J M HODGKINSON. Flexure, chapter 7.

[18]: http://www.matweb.com/reference/flexuralstrength.aspx. Accessed on December 13, 2012.

[19]: http://www.instron.us/wa/applications/test_types/flexure/default.aspx Accessed on December 13, 2012.

[20]: http://www.olsa.com/index.php?sezione=products&page=Speedymix. Accessed on December 13, 2012.