WATER DISPERSED EPOXY RESIN FOR SURFACE COATINGS

A THESIS SUBMITTED TO

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

OF

THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

EVRİM ŞEN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

THE DEPARTMENT OF CHEMICAL ENGINEERING

DECEMBER 2003

Approval of the Graduate School of Natural and Applied Sciences

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

WATER DISPERSED EPOXY RESIN FOR SURFACE COATINGS

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December 2003, 61 pages

In this research water dispersed epoxy varnishes were produced by reacting solid epoxy resin with ethylene diamine (EDA) and maleinized fatty acids of linseed oil.

Maleinized fatty acid (MFA) was produced by the maleinization process, in which, fatty acid and maleic anhydride were reacted under nitrogen atmosphere.

Maleinization was performed in order to insert hydrophilic groups to the fatty acid chains, which were then inserted to the backbone of the epoxy resin. This was done to give water dispersibility to the hydrophobic epoxy resin.

Solid epoxy resin was dissolved in 1,4-dioxane. Ethylene diamine was then added to the solution at 50°C, and stirred for 4 hours. Then the temperature was increased to 80°C and kept for 2 hours.

Maleinized fatty acids were then introduced, and the reaction was carried out at 90°C for 10 hours. 1,4-dioxane was used for the removal of the water, which forms as the byproduct. Then the driers were added. The carboxylic groups of the maleinized fatty acid were neutralized by morpholine and the product was dispersed in water. The varnish was applied on test panels and left for air-drying for 24 hours and then baked at 140°C for 5 hours.

The free epoxy content was determined by pyridinium-chloride titration and it was seen that all the epoxy groups reacted. Also, produced fatty acid was characterized by FTIR spectroscopy and maleinized fatty acid was characterized by H-NMR and FTIR spectroscopy.

Hardness, bending, impact resistance, gloss, and abrasion resistance tests were carried out on hardened varnish specimens. The samples generally showed good mechanical and physical properties. While the baking time was increased the hardness of product increased. Samples showed superior impact resistance, gloss, and flexibility.

Key words: Water dispersed, water borne, epoxy, ethylene diamine, maleinized fatty acid.

ÖZ

YÜZEY KAPLAMALARI İÇİN SUDA YAYINIK EPOKSİ REÇİNE ÜRETİMİ

Şen, Evrim
Yüksek Lisans, Kimya Mühendisliği Bölümü
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Aralık 2003, 61 sayfa

Bu çalışmada katı epoksi reçine, etilen diamin (EDA), ve keten yağının maleinlenmiş yağ asitleri kullanılarak suda yayınık epoksi vernikler üretilmiştir.

Maleiklendirilmiş yağ asidi (MFA), yağ asidinin maleik anhidritle azot atmosferi altında maleinlenmesinden elde edilmiştir.

Maleiklendirme işlemi epoksi reçinenin ana zincirine daha sonra takılacak olan yağ asidi zincirlerine hidrofilik gruplar ekleyebilmek için yapıldı ve hidrofobik epoksi reçinenin suda yayınması sağlandı.

Katı epoksi reçine 1,4-dioksanda çözülerek üzerine 50°C’de etilen diamin eklenmiş ve 4 saat karıştırılmıştır. Daha sonra sıcaklık 80^{o}C’ye çıkarılıp 2 saat bu sıcaklıkta tutulmuştur.

Bundan sonra maleiklendirilmiş yağ asitleri eklenmiş ve 90^{o}C’de 10 saat tepkimeye sokulmuştur. Tepkime sonucu oluşan suyu uzaklaştırmak için 1,4-dioksan kullanılmıştır. Nötrleştirme işleminden önce verniğe kurutucular konulmuştur. Maleiklendirilmiş yağ asitlerinin karboksilik grupları morfolin ile nötrleştirilmiş ve ürün suda yayınık hale getirilmiştir. Vernik test plakaları üzerine sürülmüş ve 24 saat havada kuruduktan sonra 140°C’de 5 saat fırınlanmıştır.

Serbest epoksi miktarı piridinyum-klorür titrasyonu ile hesaplanmıştır ve epoksi gruplarının tamamının tepkimeye girdiği görülmüştür. Üretilen yağ asidinin yapı özelliği FTIR spektroskopisi ve maleiklendirilmiş yağ asidinin yapı özelliği ise H-NMR ve FTIR spektroskopisi ile belirlenmiştir.

Hazırlanan örneklere sertlik, bükülme, çarpma dayanımı, parlaklık ve aşınma dayanımı testleri uygulandı. Örnekler genel olarak iyi mekanik ve fiziksel özellikler gösterdiler. Pişirme süresi arttırılınca ürünün sertliği artmıştır. Örnekler üstün çarpma direnci, parlaklık ve esneklik göstermişlerdir.

Anahtar sözcükler: Suda yayınık, su esaslı, epoksi, etilen diamin, maleinlenmiş yağ asidi.

To my family…

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and gratitude to my supervisors Güngör Gündüz, Prof.Dr., for his invaluable suggestions and support throughout this study. I also wish to express my special thank to my co-supervisor Leyla Aras, Prof.Dr., for her encouragement, endless help, and valuable guidance. I wish to express my heartfelt thank to İdris M. Akhmedov, Prof.Dr., from the Department of Chemistry, METU, for his help, advice and patience during my thesis.

I want to thank especially to Yavuz S. Şengün for his encouragement and great patience. He was always with me. Without his boundless support and helps this thesis would not be realized.

I am also very grateful to Cemil Alkan and Funda Çelebi for their assistance, suggestions friendships, and helps during this study. Many thanks to my labmates, Tuba Ecevit, Arzu Büyükyağcı, Özlem Akın, Umut B. Ayhan, and Ahu G. Dumanlı; with their helps and friendship METU would be a different place for me.

I am grateful to Murat Gafaroğulları, Research and Development Manager of Akzo-Nobel for supplying epoxy resin.

I am indebted to my precious family due to their endless support, understanding and belief in me during my long long study in this university. Without you I could not have been successful.

TABLE OF CONTENTS

CHAPTER

APPENDECIES

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

NOMENCLATURE

EDA : Ethylene Diamine
MA : Maleic Anhydride
MFA : Maleinized Fatty Acid
PTSA : para-Toluene Sulfonic Acid
^{1}H-NMR : Proton Nuclear Magnetic Resonance
FTIR : Fourier Transform Infrared

CHAPTER 1

INTRODUCTION

1.1 General Aspects of Surface Coatings

In any civilized society, the varying forms of surface coatings are used in different areas of everyday life. They are used mainly for two purposes. The first one is the protection of materials from chemical and physical external attacks, and the other one is the decoration of objects for attractive appearance. The protective function includes resistance against weather damage, decay and corrosion, combined with improved superficial mechanical properties, such as greater impact and abrasion resistance. The decorative effect maybe obtained through colour, gloss or texture or combinations of these properties.

The surface coating materials, which we include in the categories, paint, varnish and lacquer, have the following properties in common.

The material is either fluid or plastic, or may readily be brought into one of these states, so that it may be applied mechanically, e.g. by brushing or spraying, as one or more thin layers to the surface of an object.

The material after application undergoes a process known as drying. In this process the material is converted from the fluid to the solid state, giving a layer firmly anchored to the surface on which it is applied-such a layer being often referred to as a film.

Generally, paint is a dispersion of a finely divided pigment in a liquid composed of a resin or binder and a volatile solvent and it also contains small quantity of additives. The term paint is used when the primary consideration is the decorative purposes, on the other hand when the primary consideration is the protection of the materials the term coating is used.

The primitive paintings of prehistoric times were done with quite different ends in view. Certain objects were coloured in order to ensure good fortune in hunting, to hold evil spirits at bay or to honor the dead in their graves. The Egyptians, starting very early, developed the art of painting and discovered the protective function of the paints. However, it is only at a higher level of cultural development that the purely artistic motive becomes dominant, and it was late in history, with the birth of industrialism, that painting came to be used extensively to protect objects and extend their useful lives. In our own technical era the protective use of paint is as least as important as its decorative function.

Varnish word, from mediaeval Latin, is derived from the classical words verenice or berenice. The original meaning of these words is uncertain but in the Middle Ages they had come to mean amber. After the sixteenth century varnish or vernix was used to denote a fluid mixture of amber and oil or, more generally, of resin and oil. The latter meaning has survived to the present day. In this thesis the term varnish is used to mean a liquid coating material comprising resin, drying oil, solvent and drier. The mixture, applied as a thin coat and exposed to air, dries to a relatively hard, smooth, transparent film. The first step in this process is the evaporation of the solvent followed by oxidation of the drying oil.

Lacquer term is frequently applied to almost any coating composition which dries solely, and rapidly, by evaporation of the solvent. The term, although derived from the Hindu word lakh (meaning 100,000) which referred to the lac insect and its secretion (shellac), came to be associated almost exclusively with nitrocellulose-based coatings after the First World War. Even today, the term lacquer, if used without further qualification, would normally be taken to refer to a coating having nitrocellulose, or possibly another cellulose derivative, as the primary film-former.

1.2 Main Constituents of Paints, Varnishes and Lacquers

A paint consists of three main components: the binder, the pigment and the solvent.

The function of the binder is to provide the forces which hold the film together-cohesive forces-and which hold film and substrate together adhesive forces.

The pigment is a fine powder whose function is to give the film its desired colour and hiding properties. The pigment has a considerable influence on the consistency of the paint and hence on its application properties. Pigments are also of importance for the resistance of the film to external attack, in that they are partially responsible for such properties as hardness and resistance to abrasion and weathering.

The solvent is a volatile liquid whose function is to dissolve such binders which would be solid or semi-solid at normal temperature; this is so in the case of many resins and other binders such as glue. On the other hand, an oil paint containing a free-flowing oil as binder requires no solvent, but solvent may nevertheless be used as a diluent, or 'thinner', to obtain a suitable consistency for application. In many cases the same liquid fulfills the functions of solvent and diluent, whereas in cases such as nitrocellulose lacquers, solvent and diluent are quite distinct materials.

In addition of these three components, modern paints may contain additives of various kinds, such as plasticizers, driers, wetting agents, flatting agents and emulsifiers or other stabilizers [1].

1.3 Methods of Film Formation

There are three general methods by which film-formers change from the liquid to the solid state:

1. Evaporation of the solvent.
2. Oxidation.
3. Polymerization.

Method 1 may be illustrated by the drying of shellac. A solution of shellac in alcohol, when applied in a thin layer, dries by simple evaporation of the alcohol, leaving a continuous film of shellac as the coating. The solvent may be allowed to evaporate from these coatings under normal room conditions, or evaporation may be accelerated by heating the coated object in an oven.

Method 2 may be illustrated by the drying of linseed oil. When linseed oil is spread as a thin film, it absorbs oxygen from the air, and changes from the liquid oil to the solid film of linoxyn. This method applies to drying oils, oleoresinous varnishes, oxidizing alkyd resins, and many other film forming materials. As a result of the oxidation of these materials, linkages are formed between two or more molecules, thereby producing a polymeric structure. The general process is referred to as autoxidative polymerization.

Method 3 is designated as polymerization, but we have seen that one type of polymerization occurs in method 2. There are two other general types, namely, condensation polymerization and addition polymerization. In this process a small molecule, usually water, is split off between two film-forming molecules, thereby producing a chemical bond between them. Addition polymerization occurs when unsaturated molecules, such as styrene or vinyl chloride, are activated by a suitable catalyst so that they add together to form large molecules.

The particular process which is used to form a film of coating material depends on the chemical composition of the film-former and on a characteristic usually referred to as its functionality. If a film-former has a functionality no greater than 2, it is capable of forming linear polymers only. If the film-former has a functionality of 3, it is capable of forming three-dimensional polymeric structures. The materials made up of linear polymers are known as thermoplastic, and also as non-convertible materials, since they soften when heat is applied, and remain soluble instead of being converted into insoluble materials. The materials consisting of three-dimensional polymeric structures are known as thermosetting, and also as convertible materials, since they do not soften appreciably when heated, and they become insoluble in the solvents from which they were applied [2].

1.4 Water-Borne Coatings

Before about 1950, almost all coatings were solvent-borne. The introduction of latex paints for architectural uses was the first major step away from solvent-borne coatings. Since 1970, there has been a further trend away from solvent-borne coatings because of higher solvent prices and particularly the need to reduce VOC (volatile organic chemical) emissions to meet air quality standards.

Because the solvents play a variety of important roles in resin manufacture, coating production, application, film formation and the properties of water are very different from those of organic solvents; this leads to distinct differences in characteristics of water-borne coatings as compared to solvent-borne coatings. Some of these differences are advantageous. For example, water presents no toxic hazard and it is odor-free. Water is not flammable; this reduces risks and thus insurance costs. There are no emission or disposal problems directly attributable to the use of water. With some formulations cleanup of personnel and equipment is easy and the cost of water-borne coatings is usually low.

On the other hand, there are some disadvantages to the use of water. For example, the heat capacity and heat of vaporization of water are high, resulting in high-energy requirements for evaporation. A further problem with water-borne coatings is that the water tends to increase corrosion of storage tanks, paint lines, ovens, and so forth. This requires that corrosion resistant equipment be used in water-borne coatings, increasing the capital cost [3].

1.5 Water-Borne Epoxy Resin

In recent years with the environmental legislation in various countries becoming stricter, water-borne coating has been becoming more important in the industrial coatings. Epoxy resin has outstanding chemical resistance and protective properties and because of this it is one of the most important materials in coating industry. Nowadays, the properties of water-based epoxy systems can generally match with their solvent-based counterparts in the many important application fields including the construction industry, building engineering, and corrosion protection [4]. In addition to water-borne coatings, waterborne epoxy systems have some main advantages and disadvantages. They are illustrated in Table 1[4-6] on the next page.

There are two ways to produce waterborne coating systems. The old method is to give a hydrophobic resin to water via an emulsion polymerization. To make the resin dispersed in water the use of emulsifiers is necessary [4, 5, 7-13]. While the former technology is simpler and cheaper, the latter one can achieve very fine and well distributed dispersion (nm particles) [14]. The new method is called water dispersed, or water reducible, where the resin is prepared in a solvent. To achieve water dispersibility, chemical modification is done to introduce polar groups to the polymer backbone [14-17]. Usually, anionic charges such as carboxyl groups are used to impart a salty group in the next step. After most of the solvent has been

Table 1.1 Advantages and Disadvantages of Waterborne Coatings Compared to Solvent-Based Epoxy Systems [4-6]

Advantages	Disadvantages
• Excellent adhesion on difficult substrates (e.g., various metals, wet concrete) • Excellent interlayer adhesion (even on "old" coatings) • Coating of plastics possible	• Shorter pot life • Gloss stability depending on formulation • Somewhat lower chemical resistance, especially to organic acids • Poorer protective properties (anticorrosive coatings)

removed, a tertiary amine as a base necessary for neutralization of carboxylic groups is added. Then, water is added to reduce the coating formulation.

The epoxy resins can be dispersed in water by different means. Epoxy resin can be reacted with different hydrophilic groups such as polyethylene glycol [18] or polyethylene oxide [16] instead of carboxylic acid salts.

Another method to achieve water dispersibility is to use maleic treated oil products which dry in air [19, 20].

In this study water dispersibility was obtained by using maleinized fatty acid. Fatty acids, which were produced from linseed oil, were used to insert carboxylic acid groups into the resin backbone as side branches. To prepare waterborne epoxy coating, solid epoxy resin, ethylene diamine, maleic anhydride, fatty acids of linseed oil were used. The samples were characterized by FTIR and H-NMR spectroscopies.

To accomplish the task, epoxy resin was reacted with EDA and, also fatty acid was combined with maleic anhydride. Finally, two products were reacted with each other. The carboxylic acid groups of product were neutralized with morpholine. Driers were added to accelerate the drying.

CHAPTER 2

LITERATURE REVIEW

2.1 Epoxy Resin in Surface Coating

The chemistry of epoxy resins at the present time is one of the most vigorously developing branches of polymer chemistry [21]. Epoxy resins, since they were introduced to the paint industry in the late 1940's, have assumed an important place in the spectrum of materials available to the paint chemist. This is because the highly versatile nature of these resins allows the formulation of a wide variety of coatings systems. These epoxy coatings range from industrial baking finishes that deliver the maximum performance in solvent and chemical resistance, to maintenance systems for corrosive environments and also include can linings, overprint varnishes, durable laminates, cold solders, lightweight foams, and potting compounds for all varieties of electrical and electronic apparatus and chemically resistant floor and wall coatings [22, 23].

Epoxy polymers contain the epoxide group, also called the epoxy, oxirane or ethoxyline group, which is a three membered oxide ring. The resin can be regarded as compounds, which contain more than one epoxide group per molecule. They are polymerized through these epoxide groups or hydroxyl groups in the resin using a crosslinking agent to form a tough three dimensional network. The crosslinking element is also called curing agent or hardener [24].

In the presence of a suitable catalyst, epoxy resins can be made to link with each other or with other polymers or high molecular weight species. It is the capability of the epoxy resin to react with a variety of reactants that gives these resins great versatility in coating applications [25]. Depending upon the choice of curing agent, these versatile resins can be made to cure, or harden, either slowly (several hours) or very quickly (less than 1 min) at room temperature or at elevated temperatures. Versatility is also achieved in performance. Epoxy resins can be formulated to yield a variety of properties ranging from soft, flexible materials, to hard, tough, chemical resistant products. They can be modified into low viscosity liquids for easy pouring or converted to solid compositions for laminating and molding applications [23].

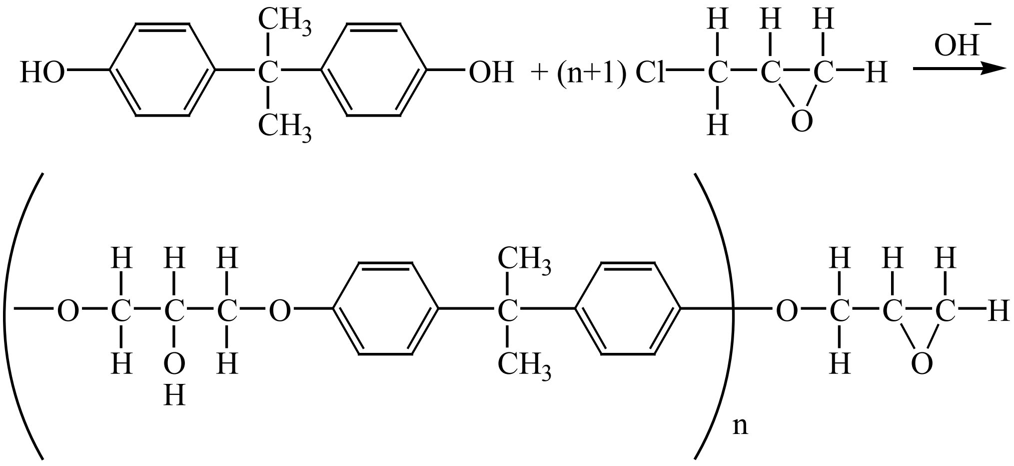
Epoxy resins are comparatively expensive and are only used in coating formulation when their superior properties are required. These properties include outstanding water resistance, good chemical resistance, particularly to alkaline environments, outstanding adhesion to a variety of substrates, excellent toughness, hardness and flexibility [25]. In addition, cured epoxy resins have good mechanical and electrical properties, superior dimensional stability, and good resistance to heat and chemical attack [23].

Epoxy resins vary in physical form as the molecular weight is increased. They range from a viscous liquid which is essentially a diepoxide and contains only a minor quantity of hydroxyl groups, to solid polyethers which are though epoxy terminated and contain principally hydroxyl groups as reaction sites [22].

Epoxy resins are characterized with their “Epoxide Equivalent Weight” (E.E.W.) which is defined as the “weight of resin containing one gram equivalent of epoxide”. The E.E.W. is also referred to as, “weight per epoxide” (W.P.E.) or “epoxy molar mass” (E.M.M.). All three terms are interchangeable. Most epoxy resins used in surface coating systems have epoxide equivalent weights (E.E.W.) between 180 and 3200. Epoxy resins with E.E.W.'s of 180 - 475 are used mainly in 'two-package' low temperature cure systems. Epoxy resins with E.E.W.'s in the range 700 – 1000 are normally used in epoxy-ester systems. Epoxy resins with E.E.W.'s in the range of 1500 - 3200 are used in stoving finishes [25].

2.1.1 Synthesis of Epoxy Resin Molecule

There are two major types of epoxy resins, the glycidyl ether epoxide resins, and epoxidized olefins. The glycidyl ether resin types are more important and they account for nearly all of the coating uses and the principle part of noncoating uses. The epoxy resins based on bisphenol A and epichlorohydrine are the most prominent of the glycidyl ether category and are produced by a condensation reaction in which the polyhydroxy compound and epichlorohydrine are reacted in the presence of alkali [22]. The reactions are shown below:



The reaction is always carried out with an excess of epichlorohydrine so that the resulting resin has terminal epoxy groups. Thus, by varying manufacturing conditions and the excess of epichlorohydrine, resins of low, intermediate, or high molecular weight may be produced [23].

The second major type of epoxy resins, the epoxidized olefins, is based on the epoxidation of the carbon-to-carbon double bond. Coating compositions derived from the epoxidized olefins have better weathering properties than analogous systems based on the bisphenol A glycidyl ether resins. However, they are inferior in general chemical resistance and for this reason they are not as widely used in the coatings field as the glycidyl ether types.

2.1.2 Curing of Epoxy Resin

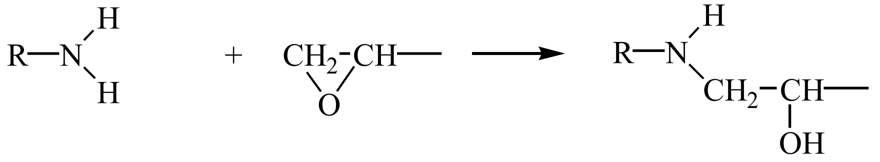
In order to proceed from the relatively low molecular weight of the coating composition, as applied, to the high molecular weight polymer necessary for optimum film properties, a "curing" or polymerization must take place. The curing mechanisms are quite diverse and may involve either the epoxide or the hydroxyl groups on the resin molecule, or a combination of both [22].

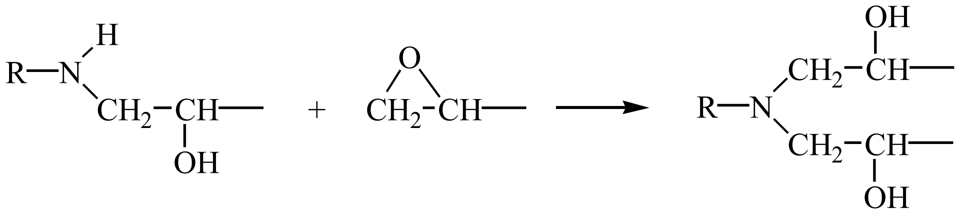
Epoxy resins can be cured or crosslinked by a large variety of chemical compounds. Namely, aliphatic and aromatic amines, acid anhydrides, and latent curing agents or catalysts. Other types of curing agents used in significant quantities in commercial applications are the phenols, carboxylic acids, ureas, inorganic acids and bases, and mercaptans. The high molecular weight epoxy resins are cured through the hydroxyl groups with phenols or ureas [23].

2.1.2.1 Amine – Epoxide Reaction

The terminal epoxy groups of the epoxy resins react with the active hydrogen groups of primary and secondary amines. Kinetic studies have shown that the conversion of primary amine to secondary amine proceeds at approximately the same rate as the conversion of the secondary amine to the tertiary amine. However, due to steric hindrance, the homopolymerization by the tertiary amine formed is a negligible reaction.

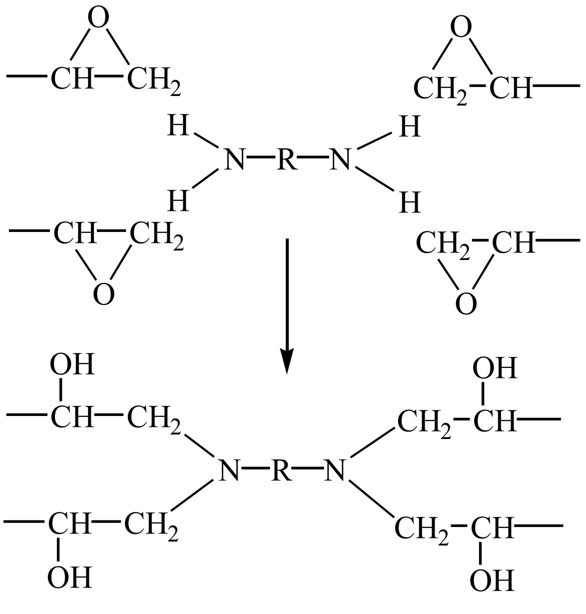
The following reactions proceed satisfactorily at room temperature, and most amine-cured systems are designed for ambient curing [22, 23].



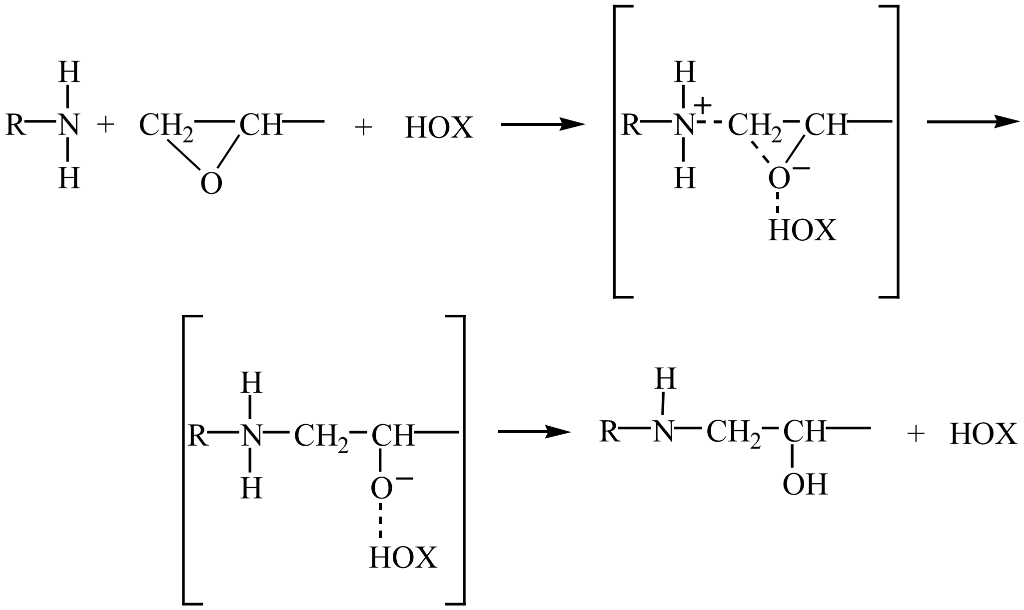


The aliphatic amines have higher reactivities than the aromatic amines therefore the former ones are preferred over the second ones [26, 27]. Several works has been reported in the literature concerning the mechanism of the reaction of epoxides with aliphatic amines [28-32].

The following illustration shows that a polyamine, in this case a diprimary amine, reacts with epoxide groups to form a crosslinked structure. Each of the four active hydrogens reacts with one epoxide group [23]. On the contrary, if excessive amine curing agent is used, it tends to stop chain building at low molecular weights, thereby embrittling the resin [33].



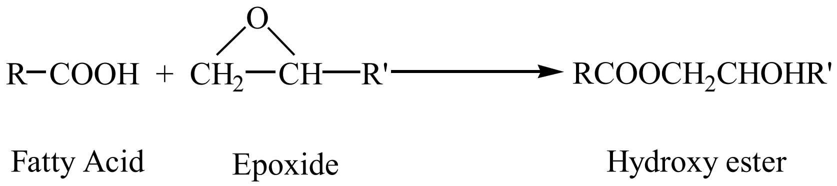
Several workers have shown that hydroxyl compounds or other materials capable of hydrogen bonding accelerate the reaction of amines with glycidyl ether resins, whereas some polar, non-hydrogen bonding compounds actually retard the reaction. The specificity of hydroxyl groups in accelerating the amine-epoxide reaction is illustrated below [23]. The effect of hydroxyl group on epoxy-amine reaction has been studied by many workers [29, 32, 34, 35].



2.1.2.2 Esterification Reaction

The esterification reaction between solid grade epoxy resins and carboxyl-containing compounds, particularly drying oil fatty acids, is of great commercial importance. The reaction products of epoxy resins and drying oil fatty acids represent an important class of coating vehicles.

Both the epoxide and hydroxyl groups on the epoxy resin molecule can take part in esterification. The epoxide group first reacts to form a hydroxy ester. This reaction is favored by basic catalysts, for example by sodium carbonate.



The carboxyl/hydroxyl reaction also takes place, both with the hydroxyl formed in the above reaction, and with hydroxyl already present on the solid epoxy resin molecule:

$$R{-}COOH + HO{-}R' \longrightarrow RCOOR' + H_2O$$

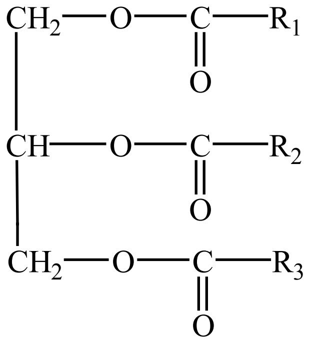
The esterification reactions require elevated temperatures (232-260°C) to proceed at a reasonable rate [22].

2.2 Oils and Fatty Acids

Glyceride oils are naturally occurring vegetable oils and marine animal oils. They occur as tri-glycerides of long chain fatty acids and are the reaction products of one molecule of glycerol and three molecules of fatty acid. The chain length of the acid can vary from C_{12} to C_{22}, but C_{18} is the most common species [25]. Oils are used by themselves as vehicles for coatings or in varnishes, alkyds, epoxies, urethanes and other polymers to impart drying properties as well as flexibility to the coating. Nondrying oils serve as plasticizers for many polymers used in coatings [36].

2.2.1 The Structure of Oils

Glyceride oils have the following general structure shown below:



where R_1, R_2, and R_3 are the fatty acid residues.

The variations in properties, encountered with different oils, are a function of the variation of fatty acid structure. Since more than one type of fatty acid can be present per oil molecule, the properties of a particular type can be directly related to the fatty acid composition [25].

2.2.2 Classification of Oils

Glyceride oils are usually classified as drying, semi-drying, or nondrying, and these deviations reflect the ability of the oil to 'air-dry', i.e. to form a coherent film on exposure to atmosphere. This ability is directly related to the fatty acid composition.

In general, when fatty acids containing at least two double bonds are present, the oil will react with oxygen from air to form a cross-linked network. The speed with which this occurs becomes greater if the double bonds are conjugated. Non-drying oils are unable to form a cross-linked structure by oxidation.

Greaves [25] attempted to quantify air drying of oil by using a drying index. This drying index is defined as the percentage of linoleic acid present, plus two times the percentage of linolenic acid present in the oil, that is:

Drying index = (% Linoleic acid + (2 × % Linolenic acid))

Drying indexes of greater than 70 indicate a drying oil.

Iodine value determinations can be used to measure the degree of unsaturation of oil, and this is useful in predicting the drying nature of the oil. It is the grams of iodine required per 100 grams of oil.

Saponification value defines the number of milligrams of potassium hydroxide required to saponify one gram of oil.

The acid value reflects the amount of free fatty acids in an oil. It is expressed as the number of milligrams of potassium hydroxide required to neutralize the acids in one gram of the oil. Table 2.1 on the next page shows the compositions and properties of drying oils [37].

2.2.3 Fatty Acids

Fatty acids are widely distributed in nature as components of lipids such as fats (esters of fatty acids with glycerol), waxes (esters of fatty acids with fatty alcohols), and sterol esters of triterpene alcohols. For manufacture of fatty acids on a commercial scale, only fats and oils available in large quantities are used as raw materials.

Although they have the same general formula, the fatty acids can vary considerably in terms of:

(i) the number of C=C double bonds (degree of unsaturation).
(ii) the relative positions of the double bonds (degree of conjugation).
(iii) the presence (or absence) of polar groups (such as OH or C=O) on the carbon backbone [25].

Table 2.1 Composition and Properties of Some Drying Oils [37]

	Special acids mol %	**Linolenic acid mol %**	**Linoleic acid mol %**	**Oleic acid mol %**	**Saturated acids mol %**	**Iodine value %**	**Specific gravity**	**Saponification value**	**Acid value**	**Refractive index**
Arachis (ground nut)	-	-	13-26	51-71	14-22	85-89	0.916-0.920	188-196	4-10	1.470-1.472
Cashew nut	-	-	7.7	74-77	16.5-18	79-85	0.911-0.918	187-195	1.4-1.6	1.462-1.463
Castor	Ricinoleic 80-85	-	3-4	7-9	10	82-90	0.958-0.969	176-187	1-4	1.477-1.479
Chia	-	41	47	0.7	8.4	200	0.934	192	0.6	1.485
Corn(maize)	-	-	39	43.4	8-10	103-125	0.921-0.928	188-193	4-8	1.467-1.474
Cotton seed	-	-	30-39	33-50	20-25	103-113	0.921-0.932	190-193	0.5-4	1.460-1.475
Hemp	-	24	53	12.6	10	148-155	0.927-0.932	190-193	4	1.477-1.482
Linseed(raw)	-	37-42	31.7-37	9-16	6-9	175-185	0.931-0.936	190-195	1-3	1.480-1.484
Lumbang(candle nut)	-	20.8	39.6	26.2	8.4	155-160	0.920-0.927	190-193	0.5-1	1.477-1.478
Niger seed	-	-	54-57	31-33	10-17	126-134	0.924-0.928	189-198	8	1.467-1.469
Oiticica	Licanic 73-75 Elaeostearic 4-9	-	-	4-6	11-13	179-218	0.966-0.969	188-192	3-15	1.514-1.516
Perilla	-	42.5	32-42	4-10	6-7	193-201	0.932-0.935	190-205	1-6	1.475-1.485
Poppy	-	-	62-65	25-30	7-8	133-169	0.924-0.927	190-198	0.7-3	1.475-1.478
Po-yok	Coupeic 41	-	-	9-10	12	140-157	0.955-0.965	188-192	1-17	1.502-1.516
Rubber seed	-	19.6	31.5	27.3	16	133-143	0.924-0.930	186-195	-	1.466-1.468
Safflower	-	0.7-1	51-67	26-38	6-10	140-150	0.925-0.928	188-194	5-6	1.468-1.469
Soya	-	2-6	50-60	26-30	11-14	125-140	0.923-0.929	188-194	0.3-3	1.468-1.478
Stillingia	-	8-11	52-58	25-26	6-9	160-180	0.936-0.946	204-210	3-10	1.482-1.483
Sunflower	-	-	52-58.5	34-42	6-9	120-135	0.924-0.926	189-194	4-7	1.474-1.479
Tobacco seed	-	-	60-70	16-20	9-10	130-145	0.923-0.925	186-197	1-8	1.474-1.482
Tung	Elaeostearic 72-86	-	-	4-18	4-6	155-170	0.939-0.943	189-197	5-10	1.519-1.522
Walnut	-	10-16	73	17-29	5-9	132-160	0.925-0.927	190-196	-	1.469-1.471

Properties of some fatty acids are shown in Table 2.2.

Table 2.2 Fatty Acids [37]

Acid	**Molecular formula**	**Number of double bonds/molecule**	**Occurrence**
Myristic	$C_{14}H_{28}O_2$	None	Non drying oils. Small quantities occur in some drying and semi-drying oils
Palmitic	$C_{16}H_{23}O_2$	None	
Stearic	$C_{18}H_{36}O_2$	None	
Arachidic	$C_{20}H_{40}O_2$	None	
Oleic	$C_{18}H_{34}O_2$	1	Majority of vegetable oils
Erucic	$C_{18}H_{34}O_2$	1	Rape oil
Ricinoleic	$C_{18}H_{34}O_3$	1	Castor oil
Linoleic	$C_{18}H_{32}O_2$	2	Most vegetable oils. High percentage in poppy seed, safflower, soybean, sunflower and tobacco seed
Linolenic	$C_{18}H_{30}O_2$	3	Linseed, perilla and stillingia oil
Elaeostearic	$C_{18}H_{30}O_2$	3	Tung oil
Licanic	$C_{18}H_{24}O_2$	3	Oiticica oil
Clupanodonic	$C_{22}H_{34}O_2$	4	Some fish oils

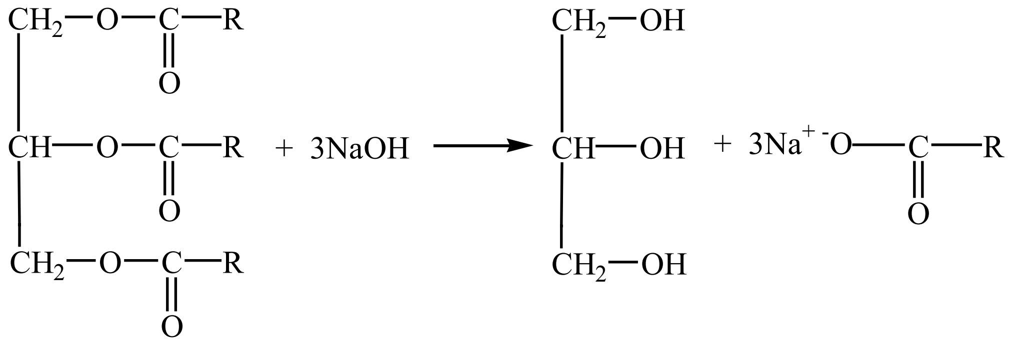
By splitting the glycerides, fatty acids and glycerol can be recovered. The most important splitting agents are water (hydrolysis), methanol (methanolysis), caustic soda (saponification), and amines (aminolysis). Because of drawbacks in the subsequent purification of glycerol, saponification and aminolysis are no longer commercially important. Exceptions are ricinoleic acid and hydroxystearic acid, which are produced commercially by saponification of castor oil and hardened castor oil, respectively. In this way, the esterification reactions that occur with the hydroxyl groups of ricinoleic and hydroxystearic acids during hydrolysis are avoided.

The reactants in the hydrolysis of fats form a heterogeneous reaction system made up of two liquid phases. The disperse aqueous phase consists of water and glycerol; the homogeneous lipid phase contains glycerides and fatty acids.

The hydrolysis reaction can be summarized as following:

Triglyceride + 3 Water → 3 Fatty acid + Glycerol

The hydrolysis of a fat or an oil in alkaline solution is called "saponification", and produces glycerol and a mixture of long chain carboxylic acid salts:



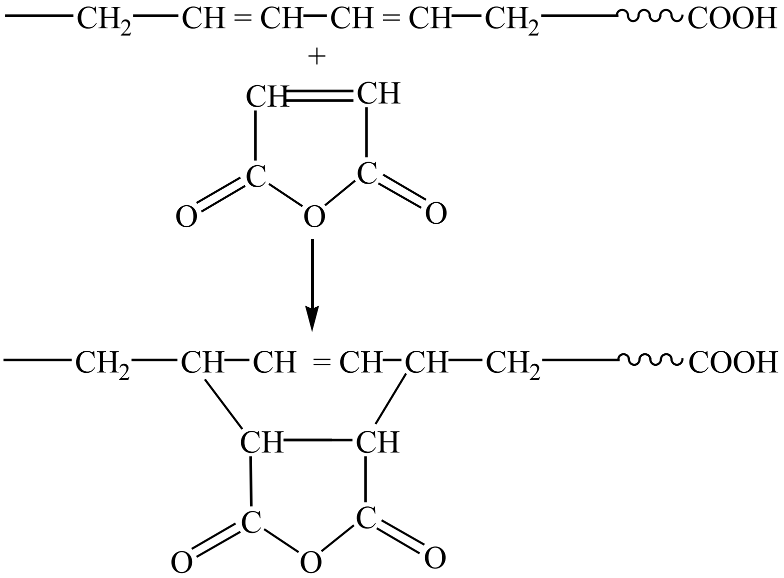
The fatty acids are obtained from soap by acidifying it with a mineral acid [38].

2.2.4 Maleinization

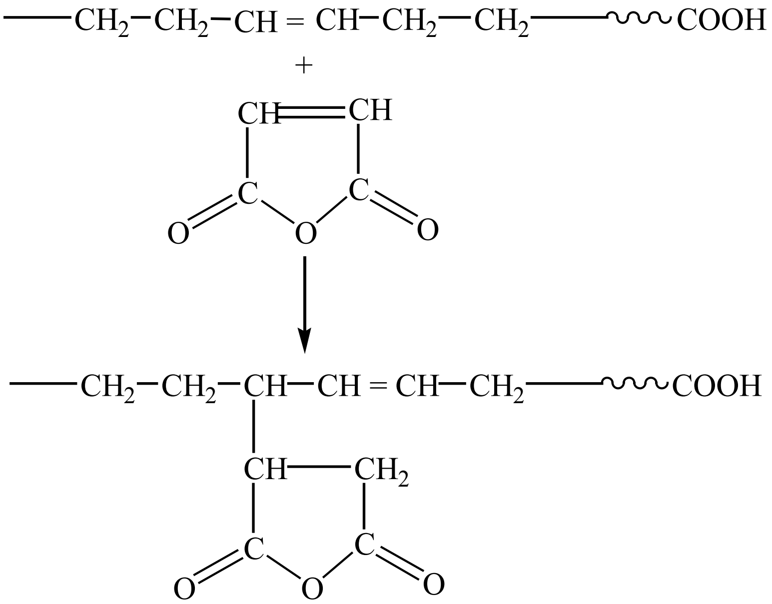
Oils are modified in several ways to improve their properties. Modification processes include isomerization, segregation, dehydration, and maleinization.

Maleinization of oils and fatty acids is of particular importance as a first step in the manufacture of water dispersible and water soluble systems. It is also a useful method of introducing controlled chain branching into an alkyd resin.

The reaction between maleic anhydride and conjugated fatty acids proceeds readily by Diels Alder type addition at moderate temperatures of about 120°C, in the following way:



When the non-conjugated fatty acids are involved, the reaction proceeds by attack on the active methylene groups and requires temperatures of about 200°C. This type of reaction is more commonly encountered in resin manufacture than the Diels Alder type. It takes place as follows:



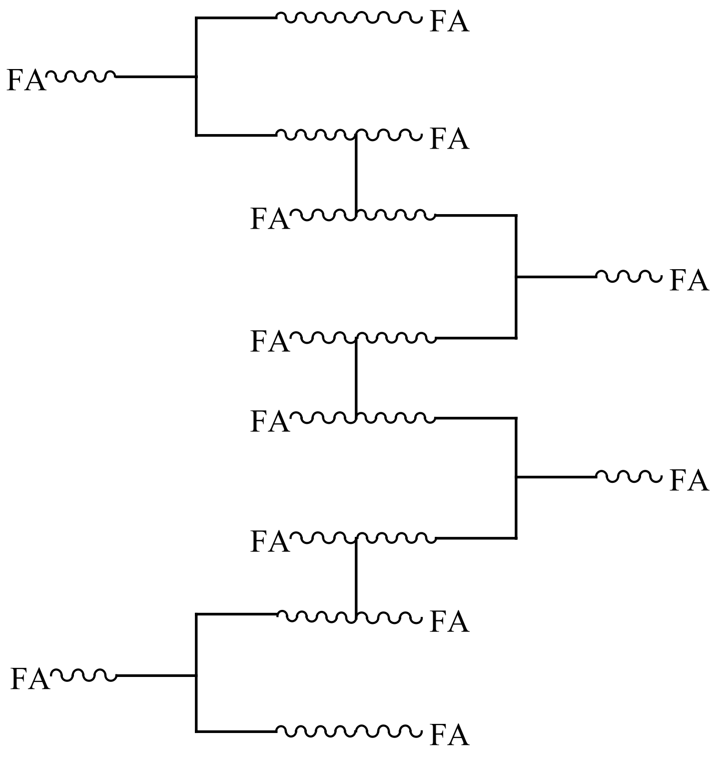
Although the ratio of maleic anhydride to oil may be varied from 1 to 6 moles maleic anhydride per 1 mole of oil, most promising results are usually obtained with 1-3 moles of maleic anhydride to 1 mole of oil.

The maleinized oils tend to be dark in colour coatings based upon them, obviously have tendency to yellow due to the use of unsaturated drying oils [25].

2.2.5 The Chemistry of Drying Process

There is general agreement that the drying of thin films of vegetable oils is characterized by a quiescent period, which is followed by oxygen absorption, peroxide formation, and peroxide decomposition [22].

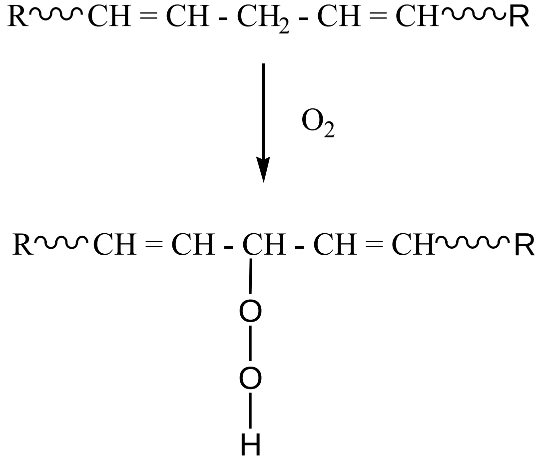
In general, conjugated and non-conjugated systems 'dry', or film form, by cross-linking. A cross-linked oil film may be represented as follows:



Where FA represents the fatty acid and —[represents the glycerol portion the of the oil molecule [25].

The simplest approach is to postulate oxygen attack at the site of the activated methylene, which is alpha to the C=C bond. This gives rise to hydroperoxide formation of a link to a neighboring fatty acid chain. The process differs somewhat for non-conjugated and conjugated systems, and there are several secondary reactions.

2.2.5.1 Non-conjugated Systems



$$R\sim\sim CH = CH - CH_2 - CH = CH\sim\sim R \xrightarrow{O_2} R\sim\sim CH = CH - \underset{\substack{|\\O\\|\\O\\|\\H}}{CH} - CH = CH\sim\sim R$$

The hydroperoxides then decompose, by dissociation of the O-O bond, leading to a variety of reaction products including intermolecular linkage, i.e. cross-linking:

$$R—OOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$2\,R—OOH \longrightarrow RO^{\bullet} + ROO^{\bullet} + H_2O$$

Then:

$RO^{\bullet} + R'H \longrightarrow ROH + {}^{\bullet}R'$ radical transfer to another molecule

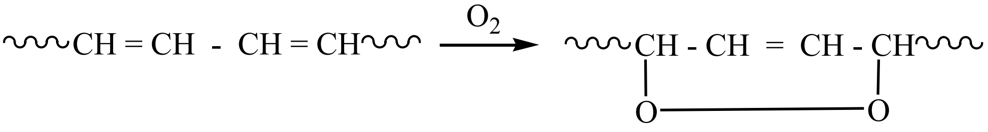
$${}^{\bullet}R' + {}^{\bullet}R' \longrightarrow R'-R'$$

$$RO^{\bullet} + {}^{\bullet}R' \longrightarrow R-O-R'$$

$$RO^{\bullet} + RO^{\bullet} \longrightarrow R-O-O-R$$

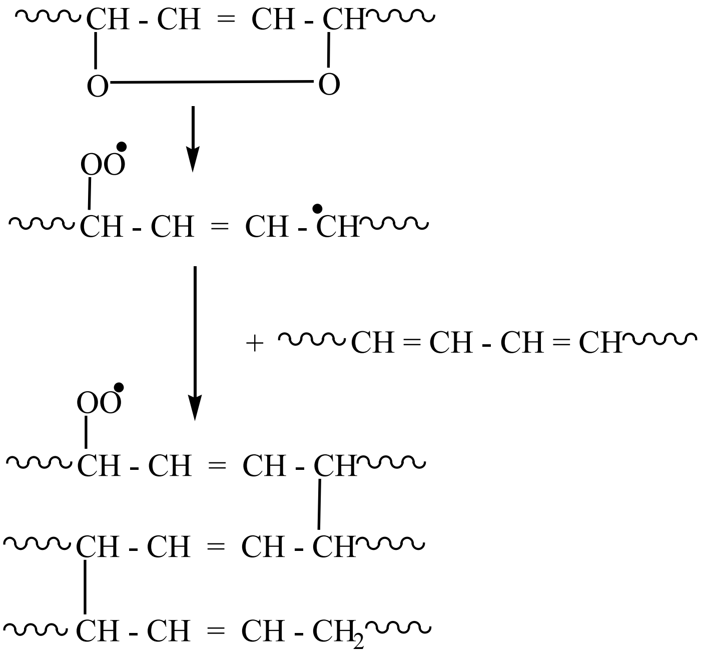
2.2.5.2 Conjugated Systems

In conjugated systems, the hydroperoxide formed is predominantly 1,4;



$$\sim\sim CH=CH-CH=CH\sim\sim \xrightarrow{O_2} \sim\sim \underset{|}{CH}-CH=CH-\underset{|}{CH}\sim\sim \quad (O-O)$$

The film formed differs from that formed by a non-conjugated structure in that the linkages are predominantly C-C suggesting a vinyl polymerization mechanism.

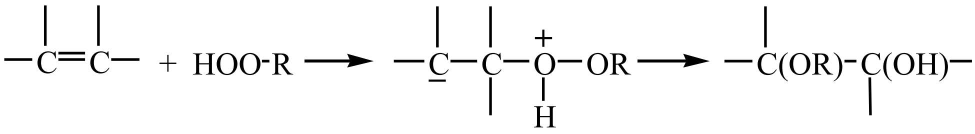


In practice the length of the polymerization chain is short because the probability of chain termination by oxygen is high.

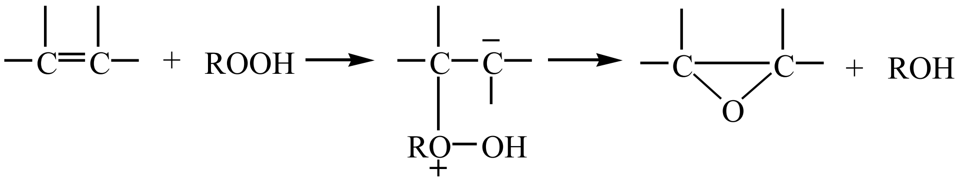
2.2.5.3 The Secondary Reactions in Drying Process

Several basic secondary reactions are presented to explain the presence of observed products of the oxidation of oils; among them are:

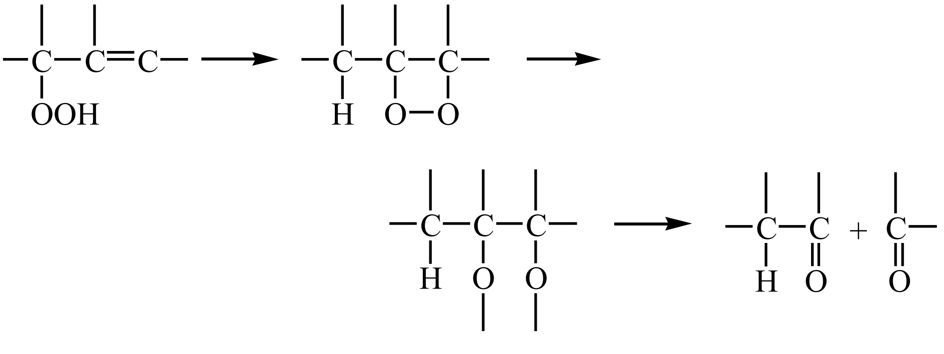
(a) Polymerization to give ether-type dimerides:



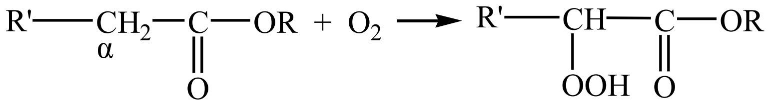
(b) Reaction of hydroperoxide with double bond:



(c) Scission of carbon chain at the double bond [39]:



(d) Oxidation of the alpha methylene group to the ester group in fully saturated oils:



However, this reaction takes place much more slowly than the oxygen attack on the carbon-carbon double bond, and it is a potential source of weakness, which can eventually play a role in film degradation [25].

2.2.6 Factors Affecting Film Formation

Several factors are of importance in influencing the crosslinking reactions.

The presence of several transition metals increases the possibility of peroxide breakdown by the formation of a redox system with the hydroperoxide:

$$\mathrm{ROOH} + \mathrm{Co}^{2+} \longrightarrow \mathrm{Co}^{3+} + \mathrm{RO}^{\bullet} + \mathrm{OH}^{-}$$

$$\mathrm{ROOH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{Co}^{2+} + \mathrm{ROO}^{\bullet} + \mathrm{H}^{+}$$

They may also act as oxygen carriers to initiate free radical formation:

$$\mathrm{Co}^{3+} + \mathrm{O}_2 \longrightarrow \mathrm{Co}^{3+}\!-\!\mathrm{O}\!-\!\mathrm{O}^{\bullet}$$

$$\downarrow$$

$$\mathrm{Co}^{3+}\!-\!\mathrm{O}\!-\!\mathrm{O}^{\bullet} + \mathrm{R}\!-\!\mathrm{CH}_2\!-\!\mathrm{CH}=\mathrm{CH}\!-\!\mathrm{R'}$$

$$\downarrow$$

$$\mathrm{Co}^{3+}\!-\!\mathrm{OOH} + \mathrm{R}\!-\!{}^{\bullet}\mathrm{CH}\!-\!\mathrm{CH}=\mathrm{CH}\!-\!\mathrm{R'}$$

$$\downarrow$$

$$\mathrm{Co}^{3+} + \mathrm{R}\!-\!{}^{\bullet}\mathrm{CH}\!-\!\mathrm{CH}=\mathrm{CH}\!-\!\mathrm{R'} + {}^{\bullet}\mathrm{OOH}$$

These metals are collectively referred to as driers and are of great importance in surface coating systems. Without the use of these catalysts, film formation would be so slow as to be commercially unacceptable particularly with non-conjugated oils [25].

The important driers are metallic soaps of lead, manganese, cobalt, calcium, and zirconium. The usual compounds are naphthenates, octoates (2-ethyl hexoates), and tallates [22]. Naphthenate driers remain the most widely employed and offer excellent overall properties such as good stability, light colour, low viscosity, high oxidation resistance and very good compatibility with solvents, oils and resins.

Octoate driers, prepared from 2-ethylhexoic acid, a synthetic acid of precise and uniform composition, also give excellent performance. The octoates have the best colour, lowest odor and lowest nonvolatile content of the three drier groups. In some alkyd systems, octoates function more efficiently than naphthenates. Octoates are especially effective under drying conditions of high atmospheric humidity.

Tallate driers, in many applications, can replace naphthenates on a direct pound-for-pound basis. Although tallates can occasionally demonstrate less stability and lower oxidation resistance than naphthenates and octoates, their overall good performance has established them as highly acceptable materials. Through constant developmental effort and progressive improvement in available tall oil acid raw materials, drier producers have consistently enhanced the colour and stability of tallate driers over the past decade [36].

There are three classes of dries:

1. Primary Driers: These are organic salts (e.g. octoates, tallates, and naphthenates) of transition metals, most usually manganese or cobalt. They directly catalyze the oxidation of the oil, and are normally employed in amounts varying from 0.005 to 0.1 % metal based on the oil. Their primary function is to promote rapid surface drying of the oil film [25]. Cobalt promotes rapid surface or top drying but poor through drying. Lead has weak surface drying effect but helps through drying. Manganese is similar to cobalt in effect but weaker [22].

2. Secondary Driers or Promotors: These are organic salts of zinc, calcium, lead, or barium. They do not have any direct catalytic effect on the oxidation when used on their own, but when used in conjunction with a primary drier, they act as synergists and considerably increase the oxygen uptake of the oil.

3. Co-ordination Driers: These are compounds of usually zirconium or aluminum, which assist the polymerization process by formation of co-ordination compounds. Zirconium acts as a through drier and is used as a replacement for the more toxic lead salts.

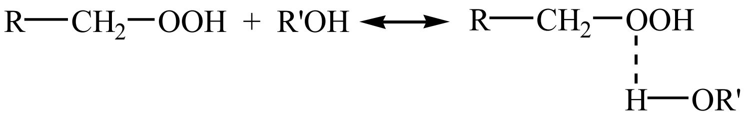
Promotors are usually used in the amounts varying from 0.05 to 0.5% metal, based on the oil, and improve the stability of the drier/oil combination, reduce the surface tension and promote through drying of the film [25].

Drier recommendations for aqueous systems usually show the active drier metal to be at least twice as high as for a solvent counterpart and should indicate the use of zirconium as the preferred auxiliary drier because of the susceptibility of lead to hydrolysis [22].

Water-dispersible driers may be prepared by adding non-ionic surfactants to naphthenate or synthetic acid driers. However, proprietary cobalt and manganese drier compounds are available that are purported to be more suitable for water-based coatings [40].

2.2.7 Effect of Polarity

The polarity of the medium or solvent has an effect on the rate of hydroperoxide breakdown and hence the drying of the oil. In the presence of high boiling polar solvents, the peroxides can be stabilized via hydrogen bond formation, hence this causes a decrease in the rate of drying.



$$R-CH_2-OOH + R'OH \longleftrightarrow R-CH_2-\underset{\underset{H-OR'}{\vdots}}{O}OH$$

This can occur also where polar groups are present in the oil either as natural impurities (e.g. phosphatides) or as part of the fatty acid structure (e.g. castor oil) [25].

CHAPTER 3

EXPERIMENTAL WORK

3.1 Raw Materials

The materials used to prepare samples are given as follows:

1. Liquid Epoxy Resin: It was commercially available from Paksoy Kimyevi Maddeler San. and Tic. A.Ş. and had an E.E.W. of 182-192.

2. Solid Epoxy Resin: It was commercially available from Akzo-Nobel Kemipol A.Ş. and had an E.E.W. of 475-550.

3. Ethylene Diamine (EDA): It was used as chain extender. (From Acros Organics, 99%)

4. 1, 4-Dioxane: It was used as an azeotropic solvent in polymer synthesis. (From Merck A.G.)

5. Linseed Oil: It was used to produce fatty acid. (From Volkan Boya A.Ş.)

6. Ethyl Alcohol: It was commercial grade and used as a solvent.

7. Sodium Hydroxide: It was used as saponifying reagent. (From Merck A.G., 97%)

8. Sodium Chloride: It was commercial grade and used as precipitating reagent.

9. Sulfuric Acid: It was used as acidifying reagent. (From JT.Baker, 96% pure)

10. Anhydrous Magnesium Sulfate: It was obtained from commercial $MgSO_4.7H_2O$ by hydrolysis and used in the drying of products.

11. Maleic Anhydride (MA): It was used for maleinization of fatty acids. (From Baker G., 99%)

12. p-Toluene Sulfonic Acid (PTSA): It was used as a catalyst in polymer production. (From Aldrich A.G., 98.5%)

13. Morpholine: It was used as neutralizing agent. (From Aldrich A.G.)

14. Nitrogen Gas: It was used to keep away oxygen from reaction medium and to remove water produced in reaction. (From Habaş, 99.5%)

15. Cobalt Octoate: It was used as top drier. (From Volkan Boya A.Ş.)

16. Lead Octoate: It was used as bottom drier. (From Volkan Boya A.Ş.)

3.2 Water Dispersed Epoxy Varnish Production

3.2.1 Preliminary Experiments to Synthesize the Prepolymer

To produce water dispersed epoxy resin, the liquid epoxy resin having an epoxy equivalent of 182-192 was reacted with EDA in the presence of 4-5 drops of water. The hydroxyl group in water made simpler epoxy ring opening and for this reason it accelerated epoxy-diamine reaction.

Different preliminary experiments were performed with changing reaction temperature (20°C-50°C) and epoxy/diamine ratio (2/1 to 1/1). In this procedure low molecular weight epoxy and EDA were agitated at different temperatures without solvent until the product hardened. It was seen that when the temperature was increased, the produced prepolymer hardened at shorter time and formed a crosslinked structure. High temperature accelerated the reaction of epoxy and amine groups and enhancing crosslinking.

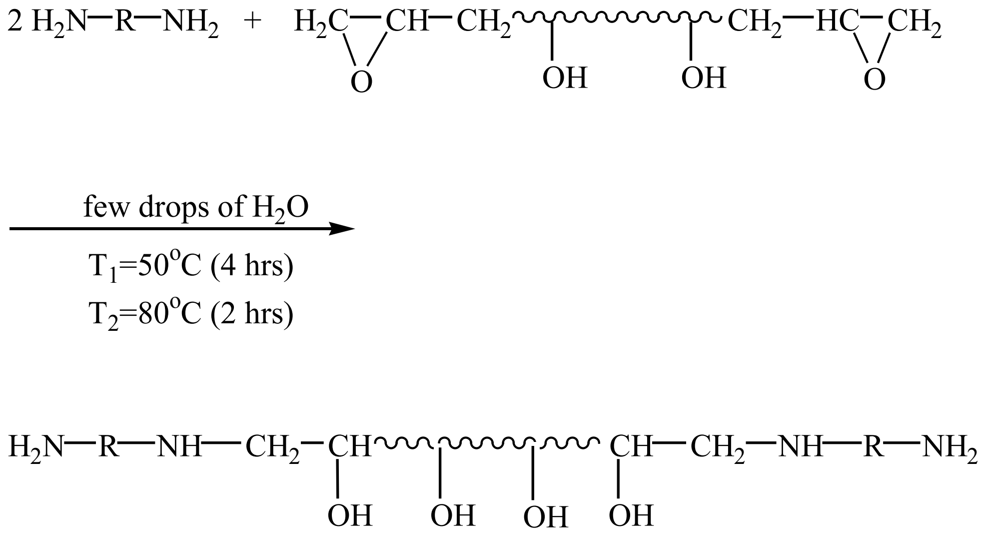
Toluene, xylene, pyridine, chloroform, acetone, and methyl ethyl ketone, which are good solvents for epoxy resin, were used as solvents for the production of the prepolymer. When the agitation time increased to 6 hours, it was seen that the produced prepolymer did not dissolve in any of these solvents. Therefore, it was decided that the epoxy/diamine ratio had to be changed to 1/2 resulting in the decrease of the number of epoxy and hydroxyl groups in the system. As a result, the liquid epoxy resin was no more preferred; instead a solid epoxy resin having higher molecular weight and consequently more hydroxyl groups was used.

By the end of 6 hours of production period, it was observed that the produced prepolymer dissolved in all solvents. However, the pyridinium chloride titration (see Appendix B) showed that the reaction did not complete in 6 hours. Relying on the results of the experiments, it was concluded that high temperature decreased the reaction time. Therefore, required reaction time was decreased with increased temperature.

In this case, the produced prepolymer could fully dissolve in only pyridine giving a dark-coloured solution, however, the sale of pyridine was quite restricted due to its harmful effects for human health. Then, other solvents were checked if they could solve the prepolymer. It was found out that the prepolymer could fully dissolve in 2-ethoxyethanol, and also 1,4-dioxane giving colourless solutions. 2-ethoxyethanol was not preferred because its hydroxyl group had the possibility of reacting with anhydride group in the next step of the course of reaction. Hence, 1,4-dioxane was used as a suitable solvent for the prepolymer.

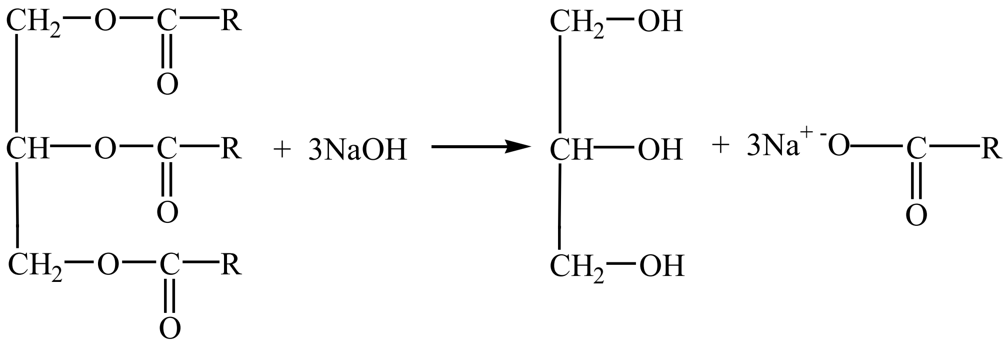
3.2.2 Synthesis of the Prepolymer

The solid epoxy resin of the bisphenol A type having an epoxy equivalent of 475-550 was dissolved in 1,4-dioxane (50% total mass). EDA was added to the solution in the presence of 4-5 drops of water at 50^oC for 4 hours under reflux and then was heated for half an hour to 80^oC and kept at 80^oC for 2 hours as shown below [41]. The end of the reaction was controlled by using pyridinium chloride titration method.



3.2.3 Synthesis of Fatty Acids

The fatty acids were obtained from linseed oil. The oil was mixed with stoichiometric amount of sodium hydroxide, which was dissolved in 1:1 ethanol-water solution. The required amount of sodium hydroxide was determined by using saponification value. The mixture was reacted at 80°C, under reflux, until a homogeneous mixture was obtained. Then, the mixture was poured into a saturated solution of sodium chloride in order to precipitate the soap. Then, soap was dissolved in water and reacted with a stoichiometric quantity of sulfuric acid. This separated the fatty acid phase from the water phase. Then, the fatty acid phase was washed with water for several times. Saturated fatty acids, which are solid at the room temperature, were separated from unsaturated fatty acid by centrifuging. Magnesium sulfate was used to remove water and saturated fatty acids suspended as colloidal particules in the produced fatty acid mixture. The saponification took place as follows:



$$\begin{array}{l} \mathrm{CH_2-O-C(=O)-R} \\ \quad | \\ \mathrm{CH-O-C(=O)-R} \\ \quad | \\ \mathrm{CH_2-O-C(=O)-R} \end{array} + \mathrm{3NaOH} \longrightarrow \begin{array}{l} \mathrm{CH_2-OH} \\ \quad | \\ \mathrm{CH-OH} \\ \quad | \\ \mathrm{CH_2-OH} \end{array} + \mathrm{3Na^{+}\,{}^{-}O-C(=O)-R}$$

Then, the fatty acid was produced in the following way:

$$\mathrm{Na^{+}\,{}^{-}O-C(=O)-R} + \mathrm{H_2SO_4} \longrightarrow \underset{\text{Fatty acid}}{\mathrm{R-COOH}} + \mathrm{NaHSO_4}$$

3.2.4 Synthesis of Maleinized Fatty Acids

The experimental set-up is shown in Figure 3.1. The experiment was performed in a 500 ml five-neck glass flask. Apparatus consisted of mechanical stirrer, condenser, thermometer, an inlet of feed and another inlet of nitrogen gas. The reactor was heated in an oil bath.

Fatty acids and maleic anhydride were reacted under inert gas atmosphere. The reactants were heated under agitation to 200^{o}C in 1.5 hrs, and then were held at 200^{o}C for 1 hr. The temperature was slowly increased to 230^{o}C (in about 30 min) and held there for about 2 hrs [2]. The unreacted maleic anhydride was removed from the reaction medium with the help of hot water, and the product was dried with magnesium sulfate.

3.2.5 Synthesis of Water Dispersed Epoxy Resin

1. The prepolymer and the MFA were reacted at 90^{o}C for totally 10 hours under N_2 atmosphere. PTSA was used as catalyst. The system was refluxed for 2 hours. Water produced in the reaction was removed with 1,4-dioxane by azeotropic distillation for 8 hours.

2. Driers were added to epoxy varnish before the neutralization step to obtain a homogeneous mixture. The mixture was stirred for 10 minutes for homogenization. The drier mixture consisted of cobalt octoate (0.08% of total solid mass) and lead octoate (0.8% of total solid mass).

3. Morpholine was added to the solution to neutralize the carboxylic groups, and the mixture was stirred for 30 minutes, while maintaining the temperature at 50^{o}C.

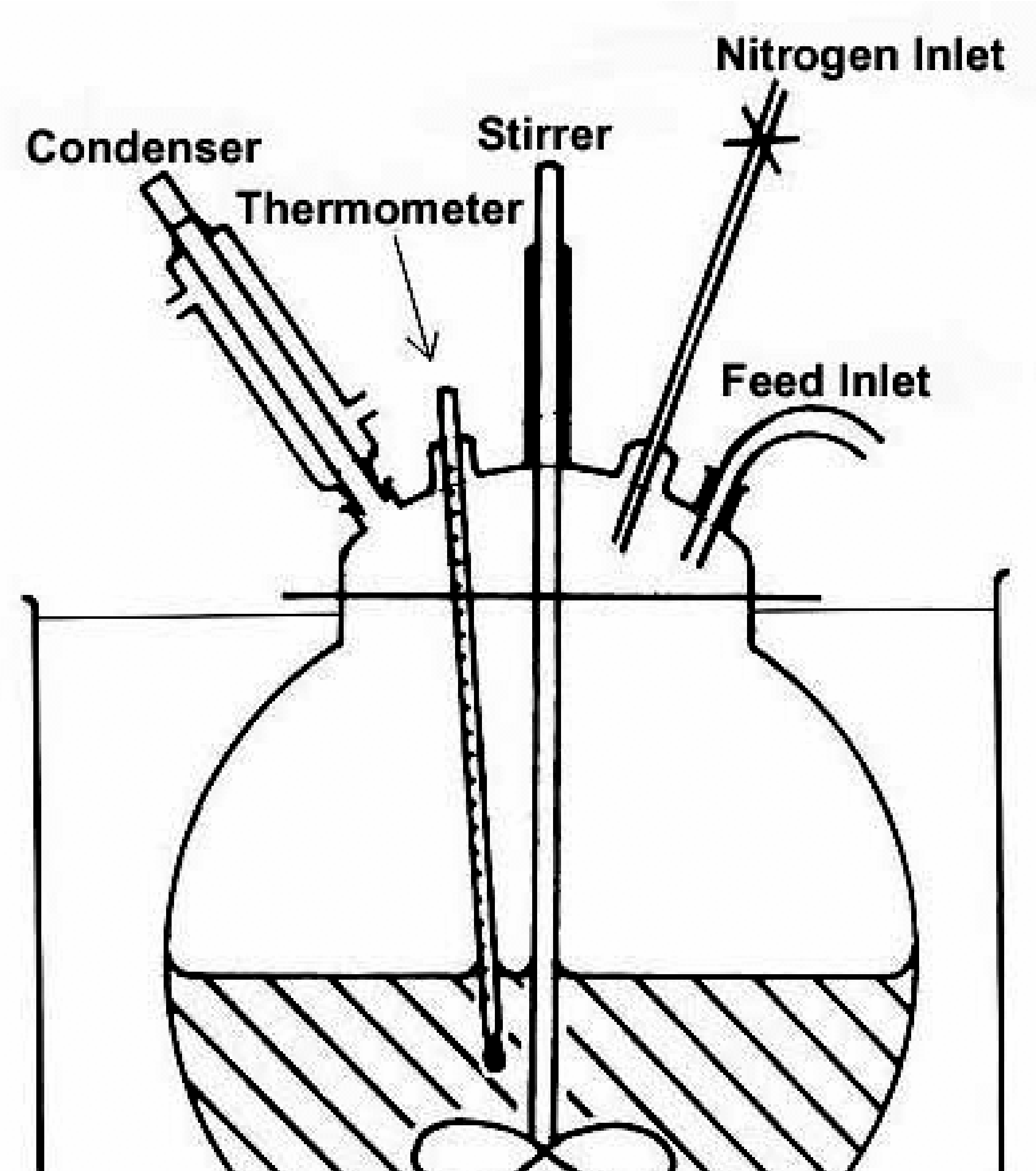


Figure 3.1 Experimental Setup for Maleinized Fatty Acid

4. For the stabilization of the dispersion, the stabilizing agents D-OP25 and D-25S were added to water. Water was added to the solution (50% of total mass) at 50°C from a stopcock burette dropwise in two or three seconds in the dispersion step. Trace amount of ammonia solution was added till the pH of the dispersion became 9. This step completed the production of water dispersed epoxy resin.

3.3 Chemical, Physical and Mechanical Tests

3.3.1 Proton Nuclear Magnetic Resonance (^{1}H-NMR)

A Bruker-Spectrospin Avance (DPX 400) Ultra-Shield Nuclear Magnetic Resonance instrument was used to characterize the maleinized fatty acid in $CDCl_3$.

3.3.2 Fourier Transform Infrared Spectrophotometer (FTIR)

Mattson 1000 FTIR Spectrophotometer was used to characterize the fatty acids and MFA by capturing a drop of the liquid sample in KBr pellets.

3.3.3 Preparation of Test Panels

50 µm wet film thickness was applied on glass and metal test panels by using film-casting knife (Braive-Instruments). Then, the test panels were left for air-drying for 24 hours and heated in an oven at 140°C for 5 hours. These test panels were used for all tests except hardness test. For hardness test, 5 hr baked period was tried for 140°C, and test panels were also baked at three different temperatures for 3 hrs, i.e. 120°C, 140°C, and 175°C.

3.3.4 Film Thickness Measurement

An Elcometer Thickness Gauge was used to measure the thickness of hardened varnish specimen on metal plates [42].

3.3.5 Gloss Measurement Test

A Braive-Instruments Glossmeter was used. It measures the intensity of light reflected from coating surface in three different directions. Metal and glass plates were used for measurements [43].

3.3.6 Pendulum Hardness Test

A Braive-Instruments Persoz Pendulum, (Model: 3034), was used. The coated glass plate was placed in hardness instrument and test was applied. Hardness of coating was measured from the number of oscillations of the pendulum swinging on the test panel. While the hardness of resin increased, the number of oscillations increased because the increase of hardness of a film decreased the effect of friction [44].

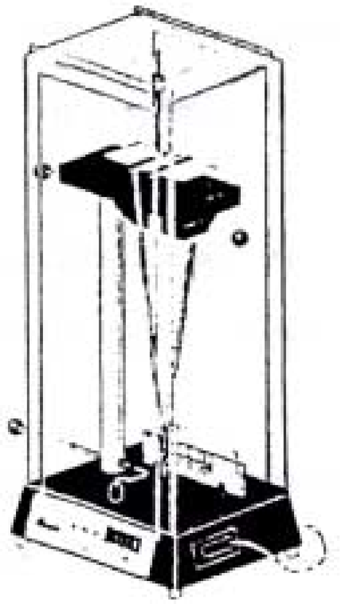


Figure 3.2 Hardness Pendulum Testing Instrument

3.3.7 Impact Resistance Test

A Gardner Impact Tester (Model: 5510) was used for impact test. A standard weight of (1+0.9) kg was dropped to a film coated on a metal plate from different heights. The value of potential energy at which failure occurred by cracking referred to impact value [45].

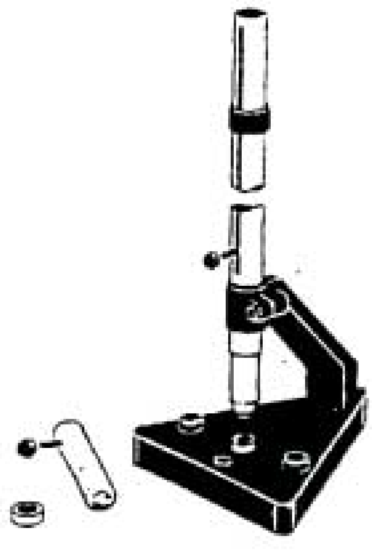


Figure 3.3 Impact Resistance Testing Instrument

3.3.8 Abrasion Resistance Test

This test method determines the resistance of coating film to abrasion produced by abrasive falling from a specified height through a guide tube onto a coated metal panel. Silica sand which was used as an abrasive agent was poured onto the coated panel until some scratching was detected. Abrasion value was determined from the change in the thickness of the film [46].

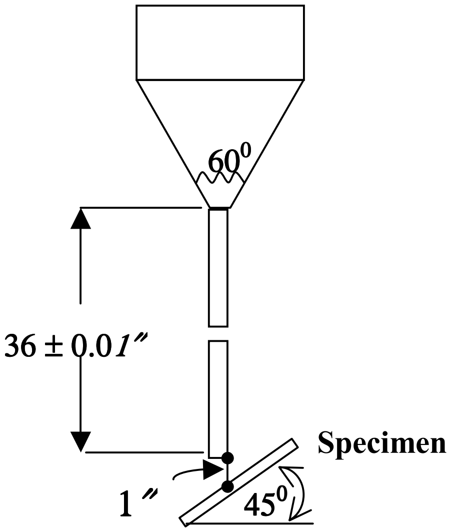


Figure 3.4 Abrasion Resistance Measurement Instrument

3.3.9 Mandrel Bending Test

A conical Mandrel Bending Tester (Braive-Instruments, Model: 1510) was used for this test. After the prepared test panel was fastened, it was bent over, and cracks were observed along the increasing radius of the conical mandrel. The ability of resin to resist cracking when elongated shows the flexibility of coatings [47].

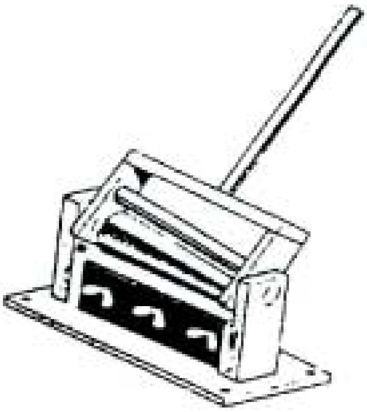


Figure 3.5 Mandrel Bending Instrument

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization

The chemical characterization of the products was done using ^{1}H-NMR and FTIR spectroscopy.

4.1.1 ^{1}H-NMR Spectroscopy

The characterization of MFA was done by using ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectroscopy of a mixture of MA and fatty acid was also obtained. Figure 4.1 shows the ^{1}H-NMR spectroscopy of MA-fatty acid mixture, and Figure 4.2 shows that of MFA.

The results showed that the double bond of MA disappeared after the reaction. In Figure 4.1, the peak at 7 ppm denotes the double bond of MA, and it disappears after the reaction of MA with fatty acid as seen in Figure 4.2. Other peaks appear in both figures because they have similar structures. The peak at 5.2 ppm covers carbon-carbon double bond of the fatty acid residue. The peak at 2.7 ppm corresponds to β-CH_2- groups adjacent to double bonds in the fatty acid residue, and the one at 2.25 ppm denotes the CH_2- groups adjacent to the ester bond (O=C-O-) and the groups that are not bonded to the carbon atoms in the double bonds. The peak

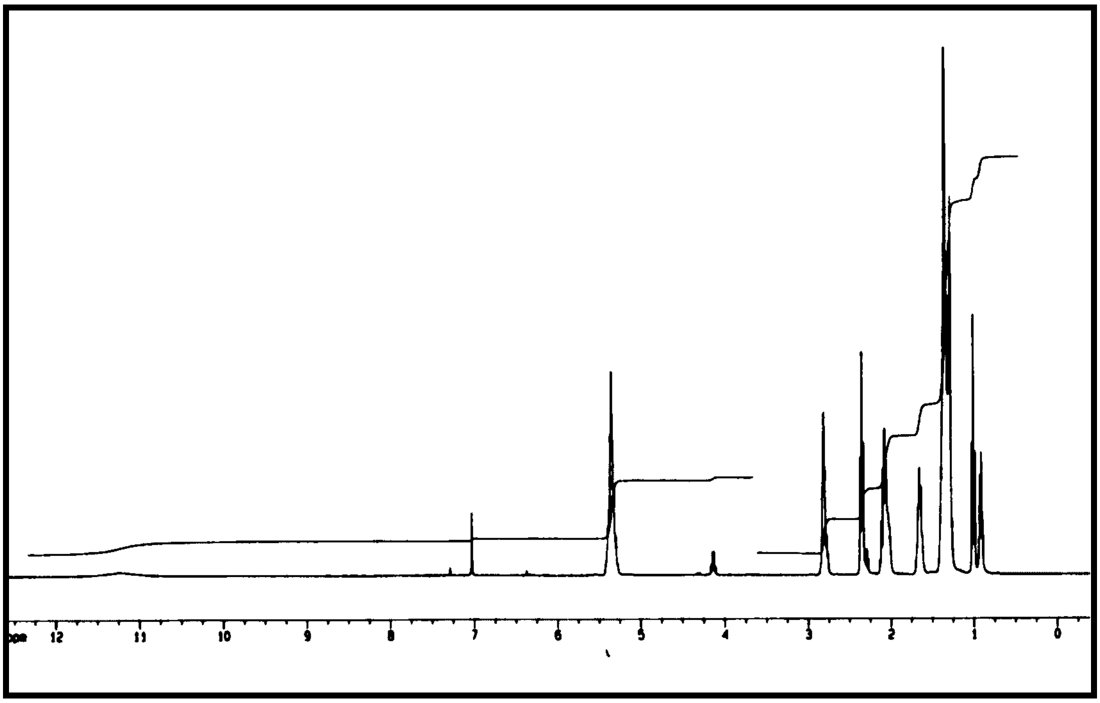


Figure 4.1 ^{1}H-NMR Spectrum of Maleic Anhydride-Fatty Acid Mixture

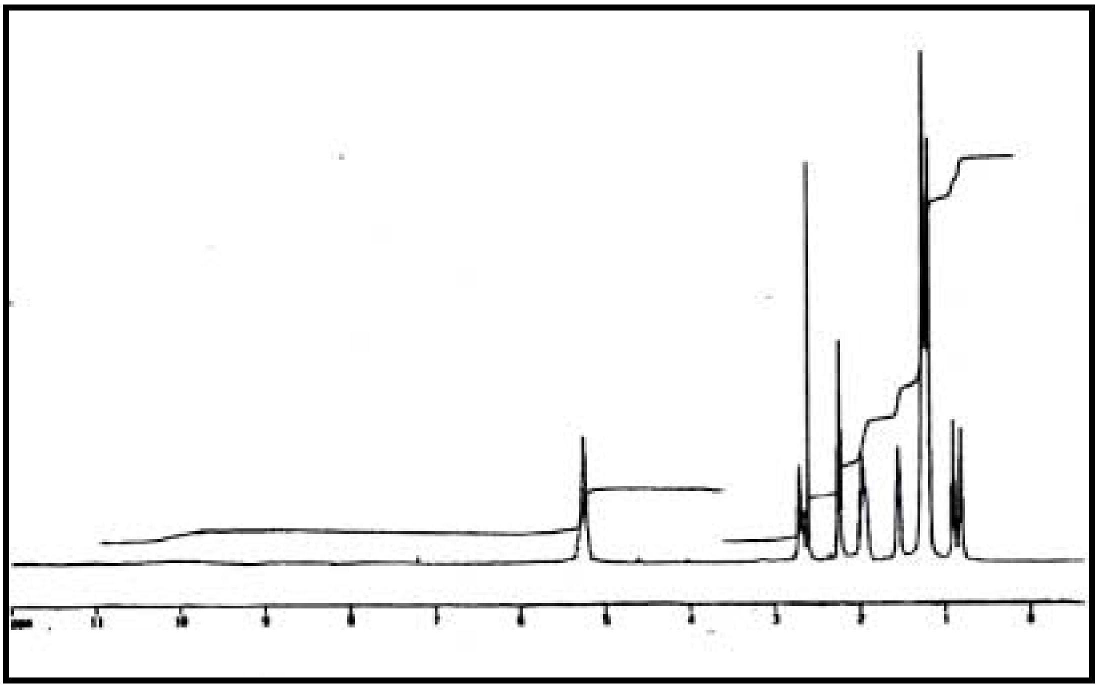


Figure 4.2 ^{1}H-NMR Spectrum of Maleinized Fatty Acid

at 1.9 ppm corresponds to the -CH_2- groups adjacent to the double bond from fatty acid. The peak at 1.6 ppm corresponds β-CH_2- adjacent to the ester bond (O=C-O-) and the one at 1.3 ppm denotes the saturated -CH_2- groups adjacent to methyl groups in the fatty acids. The peak at 0.9 ppm denotes the -CH_3 group in the fatty acid.

4.1.2 FTIR Spectroscopy

The IR spectra of fatty acid and MFA are shown in Figures 4.3, 4.4, respectively.

The IR spectrum for fatty acids of linseed oil is shown in Figure 4.3. The small shoulder at 3012 cm^{-1} corresponds to unsaturated CH stretching, and the peak at about 2900 cm^{-1} corresponds to CH stretching. The peak at 2667 cm^{-1} and the peak at 2554 cm^{-1} are due to the hydrogen bonded O-H of carboxylic acid. The carboxylic group gives two peaks at 1712 cm^{-1} from C=O stretching and at 1288 cm^{-1} from C-O stretching. The peak at 1460 cm^{-1} corresponds to –CH_2 bending and the broadening in the peak is due to O-H deformation. The bending of O-H dimer of carboxylic acid groups gives a peak at 937 cm^{-1}, and the peak at 718 cm^{-1} corresponds to multiple CH_2 split due to $(CH_2)_n$ and the broadening in the peak is due to cis C=C group.

The IR spectrum for MFA is shown in figure 4.4. The small shoulder at 3098 cm^{-1} corresponds to unsaturated CH stretching, and the peak at about 2900 cm^{-1} corresponds to CH stretching. The peak at 2667 cm^{-1} and the peak at 2567 cm^{-1} are due to the hydrogen bonded O-H of carboxylic acid. Two peaks at 1858 cm^{-1} and at 1785 cm^{-1} corresponds to the carbonyl stretching of anhydride group. The carboxyl group gives two peaks at 1712 cm^{-1} from C=O stretching and at 1288 cm^{-1} from C-O stretching. The peak at 1460 cm^{-1} corresponds to –CH_2 bending and the broadening in the peak is due to O-H deformation. The bending of O-H dimer of carboxylic acid groups gives a peak at 923 cm^{-1}, and the peak at 724 cm^{-1} corresponds to multiple CH_2 split due to $(CH_2)_n$, and the broadening in the peak is due to cis C=C group.

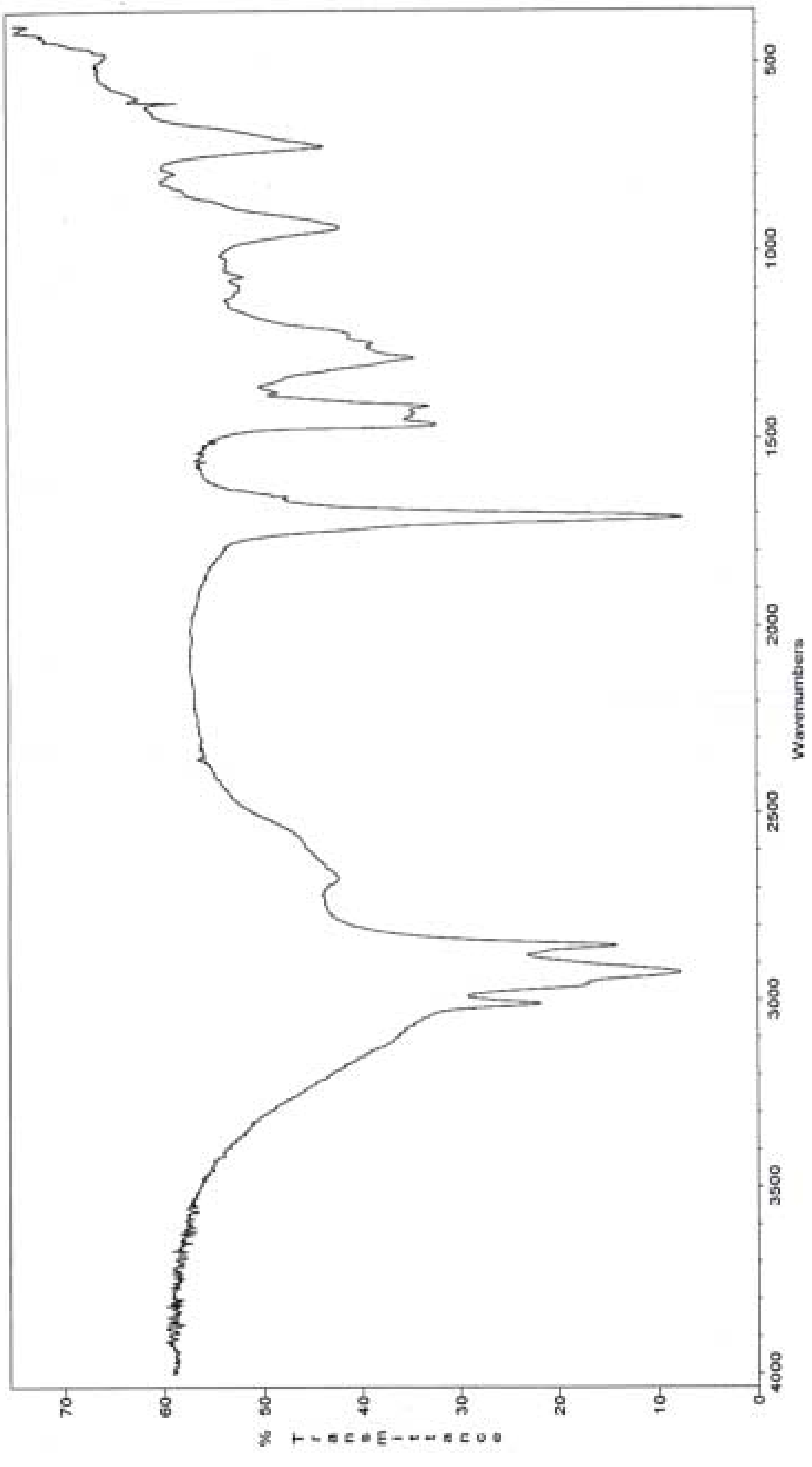


Figure 4.3 IR Spectrum of Fatty Acid

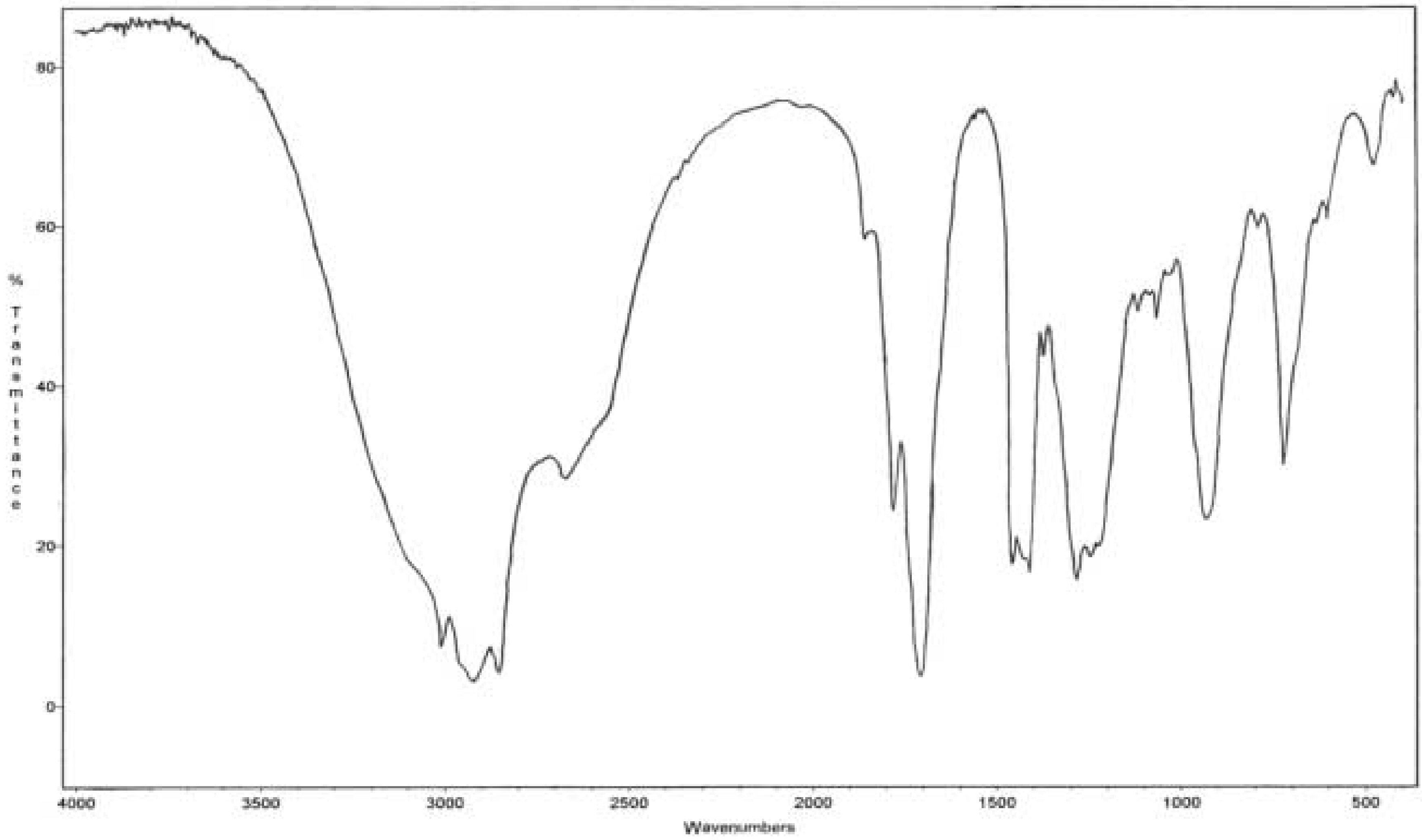


Figure 4.4 IR Spectrum of Maleinized Fatty Acid

4.2 Gloss Test

The gloss values of the produced resin are listed in Table 4.1 for metal and glass plates at angles of 20^o, 60^o, and 85^o. The resin showed outstanding gloss properties in all angles.

Table 4.1 Gloss Values of the Resin on Glass and Metal Plates

Substrate	20^o	60^o	85^o
Glass	81.3	96.5	98.3
Metal	62.4	85.8	86.3

A gloss meter measures the specular reflection. The light intensity is registered over a small range of the reflection angle. The intensity is dependent on the material and the angle of illumination. The amount of reflected light increases with the increase of the illumination angle as seen from Table 4.1. The remaining illuminated light penetrates the material and is absorbed or diffusely scattered. The gloss value of the resin on glass plate was found to be higher than one on metal plate as seen from Table 4.1.The glass plate having higher refractive index than metal has higher ability to reflect light. The glass surface reflects the diffracted light yielding higher gloss. If the gloss value observed at 60^o is higher than 70, is said to be in ‘high gloss’ range. It is in ‘semi gloss’ if it is between 10 and 70; and in ‘low gloss’ range if it is below 10. Therefore, it can be easily said that the produced resin has high gloss property.

4.3 Hardness Test

The resin was baked at three different temperatures for hardness test. The film baked at 120^oC was soft and it could be easily deformed. So it was excluded from hardness test. On the other hand, the hardness value of the baked resins at 140^oC and 175^oC was found to be 14 Persoz unit. So the increase of the baking temperature did not introduce any significant increase in hardness.

The hardness value of the resin increased from 14 to 18 Persoz unit by extending baking time from 3 hrs to 5 hrs at 140°C. The extended time of baking should have increase of crosslinking of the resin, which, in turn, increases hardness. The increase of the temperature to 175°C probably led to other reactions which adversely affected the hardness although crosslinking possibly increased.

4.4 Impact Resistance Test

The specimen showed no cracking in impact test. The impact resistance value was found to be higher than 19 J. This is the maximum value which can be measured on impact instrument.

4.5 Abrasion Resistance Test

The abrasion resistance is also a measure of the coating’s toughness as hardness and impact resistance. The test result is given in terms of the amount of sand required to remove a certain thickness from coating. The abrasion resistance value for the produced resin was found to be 16.83 kg/μm.

4.6 Mandrel Bending Test

The resin successfully passed the mandrel bending test. Any crack formation by elongation was not observed on the film surface. This implies that the baked resin has sufficient flexibility.

4.7 Colour of the Varnish Films

The varnish left at the room temperature for 24 hours formed a yellow coloured transparent film. The varnishes baked for 3 hours tended to get darker with the increase of baking temperature, i.e. 120°C, 140°C, and 175°C. The increase of baking time from 3 to 5 hrs at 140°C did not change its colour but improved the hardness of the baked product.

The linseed oil tended to get dark because of its high degree of unsaturation. While the double bonds in the linseed oil reacted with oxygen in air, the colour of the oil got dark. Therefore, the increase in baking temperature accelerated the formation of hydroperoxide resulting in darker colour of the resin.

4.8 Comparison of Some Mechanical and Physical Properties of Different Resins

Several studies about hardness and abrasion resistance properties of resins were performed in our laboratory. Different values of hardness and abrasion resistance were taken depending on the methods of syntheses and details. The studies can be separated into two different groups according to the resin types; alkyds and polyurethanes.

While the hardness of alkyd resins changed between 57 and 245 Persoz unit [48-50], the hardness of polyurethane resins changed between 22 and 140 Persoz unit [19, 20, 26, 51-53]. The effect of flame retardant agent on hardness was investigated for both types of resins [49-51, 53]. The hardness of produced epoxy varnish changed between 14 and 18 Persoz unit in my study and it gave the lowest hardness value among all resins. Hardness changes depending on branching and crosslinking of resins. It can be said that the resin produced in this work, i.e. epoxy resin, has less side branches than the other resins and less crosslinking between these branches which resulted in low hardness values.

As for the abrasion tests; one study was based on two types of alkyd resins and four different other studies were based on polyurethane resins in our laboratory. The abrasion resistance of alkyd resins changed between 15 and 120.2 kg/µm [50]. While no significant loss of film thickness was reported in two studies on polyurethane

[19, 20], the abrasion resistance of polyurethane resins changed between 4.08 L/µm (≈ 8.24 kg/µm) and 50 kg/µm in other two studies [51, 53]. The abrasion resistance of produced epoxy varnish of this work was found as 16.83 kg/µm. Therefore, the abrasion resistance value of the epoxy varnish is lower than the average value of the other resins.

CHAPTER 5

CONCLUSIONS

1. The amount of 1,4-dioxane should be at least 50% of the total mass of the prepolymer to prevent gelation.
2. The epoxy resin was extended with ethylene diamine for chain extension. The ratio of both components has to be adjusted to prevent gelation.
3. Epoxy resin could be made water dispersed by using maleinized fatty acids which join with the backbone as side branches.
4. The varnish showed excellent gloss properties in all angles.
5. The resin cured at 120^{o}C was very soft, while the ones cured at 140^{o}C and 175^{o}C were sufficiently hard.
6. The hardness of the resin showed an increasing trend as the baking time increased.
7. The cured resin showed superior impact resistance greater than 19 J.
8. The cured resin showed small abrasion.

9. No cracks on the film were observed after bending test.

10. The increase of curing temperature from 140°C to 175°C caused increased darkening, but did not increase the hardness.

CHAPTER 6

RECOMMENDATIONS

1. Different aliphatic or aromatic amines can be used in order to study their effect on the resulting film properties.

2. The dispersion properties of water dispersed epoxy resin can be investigated by changing the amount of maleic anhydride.

3. Sunflower oil fatty acids can be used instead of linseed oil fatty acids to obtain lighter colour resin.

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APPENDIX A

OPEN STRUCTURES OF SOME COMPOUNDS

1. Some fatty acids

Oleic Acid

$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COOH$

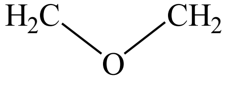
Linolenic Acid

$CH_3 - (CH_2 - CH = CH)_3 - (CH_2)_7 - COOH$

Linoleic Acid

$CH_3 - (CH_2)_4 - CH = CH - CH_2 - CH = CH - (CH_2)_7 - COOH$

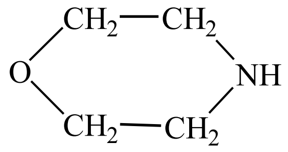
2. 1,4-Dioxane



3. Ethylene diamine (EDA)

$H_2N - CH_2 - CH_2 - NH_2$

4. Morpholine



APPENDIX B

DETERMINATION OF EPOXIDE EQUIVALENT BY THE PYRIDINIUM CHLORIDE METHOD [54]

Reagents:

1. 0.2 M pyridinium chloride in pyridine (16 ml conc. HCl per liter of pyridine)
2. Standardized 0.5 M methanolic NaOH (20 g NaOH per liter)
3. Phenolphthalein indicator (0.1 g phenolphthalein per 100 ml methyl alcohol)
4. Methyl alcohol, reagent grade

Procedure:

Place a weighed sample of epoxy compound (2 to 4 milliequiv.) into a 200-ml round-bottom flask. Pipet 25 ml of pyridinium chloride-pyridine solution into another 200-ml flask. This will be used as a blank throughout the procedure. Swirl the solution until all the sample has been dissolved, heating gently if necessary. Use a heating mantle plus a magnetic stirrer. After the sample has dissolved, add a reflux condenser, and reflux at 115^{o}C and stir the solution for 25 min. After refluxing, cool the solution with the condenser in place. Add 50 ml of methyl alcohol through the reflux condenser and let drain. Remove the reflux condenser. Add 15 drops of phenolphthalein indicator. Titrate with 0.5 M methanolic NaOH from a 10-ml buret to a pink end point.

Calculation:

$$\text{Epoxide equivalent} = \frac{(16).(\text{sample weight, g})}{(\text{g of oxirane oxygen in sample})}$$

Grams of oxirane oxygen in sample = (A – B)(M)(0.016)

A = milliliters of NaOH for blank

B = milliliters of NaOH for sample

M = molarity of NaOH

0.016 = milliequivalent weight of oxygen in grams