

EPOXIES  
THEIR RECENT APPLICATIONS  
IN AMERICAN INDUSTRY

139

by

MITHOO RAMCHANDANI

B.S., University of Poona, India, 1962

---

A MASTER'S REPORT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Industrial Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1965

Approved by

A E Hartnett  
Major Professor

LD  
2/6/68  
P4  
1965  
R.168  
CP2

TO  
MY PARENTS

## TABLE OF CONTENTS

INTRODUCTION. . . . .	1
General Information . . . . .	1
Rapid Growth of Plastics . . . . .	2
Plastics as Materials In Industry . . . . .	2
Extent of The Industry . . . . .	4
Plastics Industry . . . . .	5
The Materials Manufacturer . . . . .	6
The Processor . . . . .	6
The Fabricator and Finisher . . . . .	7
Production in The Industry . . . . .	7
Plastics - Thermoplastic and Thermosetting . . . . .	7
EPOXY RESINS . . . . .	8
History . . . . .	10
The Resin Intermediates . . . . .	11
Modified Definition of Epoxy Resin . . . . .	16
Industrial Epoxy Resins . . . . .	16
Type of Epoxy Groups . . . . .	17
Location of Epoxy Groups . . . . .	18
Number of Epoxy Groups . . . . .	18
Curing the Liquid Epoxy . . . . .	19
Catalytic Cure . . . . .	19
Crosslinking Agents . . . . .	21
Curing Agents for Epoxy Resins . . . . .	21
The Exotherm . . . . .	22

Flexibilizing Modifiers for Epoxy Resins . . . . .	23
Reinforcements, Fillers, Thixotropic Agents, Colorants.	24
PROPERTIES AND SELECTION FACTORS . . . . .	25
PRICES IN THE PLASTICS INDUSTRY . . . . .	31
HANDLING EPOXIES . . . . .	31
APPLICATIONS OF EPOXIES . . . . .	33
Tooling for Working of Metals . . . . .	33
Laminated Tools . . . . .	34
Surface Cast Tools . . . . .	34
Mass Cast Tools . . . . .	35
Paste Plastic Tools . . . . .	35
Comparison of Tooling Methods . . . . .	36
Adhesives From Epoxies . . . . .	37
Applying the Adhesive . . . . .	39
Epoxy Resins in Surface Coatings . . . . .	40
Epoxies For Electrical Embedments . . . . .	43
Miscellaneous Structural Epoxies . . . . .	45
FUTURE OF EPOXIES . . . . .	50
BIBLIOGRAPHY . . . . .	52
ACKNOWLEDGEMENT . . . . .	53
APPENDIX . . . . .	55

## INTRODUCTION

### GENERAL INFORMATION

Plastics have developed into the wonder material of the 20th century. The homes we live in, the clothes we wear, our food and our automobiles have all been improved by plastics in one form or another. Industry has made widespread use of plastics.

However, this does not mean that we are entering the age of plastics. No, we are entering the age of materials, an age where we can and must choose our materials not from one or more narrow groups, but from a broad and very nearly continuous spectrum of materials. (1)

If we look back into the history of materials, we find that in one respect at least, plastics are unique. Most materials have developed within a specific application area to satisfy a particular need. Metals, for example, were developed primarily for ornaments or machines....textiles for clothing....stone and wood for building....and glass for windows. And to a great extent, most of these materials continue to confine themselves to these same areas of application.

The entry of plastics into the materials field constitutes the only real exception to this orderly procedure. Plastics were not developed to satisfy any single pressing need but rather are emerging as competitors in all areas. Now there are plastic guns, complete with reinforced plastic barrels, and even plastic cartridges. Plastic or synthetic fibers and films

are commonplace in clothing today. There are plastic building panels, plastic windows and plastic paper. The list is endless.

#### RAPID GROWTH OF PLASTICS

Why are plastics growing so rapidly compared to other materials? There are three basic reasons. The first is cost. We are all painfully aware of the progressively increasing prices of most materials over the last ten years. However, the average price of plastics has gone down consistently, and there is every indication that this trend will continue.

The second reason involves the growing realization that plastics are not merely substitutes, but rather that they are a group of basic engineering materials. This was not always the case. During the early days of World War II, plastics were strictly substitutes for practically everything that was in short supply. And because they were considered merely temporary substitutes and not competitive materials, there was very little engineering or design time wasted on them. In many instances the word plastic was merely substituted on a blueprint for steel or aluminum or brass and then the part went directly into production. (1)

#### PLASTICS AS MATERIALS IN INDUSTRY

As one might expect, there were far more failures than successes, and plastics acquired a rather poor reputation -- a reputation that they are still trying to live down. Today plastics are accepted as basic engineering materials, subject

to the same design and engineering limitations as any other group of materials.

The growth rate of plastics in automobiles is an example of what can happen when plastics are applied properly. Plastics usage grew somewhat during World War II, but the most significant growth came much later. It came after these materials were no longer required as substitutes -- when they were accepted and used as competitive engineering materials.

The third reason for the remarkable growth of plastics lies with the materials themselves. The variety and quality of plastic materials available during World War II was quite limited. Today there are between 50 and 60 distinctly different types of plastics, representing literally thousands of compounds that vary so widely in properties that they can compete with steel and cotton simultaneously. (Polyester resin is a good example. Molded with glass fibers, it replaces steel in car and truck bodies. As fiber it competes with cotton and wool for clothing and rugs. As film, it replaces glass for greenhouses and competes with aluminum and other exotic metals in satellite applications. Cast polyester can be substituted for hard rubber in bowling balls, and polyester coatings can improve the corrosion resistance of many metals and alloys.)

Many engineers and designers in this country are unaware of the capabilities of plastics. Consequently, the great majority of plastic parts currently in production were originally designed for some other material and were eventually adapted to plastics. The plastic industry is expected to have an even more

rapid growth in the forthcoming years because the engineers will become more familiar, more adept with plastics.

#### EXTENT OF THE INDUSTRY

The modern plastics industry may be said to have started in 1930, when diversified products of plastics research laboratories first came into commercial use in appreciable volume. Table 1 shows the approximate dates when many of today's plastics first became commercially available in the United States. (10,11)

Table 1. Progress in Plastics Development  
Approximate Dates Covering Introduction of Some  
Commercial Plastics

Year	Plastics	Typical Application
1870	Nitrates (Celluloid)	Eyeglass Frames
1909	Phenolics	Telephone hand set
1909	Cold molded	Electric heater parts
1919	Casein	Knitting needles
1919	Vinyl acetates	Adhesives
1926	Alkyds	Molded electrical bases
1926	Aniline-formaldehyde	Terminal boards
1927	Cellulose acetate	Molded products
1928	Ureas	Lighting fixtures
1931	Acrylics	Brush backs, displays
1935	Ethyl cellulose	Flashlight cases
1936	Polyvinyl chloride	Raincoats
1938	Polyvinyl acetals	Safety glass interlayer
1938	Polyvinyl butyral	Safety glass
1938	Polystyrene	Housewares
1938	Cellulose acetate butyrate	Extended trim
1938	Polyamides (nylon)	Fibers
1939	Polyamide molding powders	Gears
1939	Melamines	Tableware
1939	Polyvinylidene chloride (saran)	Auto seat covers
1942	Allyl diglycol carbonate (CR-39)	Cast sheets
1942	Polyethylene	Squeeze bottles
1942	Polyesters	Laminated reinforced plastic boats



Table 1 (cont.)

Year	Plastics	Typical Application
1943	Silicones	Motor insulation
1943	Polytetrafluoroethylene (Teflon)	Gaskets
1945	Cellulose propionate	Pen casings
1947	Vinyl organosols and plastisols	Coatings, foams
1947	Epoxies	Potting compounds, ad- hesives
1948	Acrylonitrile-butadiene- styrene (ABS)	Simulated leather for luggage, etc.
1948	Polychlorotrifluoroethylene (Kel-F)	Gaskets and valve seats
1953	Polyurethanes	Sheets and foams
1955	Polyurethanes	Coatings
1957	Methylstyrene	Housewares
1958	Polyacrylamides	Adhesives
1958	Polyethylene oxide (Radel)	Packaging
1958	Polyacetals (Delrin)	Automotive parts
1959	Chlorinated polyether (Penton)	Pump parts
1959	Polycarbonate (Lexan)	Housings
1959	Polypropylene	Luggage
1962	Polyallomers	Molded hinges
1964	Surlyn	Packaging films, pipes, costume jewelry. (10)

Behind the plastics industry and closely associated with it are the chemical companies. For the most part these are large manufacturers of chemicals with plastics raw materials forming a small part of their total production. There are about 200 such chemical companies serving the plastics industry. The four largest of these have total sales averaging over one billion dollars each but their sales of plastics materials average even below 20 percent of the total. (10, 11)

#### PLASTICS INDUSTRY

The chief product of the plastics industry proper -- by

which is meant molders, extruders, fabricators and other end product companies -- is molding powder. Other products include resins, organosols and plasticols. Yet it is extremely difficult to draw a clear line of distinction between the supplier of the raw material for plastics and the companies which use them. The Society of the Plastics Industry (SPI) estimates that a minimum of 5700 companies in the United States are engaged in some sort of plastics activity. These divide into three categories, often overlapping: (1) chemical companies, that produce the resins, molding powders and other raw materials; (2) processors that convert such materials into solid or semi-solid form; and (3) fabricators or finishers that further fashion and decorate the product.

#### THE MATERIALS MANUFACTURER

The primary function here is the formulation of a plastic from basic chemicals. The plastic is usually sold in the form of granules, powders, pellets or flake. However, some of the materials manufacturers go a step further and produce sheets, rods, films and similar materials from the molding compounds. Most of these companies are chemical manufacturing companies such as Ciba, Dupont, Dow and Union Carbide.

#### THE PROCESSOR

The processors of plastics may be the molders, who form end products in molds or the extruders who, by means of extruding machines, produce sheets, film, wire covering and special shapes. The processors can also be the film and sheet makers

or the coaters who make use of spread coating and dipping or the high pressure laminators. The last group forms sheets, rods, tubes from paper, cloth and other materials by impregnating the materials with liquid resins. The reinforced plastics manufacturers would also be included in this group, being those who combine liquid resins with such materials as glass fibers, cloth, hemp fibers and even such materials as wood flour. (10)

#### THE FABRICATOR AND FINISHER

This group includes the miscellaneous companies, which for the most part, take the films, sheets, tubes, and rods produced by the processors and make them into finished products. (10)

#### PRODUCTION IN THE INDUSTRY

Recent production figures show that the plastics industry is growing several times as fast as all industry combined. Within ten years the annual production of all plastics materials has jumped from about 2,000,000,000 pounds to close to 7,500,000,000 pounds. The plastics industry is expected to reach a capacity of 9,000,000,000 pounds by 1966, with an estimated production value of more than 3,000,000,000 dollars. (10, 11, 14)

#### PLASTICS - THERMOPLASTIC AND THERMOSETTING

The term plastics refers to a group of organic materials, usually synthetic. Very few plastics occur naturally, for example, rubber, gutta percha, and some types of vegetable waxes. The molecules of plastics are composed principally of carbon,

hydrogen, oxygen and nitrogen. These are derived from petroleum, coal, salt, air and water. In the early stages of manufacture most plastics are monomer, that is, they are composed of heat and pressure, or of chemical catalysts, these small molecules combine to form complex molecules which become solid or semi-solid structures.

Plastics are broadly classified into two groups; (1) thermoplastic and (2) thermosetting.

Thermoplastic is an adjective applied to plastics that may be softened by heat and which upon cooling regain their solid state, even if the process is repeated. Typical of this group are polystyrenes, vinyls, polythylenes (alkathenes).

Thermosetting is an adjective applied to plastics that solidify or set on heating and cannot be remelted. The thermosetting property is usually associated with a cross-linking reaction which forms a three-dimensional network of molecules. In general, thermoset materials cannot be reshaped once they have been fully cured. Typical of the thermosetting materials are the phenolics and epoxies. (10, 11, 12)

#### EPOXY RESINS

In recent years one of the most versatile plastics to be used by industry is the plastic material, epoxy. Introduced in the early 1950's they achieved recognition quickly in industrial and protective coatings, where they combine good adhesion with resistance to chemicals.

The term "epoxy resin" is considered by most research scientists as a misnomer. This is because these compositions may be resinous but are not necessarily so. Hence they might be more properly termed as intermediates rather than resins because this, in fact, what they are. (18) The use of the term "resin" is somewhat confusing. It is often considered to be synonymous with "plastic" but it usually refers to the liquid polymers which are the starting materials in the production of molded or fabricated solid or semi-solid products. (10, 11)

An epoxy resin is never used per se. Rather, the virtue of an epoxy resin lies in its functionality, in its chemical hooks, as it were -- hooks which are continually eager to grab on to other molecules to form a chemical "alloy", by chemical interaction. It is this "alloy", this combination of the epoxy resin with another material which has useful properties and, in some instances, unique properties. (18)

It is interesting at this time, however, to see where the term epoxy comes from. It is derived from the Greek prefix, 'ep', which means "over" or "between". The 'oxy', of course, is a suffix denoting oxygen. Thus, epoxy designates "oxygen between"-- that is, a compound which has an oxygen atom between two other atoms. And, indeed, one way to form an epoxy group is to insert an oxygen atom between two carbon atoms which initially are linked together. (18)

And hence, chemically the term epoxy means a three-membered ring containing one oxygen and two carbon atoms arranged as follows: (16)



An epoxy resin, thus, would be a molecule which contains, on the average, more than one of such groups.



## HISTORY

The invention of epoxy resins was indeed a milestone in both the protective coatings as well as the plastics industry. As is so often the case with great inventions, the concept of preparing resins containing epoxy functional groups was conceived in several laboratories almost simultaneously. (12,18)

The commercial exploration of the epoxide resins was begun by I. G. Farbenindustrie in the thirties. A German patent 676117, issued in 1939, describes liquid polyepoxides which can be hardened by a variety of methods. Similarly, a Swiss inventor, P. Castan, was exploring these materials and, in 1943, a U.S. patent (2,324,483) was issued in his name which described the curing of epoxy resins with dibasic acids. The work of Castan was exploited by the Ciba Company of Basel, Switzerland. Castan was also involved in some work concerning the use of amines for curing epoxy resins as a subsequent patent (U.S. Patent 2,444,333) indicates. Almost at the same time, Greenlee, working at the Devoe Reynolds Company, conceived the idea of preparing epoxy resins and utilizing the hydroxyl group contained therein for esterification with fatty acids. Numerous patents issued to him describe this technology as well as the technology of preparing the resins and curing them by various procedures. This re-

search provided the coatings industry with an unique new material, which has been described as a "super-phenolic," possessing remarkable resistance to chemicals and solvents. (3, 12, 18)

Meanwhile, a capable group of researchers at Shell Development Company was investigating the utility of a large family of chemicals derived from propylene, one of Shell's basic chemical raw materials. These propylene derivatives were converted to resins with newly discovered acidic and basic catalysts.

The fourth U. S. company to begin the manufacture of epoxy resins was Bakelite, which concentrated on the liquid casting resins rather than the solid coating resins, and which has done much to gain acceptance for epoxies in tooling, laminates and potting. (18)

#### THE RESIN INTERMEDIATES

The epoxies are thermosetting resins. Their structure is uncommon in nature except as intermediates. The uncured intermediates are either honey colored liquids or brittle amber solids which become liquid when heated. Enlarged 10 million times, the molecules of resin might resemble short pieces of thread, varying in length from half an inch in some of the liquids to several inches in the solids. When cured or hardened to become coatings glass-reinforced pipe, metal-forming tools, etc., these threads are joined together at the ends and along the sides to form large cross-linked structures. Each molecule is tied to several others, like the ropes of a fish net or the filaments of a spider's web, but in an irregular rather than neat pattern. (12)

These final products are thermoset; they are solids that may become softer when heated, but will never again liquefy. The curing of epoxies is as irreversible as the boiling of an egg; and just as a 3-minute egg differs from one boiled 15 minutes, the physical properties of an epoxy casting depend on the extent of the cure. The greater the "density of the cross-links", the better will be the electrical characteristics and resistance to heat-softening or attack by chemicals and water. (12)

Table 2. Symbols of Polymer Chemistry -- A Handy Reference Glossary of Chemical Terms

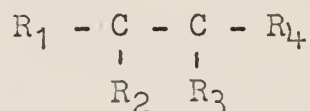
Letter	Meaning
$\begin{array}{c}   \\ -C- \\   \end{array}$	Carbon atom. Normally needs four bonds either to adjacent carbons or to other atoms (hydrogen, oxygen, nitrogen, phosphorous, etc.)
H-	Hydrogen atom (monovalent)
-O-	Oxygen atom (divalent)
-N<	Nitrogen atom (trivalent)
P	Phosphorous atom
S	Sulfur atom
R, R' R''	General purpose symbols meaning radical or group such as methyl, ethyl, etc. Often used to stand for the "rest of the molecule" so that attention can be focused on the reacting group.
-OH	Hydroxyl group (alcohol)
$\begin{array}{c} O \\    \\ -C- \end{array}$	Carbonyl group
$\begin{array}{c} O \\    \\ -C-OH \end{array}$	Carboxyl or organic acid



Table 2. (cont.)

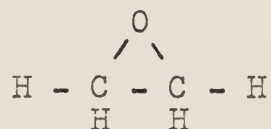
Letter	Meaning
$-\text{NH}_2$	Primary amine
$>\text{NH}$	Secondary amine
$-\text{N}<$	Tertiary amine
$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{N}-\text{H} \\   \end{array}$	Amide
$\begin{array}{c} \text{O} \\    \\ -\text{C} \\ \diagdown \\ \text{O} \\ \diagup \\ -\text{C} \\    \\ \text{O} \end{array}$	Acid Anhydride
$\begin{array}{c} \text{O} \\    \\ \text{R}'-\text{C}-\text{O}-\text{R} \end{array}$	Ester
$\begin{array}{c} \text{H} \\   \\ \text{C} \\ // \quad \backslash \\ \text{HC} \quad \text{CH} \\   \quad \quad    \\ \text{HC} \quad \text{CH} \\ \backslash \quad / \\ \text{C} \\   \\ \text{H} \end{array}$	Benzene ring. Usually written as shown at the right.
$\left[ \text{CH}_2-\text{CH}_2 \right]_n$	Subfix n denotes that radical in bracket occurs a large number of times in repetition - thus leading to the term "polymer" from "monomer."
$\begin{array}{c} \text{O} \\ / \quad \backslash \\ -\text{C} \quad - \quad \text{C}- \end{array}$	Generalized epoxy group
$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad - \quad \text{CH} \end{array} - \text{CH}_2 - \text{O} -$	Glycidyl group type epoxy group

It has been mentioned before that the epoxy ring is highly reactive, and that there is great strain on the interatomic chemical bonds. Hence five-membered and six-membered rings are preferred because these are considerably more stable. The complete and generalized structure for an epoxy group involving the epoxy ring before treating the resin directly is as follows:



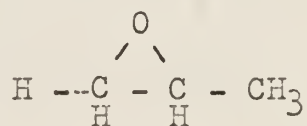
The carbon atoms are generally tetrafunctional and hence the structure is as above. (16)

Now, if in the generalized epoxy group  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen atoms, we have



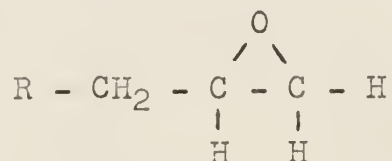
ethylene oxide, which is a highly reactive gas.

If  $R_4$  is methyl ( $CH_3 -$ ) we have



propylene oxide, another reactive gas.

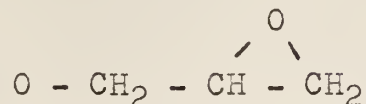
Examining the epoxy further, if  $R_1$  is a methylene group ( $R - CH_2-$ ), containing some other, as yet, undefined substitution, and the other radicals are hydrogen, we have



which is defined as a substituted glycidyl group.

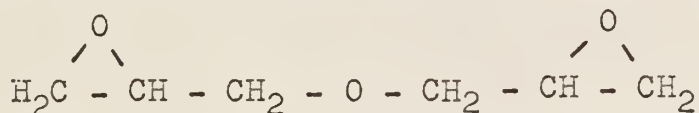
Depending on the nature of the R, this molecule may be either a gas, a liquid, or a solid. Similarly its chemical reactivity will depend on the substituted radical. (16)

The addition of an oxygen beyond the glycidyl radical gives

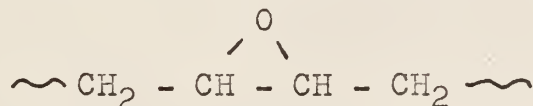


which is a glycidyl ether radical. The electronegative nature of the oxygen exerts a strong effect upon the strained, therr-membered ring. It produces a marked change in the solubility, chemical resistance and reactivity of the epoxy group.

Many commercial epoxy resins contain a plurality of these glycidyl ehter groups, the simplest example of which would be diglycidyl ether, a basic epoxide:

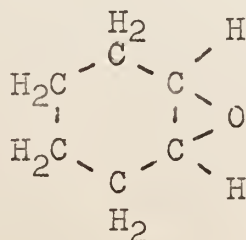


But this by no means exhausts the possibilities for an epoxy resin. Returning to examination of the substitutions on the epoxy ring, if both  $R_1$  and  $R_4$  are methylene groups



then the epoxy group is considered to be internal rather than terminal and is located along the "inside" of a chain rather than at its end.

If in the generalized structure,  $R_1$  and  $R_4$  happen to be connected through a bridge of other atoms



then we have the epoxy-ring situated on another ring.

On the basis of the short descriptions above, it may be concluded that numerous chemical structures, all containing epoxy groups, are possible. (2, 16)

#### MODIFIED DEFINITION OF EPOXY RESIN

An epoxy resin has been defined as any molecule containing more than one epoxy group. The groups may be glycidyl, terminal, internal, ring situated, etc., or combinations of any of these. This definition is often modified by adding the qualification... "and which is capable of curing or reacting to a hard, tough, durable solid." This qualification is considered to stem from older connotations wherein the natural resinous products - shellac, amber, rosin, etc. - were mostly hard solids initially. To some extent this connotation is still useful in that some diepoxides, when cured, do not develop the good strength of others (due to steric hindrances to cure, for example) and as such are more suitable as diluents for other epoxy resins. However, for the purpose of convenience all diepoxy or polyepoxy molecules will be referred to as epoxy resins, since this is common practice in the field. (16)

#### INDUSTRIAL EPOXY RESINS

On the basis of the numerous generalized structures drawn above, it may be assumed that there are numerous types of diepoxides referred to as epoxy resin. And this is actually the case in industry. There are slightly over 25 different types of epoxy resins available today, commercially or experimentally,

from 20 base chemical sources. (10, 11, 16)

These many resins are but building blocks in the development of an epoxy resin compound. An epoxy resin compound - or formulation - involves one or more epoxy resins, curing agents and modifiers such as plasticizers, flexibilizers, accelerators, stabilizers, flow control agents, pigments and selected fillers which modify various properties further.

#### TYPE OF EPOXY GROUPS

The type of epoxy groups in a resin is important since they determine what type of curing agent may be used and with what resin. They also determine whether heat cure will be required, or whether sufficient exothermic energy will be given off by the reaction of the epoxy and curing agent to drive the cure to a satisfactory degree of completion. In general, very definite reactivities exist among the various different types of epoxy groups, some types preferring electrophilic curing agents, others nucleophilic curing agents.

Electrophilic substances are those which react with the epoxy ring by attacking the oxygen atom and straining its bonding to one of the carbons so as to break the bond open and to allow the atoms of the curing agent to establish new bonds with the atoms initially in the epoxy group. A nucleophilic substance is one which prefers to attack the carbons in the epoxy group, rather than the oxygen. To do this, the curing agent must be able to get behind the carbons on the side of the epoxy group away from the oxygen. Obviously, then, the location of the epoxy

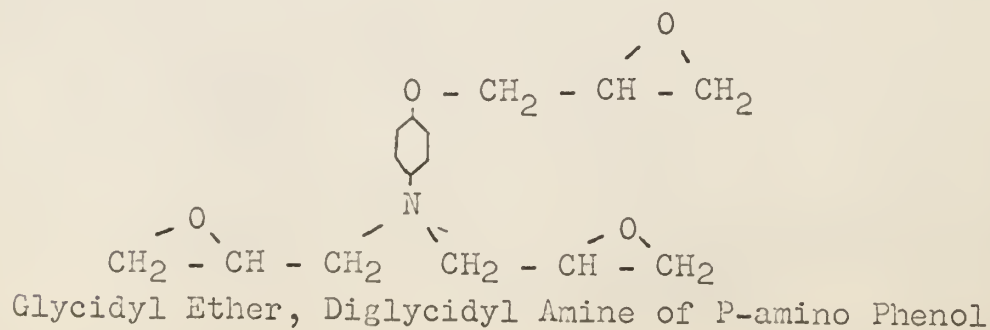
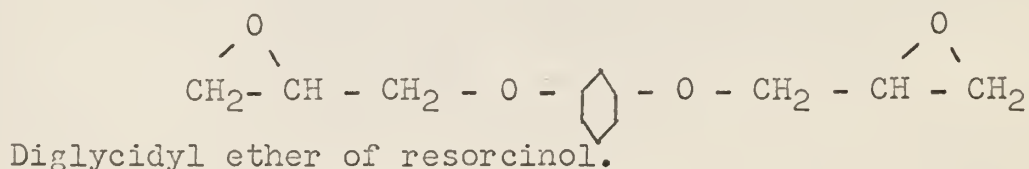
group is important. (16)

#### LOCATION OF EPOXY GROUPS

Both, the terminal and the ring type groups are attacked either by the electrophilic or by the nucleophilic substance or by both. The terminal groups may most readily be attacked by both types since they are exposed. The ring situated groups may most easily be attacked by electrophilic curing agents, and are almost unreactive with nucleophilic reagents because the chemical ring on which the epoxy group is located prevents the curing agent from approaching the backside of the epoxy group. In addition, the presence of oxygen atoms or aromatic groups adjacent to the epoxy group can markedly influence the reaction rate of a given type of epoxy group, so that all in all, the curing of epoxy resins is one of great complexity. (16)

#### NUMBER OF EPOXY GROUPS

The number of epoxy groups in a molecule may be referred to as the molecule's epoxy functionality. A resin with many epoxy groups provides more reactive sites than a similarly sized molecule with fewer epoxy groups.



When cured, a resin with high functionality will have a higher crosslinked density. Crosslinked density means the number of primary chemical bonds in a given volume of space occupied by the cured resin.

Once the basic resin has been reviewed, then the potential curing agents must be reviewed in regard to their functionality, chemical chain make up and hence heat stability, solubility characteristics etc. (16)

#### CURING THE LIQUID EPOXY

Cure of epoxy resins is said to occur when substantially all of the potentially reactive sites within the epoxy resin-curing agent have been reacted with one another and the epoxy resin has been converted from a group of discrete molecules into huge macromolecules, bonded together in all three dimensions, such that the resin will not remelt or flow upon the application of heat. (12)

Cure of epoxy resins may be accomplished by two means: (1) where the linkage is directly to other epoxy intermediate molecules, with aid of a catalyst and (2) where the linkage is to a reactive hardener which combines with one or more additional molecules of resin. (12, 16)

#### CATALYTIC CURE

The essential feature about catalytic cure is that one epoxy resin is caused to react directly with another epoxy resin molecule. This reaction is initiated by a catalyst and then proceeds rapidly until the epoxy groups are consumed or

become end - stopped by impurities. The essential constituent of the catalytically cured structure will be the epoxy resin molecule itself. The functionality and the reactive density of the resin - together with the nature of the chemical bonds - will determine the cured properties.

Theoretically, a given epoxy resin system should cure up to give substantially the same properties irrespective of which catalyst is employed to effect the cure. In practice, this is not the case, in so far as catalysts will differ in reactivity notes, and greater or lesser concentrations will be employed. Obviously the amount of catalyst is critical. Under-catalysis provides under cure. Over catalysis causes the system to be "degraded" from the theoretical optimum, since either the free catalyst will be locked in unreacted as a diluent, or the catalyst will have initiated polymerization at so many sites that the resin polymerization will be in effect end=stopped at a low degree of crosslinking due to the early exhaustion of unreacted resin before large crosslinked chains are built. Or other hindrances on the part of catalyst-resin complexes may prevent complete cure.

Catalysts are usually used in concentrations ranging from 1 - 10 parts per 100 parts of resin (phr) by weight. The reaction may, with some catalysts, be achieved at room temperature; whereas with others a heat cure may be required.

The amount of catalyst used is usually dictated by the reaction time desired; and all other things being equal, the lesser amount is to be preferred to the greater amount. (12, 16)



## CROSSLINKING AGENTS

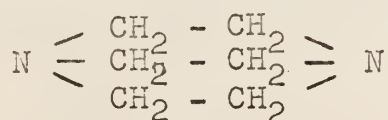
To distinguish the crosslinking agents from the catalysts: the crosslinking agents react with the epoxy molecules and are coupled directly into the cured system as structural members of the molecular network. They become a vital part of the cured resin chain, and their properties affect final properties in proportion to their type and the percentages present to a greater extent.

The crosslinking agents contain sites or radicals which are reactive with the epoxy groups in the epoxy resin. The crosslinking agents are provided in an amount intended to assure the consumption of epoxy groups. In many cases, the amount will be such that one reactive group of the curing agent is provided for each epoxy group in the system. In other cases, competing reactions will dictate the use of amounts somewhat below or over the 1 = 1 ratio. In any case, there is an optimum amount of curing agent which will assure substantially complete reaction and amounts above or below this will result in some reduction of cured properties.

It follows, then, that crosslinking agents may be present in substantial quantities (from 10 - 100 phr or more) and the properties of the cured system will be influenced by the specific curing agent employed. (12, 16)

## CURING AGENTS FOR EPOXY RESINS

### 1. Trimethylenediamine



Concentration used: 8.5 parts per hundred parts of resin

Type: Catalytic

Application: Suitable for applying, at temperatures over 60° F.

2. Diethylenetriamine (DTA)

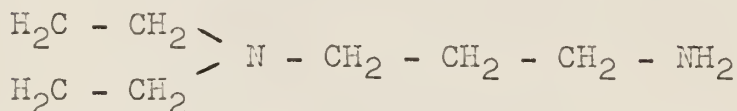


Concentration used: 10 - 12 parts per hundred parts of resin.

Type: Crosslinking.

Applications: Castings, laminates and adhesives at 60 - 300° F.

3. Diethylaminopropylamine (A)



Concentration used: 4 - 8 parts per hundred parts of resin.

Type: Crosslinking.

Applications: Castings, laminates and adhesives at 80 to 300° F. (2, 16)

## THE EXOTHERM

The reaction of epoxides is highly exothermic; that is, a large amount of heat is given off when the epoxide ring is opened, whether by polymerization with other epoxides or by reaction with a hardener.

These hardening agents will often bring about curing starting at room temperature, without application of heat. As the temperature rises, the curing takes place at a faster rate.

From a production point of view, the shorter cure time is welcome, but the temperature must not be allowed to climb too high, or the strength of the cured product will be impaired.

Best results seem to come from a two-stage cure. In the first stage the small molecules are for the most part combined into larger units having only occasional interconnections. Then the temperature is raised, and in the second stage these clusters are rejoined together at many points to form one big molecule. (12)

#### FLEXIBILIZING MODIFIERS FOR EPOXY RESINS

Cured epoxies which are unmodified tend to be brittle. When subjected to sharp impact, they may break. In thin films as adhesives or coatings, they may crack when flexed. Their peel strength is low. In contact with glass fiber, or with the components of potted electronic assemblies, they have far better resistance to temperature cycling than other resins, yet at extremely low temperatures they may separate from glass or metal.

Unmodified epoxies are hard materials with high tensile strength but low elongation. At the other extreme, with low tensile strength and moderate to large elongation, are materials such as Swiss cheese. Both have low areas under the stress - strain curve; both are brittle. (12)

In thermoplastics, to improve elongation and toughness, some of these bonds are loosened by the addition of plasticizers. Plasticizers are materials added to a plastic to improve flexibility or to facilitate compounding. But these have been found to be unsatisfactory in the case of epoxies. For epoxies, a better solution is to build more flexibility into the resin

molecule itself.

"Thiokol," "Versamid", and "Cardolites" are common flexibilizers used with the epoxies and the hardeners. (12)

#### REINFORCEMENTS, FILLERS, THIXOTROPIC AGENTS, COLORANTS

There are various inert solid additives which are capable of improving the properties of epoxies.

Reinforcements are fibers in the form of cloth, mat or chopped strands. They form a continuous framework which buttresses the resin. Glass fiber, the most common reinforcement, confers increased tensile, compressive, flexural and impact strength, improves heat resistance, and reduces shrinkage and thermal expansion.

Inert addends which are not expected to increase strength are termed fillers. They are usually inorganic particles, granular rather than fibrillar in shape. Fillers also improve heat resistance, shrinkage on curing, and the thermal expansion coefficient. Their low cost, plus the capacity of epoxy to swallow more than its own weight of the, make it possible to bring epoxy formulations down to the price range of competitive materials for many applications.

Thixotropic or thickening agents are finely divided particles which can clot a liquid epoxy so that it will not drain from an inclined or even a vertical surface. They may be porous granules such as special silicas; platelets, such as mica, or short fibers such as asbestos. Because of their noncompact shapes, they are able to make contact with each other even when present to the

extent of only a few per cent. Thus they form webs which immobilize the liquid; but stirring breaks up the mass so that the composition can be poured or brushed.

Colorants are inorganic or organic pigments, usually added to the epoxy before cure. The amber cast of epoxies is easily overcome either by organic dyestuffs or by inorganic pigments such as carbon black, chrome green, iron earths, etc. The inorganic pastes are employed in 1 to 2 per cent concentration, the stronger organics in 0.5 to 1 per cent. An important use for colorants is to distinguish the curing agent from the resin, so that the completeness of mixing may be appraised visually. A safe rule, when the components are differentiated colorwise, is to mix to a homogenous color and then continue mixing for at least an equal length of time. (12)

#### PROPERTIES AND SELECTION FACTORS

Thermosetting epoxy resins have properties which make them very useful in the formulation of coatings, castings, laminatives and adhesives. Epoxies exhibit versatility, toughness and good handling characteristics. The linear shrinkage of filled epoxy resin systems is on the order of 0.002 percent. Epoxies are practically unaffected by a wide range of acids, alkalies and solvents. (10, 11)

Considering the properties of a commonly used epoxy resin with silica filler:

Specific Gravity	1.6	-	2.0
Specific Volume (cu.in/16.)	13.9	-	17.3
Tensile strength (p.s.i.)	6000	-	13000

Compressive Strength (p.s.i.)	15000	-	35000
Impact Strength (ft.lb./in of notch)	0.3	-	0.5
Rockwell Hardness (M)	M85	-	M120
Resistance to heat (°F)	250	-	500
Water absorption, 24 hrs. 1/8" thick	0.04%	-	0.10%
Burning rate	Self extinguishing		
Effect of sunlight	None		
Effect of weak acids	None		
Effect of strong acids	Attacked by few		
Effect of weak alkalies	None		
Effect of strong alkalies	Very slight		
Organic solvents	Generally resistant		
Clarity	Opaque		

Trial and error, as a means of selection of plastics is exceedingly costly, and therefore careful study of the problem is warranted. The more rigid the specifications covering end use, the easier the selection becomes. (5, 10, 11, 15)

The succeeding tables exhibit the rating of various materials in the order of preference of one particular property. Thus under relative specific gravity, polypropylene is rated 1, as being the lightest of all plastics and the similar procedure is adopted in the following tables thus making them very useful in the selection of materials.

Table A. Specific Gravity

Specific Gravity is the ratio of the weight of a material compared to the weight of an equal volume of water. A value less than 1.00 indicates that the material will float. (10,11)

Rating		
1.	Polypropylene	0.90
2.	Low-density Polyethylene	0.910 - 0.925
3.	High-density Polyethylene	0.926 - 0.940
4.	Polyester	0.99 - 1.20
5.	Polystyrene	1.04 - 1.10
6.	<u>Epoxy</u>	1.11
7.	Cellulose Ethyl	1.14
8.	Nylon	1.17
9.	Acrylate	1.18
10.	Polycarbonate	1.20
11.	Butyrate	1.21
12.	Cellulose Acetate	1.30
13.	Phenolic (Wood Flour)	1.36
14.	Urea	1.48
15.	Melamine	1.49
16.	Silicones	1.75

Table B. Tensile Strength

Rating		
1.	Polyester (glass-reinforced)	30,000 psi
2.	Silicone (asbestos-filler)	28,000
3.	<u>Epoxy</u> (glass-reinforced)	17,000
4.	Nylon	15,000
5.	Polycarbonate	9,500
6.	Acetals	9,000
7.	Phenolics	8,500
8.	Melamines	8,300
9.	Cellulose Acetate	8,000
10.	Polystyrene	7,000
11.	Polypropylene	5,500
12.	Vinyls	4,800
13.	Polyethylene (High-density)	4.600

Table C. Thermal Expansion

---

The increase in length per unit length per degree C.

Rating	Type	In./in.°C x 10 <sup>-5</sup>
1.	Silicone (glass-fiber)	0.8
2.	<u>Epoxy</u> (glass-fiber)	1.2
3.	Phenolic (glass-fiber)	1.6
4.	Urea	2.8
5.	Melamine	4.0
6.	Polystyrene	6.5
7.	Polycarbonate	7.0
8.	Acrylic	9.0
9.	Nylon	10.0
10.	Polyethylene (high-density)	12.0
11.	Vinyl	23.0

---

Table D. Modulus of Elasticity

---

Rating	Type	x 10 <sup>5</sup> psi.
1.	<u>Epoxy</u> (glass-fiber)	30.00
2.	Phenolic (mineral-filled)	14.00
3.	Urea	13.00
4.	Phenolic (wood-flour filled)	9.00
5.	Polystyrene	4.50
6.	Vinyl	3.50
7.	Polycarbonate	3.20
8.	Polyether (chlorinated)	1.60
9.	Cellulose Acetate	1.40
10.	Polypropylene	1.30

---

Table E. Flexural Strength

---

Rating	Type	psi
1.	Phenolic (laminated)	27,000
2.	<u>Epoxy</u>	24,000
3.	Nylon	17,000
4.	Phenolic	15,000
5.	Melamine	14,000
6.	Polycarbonate	12,000
7.	Polystyrene	11,500
8.	Vinyl	11,000
9.	Polyester	9,000
10.	Polyethylene (med-density)	6,000

---



Table F. Water Immersion

---

24 hour immersion, 1/8 inch thick, per cent absorbed.

Rating	Type	Per Cent
1.	Polypropylene	0.01
2.	Polyethylene	0.015
3.	Polystyrene	0.04
5.	<u>Epoxy</u>	0.10
6.	Silicone	0.15
7.	Polycarbonate	0.30
8.	Melamine	0.35
9.	Phenolic	0.60
10.	Urea	0.65
11.	Nylon	1.50

---

Table G. Hardness

---

Rating	Type	Reading
Rockwell M		
1.	Phenolic	126
2.	Melamine	120
3.	Urea	115
4.	Polyester	100
5.	Nylon (glass-fiber)	94
6.	<u>Epoxy</u>	90
7.	Silicone	89
8.	Polystyrene	80

---

Table H. Impact Strength

The mechanical energy absorbed by a standard test piece during fracture by a glow form a pendulum hammer. Comparative value.

---

Rating	Type	Foot Pounds
1.	Polycarbonate	8.0
2.	Phenolic	4.0
3.	Polyethylene (high-density)	3.0
4.	Cellulose Acetate	2.2
5.	Polypropylene	2.0
6.	Nylon	1.5
7.	<u>Epoxy</u>	1.0

---

Table H. (cont.)

Rating	Type	Foot Pounds
8.	Cast Phenolic	0.35
9.	Silicone	0.30
9.	Urea	0.30
9.	Melamine	0.30

Table I. Compressive Strength

Rating	Type	psi
1.	Phenolic (laminated)	34,000
2.	Melamine	30,000
3.	Cellulose Acetate	28,000
4.	Polyester	25,000
5.	Silicones	17,000
6.	Polystyrene	15,000
7.	Nylon	13,000
8.	Vinyl	11,000
9.	Polycarbonate	10,000

Table J. Safe Top Operating Temperatures for Some Plastics

Rating	Type	°F
1.	Silicones	600
2.	Phenolics	450
3.	Epoxy	400
4.	Nylons	325
5.	Polypropylenes	300
6.	Polyether (chlorinated)	290
7.	Polycarbonate	250
8.	Polyethylene	225

## PRICES IN THE PLASTICS INDUSTRY

Any attempt to list prices is difficult because they change very often, and also because of the many variations in types of any one plastic. The prices listed below are, hence, the approximate prices in 1964 and are indicative of a general level only. (11)

	cents per pound
Acetal	62
Acetates	38
Acrylics	51
Epoxy resins	60
Fluorocarbons (TFE)	310
Melamine	46
Phenolics	21
Polyamides (Nylon)	92
Polyesters	35
Polyethylene (L.D)	22
Polyethylene (H.D)	30
Polystyrene	16
Polyvinyl Chloride (PVC)	16
Polyvinyl Chloride Acetate	44
Ureas	31

## HANDLING EPOXIES

Epoxy resins and hardeners are reactive chemicals. When handled by personnel used to handling chemicals, for example, in paint factories, they generally give no trouble. But they are finding their greatest usage in nonchemical industries - electrical, aircraft, automotive. Workers in these plants must be protected from contact with diepoxides. Dermatitis is the most common complaint.

The dermatitis from epoxy-hardener exposure has been compared to that caused by poison ivy. Also, it afflicts some individuals worse than others. Women are more sensitive than men. The only preventive measure for this is good house keeping. An adequate supply of clean disposable rags should be available.

Rubber or polyethylene gloves, with cotton gloves underneath, should be worn. Ventilation should be adequate to draw fumes away from the operator. A thorough wash with soap and water should end each work period. (12)

## APPLICATIONS OF EPOXIES

## TOOLING FOR WORKING OF METALS

The epoxies are enjoying their greatest growth as casting and laminating resins for the manufacture of metal forming tools. Reinforced with glass cloth, they make light weight models, jigs, fixtures, inspection gauges and other secondary tools. They are used either by themselves or in conjunction with other materials for draw dies, drop hammer dies, etc.

The automotive and aircraft industries are very enthusiastic about the epoxies. Chrysler Corporation has approximately one-third of its tooling done in plastics, and that proportion is growing. General Motors uses epoxies for die models, spotting racks, prototypes, water test fixtures, paint spray masks, contour templates, assembly fixtures, inspection fixtures, drill baskets, etc. (8, 12)

Although the resins are high priced, the finished epoxy tools are almost invariably cheaper than their metal counterparts. They require fewer man-hours, and are especially frugal in regard to precious tool-and-diemakers' time. They cut down the lead time required to develop new models. They provide economical prototypes so that various departments and plants within an organization can work on new models simultaneously. They permit the quick evaluation of design changes, so that the ideas and corrections of designer and engineer can be fed back into the working model. Irving Skeist said, "If a picture is worth a thousand words, a "live" three-dimensional model is worth a thousand blueprints."

At present, epoxy plastic tooling may be divided into four general categories: laminating, surface casting, mass casting and paste plastic tooling .... each of which may be used singly or any combination.

#### LAMINATED TOOLS

A laminated plastic tool is made of alternate layers of glass cloth and liquid laminating plastic. After the laminations are completed, the liquid plastic solidifies into a strong rigid form. The finished piece has the exact size and shape of the surface from which it was molded.

Laminated tools are usually reinforced with, or become a part of, a framework. This framework can be made of plastic materials, fabricated steel or aluminum, and the type of framework developed depends on the end use of the tool. Ren Plastics, Inc., of Lansing, Michigan are specialists in epoxy compounding and pioneers in the epoxy tooling field and their laminated plastic tools have excellent properties especially in strength and weight. (8)

#### SURFACE CAST TOOLS

A surface cast tool usually consists of a metallic core, rough cast to the general shape of the finished tool. This core is suspended over a model of the working face of the tool and liquid plastic is then cast into the space between the metal and the metallic core. Preliminary preparations are made so that the plastic cast bonds tenaciously to the metallic core but parts cleanly from the model. The resultant tool will have the exact

shape and finish quality of the model. Generally speaking, surface casts are made against a metal core such as aluminum or steel. This type of tool is used in some industries for metal forming dies. It is used to make patterns or core boxes in the foundry industry. (8)

#### MASS CAST TOOLS

Mass cast tools usually are made entirely of the plastic material. Sometimes metal inserts are built into the unit for added strength at certain stress points. Mass casting of plastics are usually used where a large tool surface is involved such as an aircraft stretch block or hammerform. The dimensional stability of a mass cast tool is lower than that of a laminated tool but is still well within the normal tolerance of stretch forming operations.

Recent developments in mass casting materials have given this method a wider range of usefulness. The plastic materials nowadays are cast in thick or thin sections and their physical properties, especially in toughness, have improved considerably. (8)

#### PASTEPLASTIC TOOLS

Tools made with paste plastic, which is a non-flowing material, are varied and numerous. The resin and hardener of these materials are combined on a flat surface using putty knives. Due to the outstanding dimensional stability of paste materials, quite a few of the recent tools include paste plastics within the laminated portion of the unit and still provide highly accurate plastic tooling.

The aircraft industry uses these materials extensively within the aircraft industry to produce highly accurate splined master models. Past plastics are commonly used in pattern shops for small and medium size foundry patterns. Other industries find these materials useful for models, nesting fixtures, repairs of spinning blocks, hammer forms, wood patterns etc. The dimensional stability of past plastic tools is a bit less than laminated plastics but is very much within the working tolerances encountered generally in the metal working industry. (8)

#### COMPARISON OF TOOLING METHODS

Ren Plastics Inc., have developed a very convenient table which has proved helpful in determining the method to use for the various tooling requirements. The ratings shown are established from the desirability standpoint, rated as follows: A = most desirable, B = satisfactory, c = fair, d = least desirable. (8)

Desirability factors	Laminate	Surface Cast	Mass Cast	Paste
Dimensional Stability	A	C	D	B
Shrinkage (during cure)	A	C	D	B
Least Weight	A	D	C	B
Labor Cost	D	C	A	B
Material cost (lb.)	D	C	A	B
Strength	A	B	C	D
Toughness	A	B	D	C



## ADHESIVES FROM EPOXIES

In a few short years, the epoxies have been established in many applications for bonding metals, glass, ceramics, polyesters, phenolics and other materials. Because of their high strength and relative ease of application, the aircraft industry uses them extensively. They bond the aluminum sheet to itself or to other metals. They make possible the construction of thin-skinned honeycomb sandwiches. They are tougher than metal solders for joining most materials. Under repeated cycling at low stresses, the epoxy glue line often outlasts the metal "adherends," or surfaces being bonded.

In the small-parts assembly industries, epoxies perform a variety of tasks. They frequently add value to the product far out of proportion to their cost. This is shown in the bonding of a sapphire needle in a phonograph arm whose weight is critical. (12, 4. Sept., 2959)

Like many other adhesives, the epoxies offer advantages over fasteners for metal-to-metal bonding. Labor cost is generally reduced. Stress is distributed uniformly over the widest possible surface, promoting high strength and resistance to fatigue, and permitting the use of thin metal skins which would distort if riveted or welded. Even, smooth outside contours, so highly important in high speed aircraft, become feasible. Two different metals may be joined without creating corrosion problems.

Epoxies have special advantages over other resins as bonding agents. These are 1. Adhesion, 2. Cohesion, 3. 100 per

cent solids, 4. Low shrinkage, 5. Low creep and 6. Resistance to Moisture and Solvents. (12)

(1) Adhesion: Because of their epoxide, hydroxyl, and other groups, the epoxies have high specific adhesion to metals, glass and ceramics. They can be formulated to give mixes of low viscosity and good penetration. They also provide good affinity between metals and plastics. For example, epoxies are in use for the bonding of copper to phenolic laminates in printed circuits.

(2) Cohesion: When the resin is properly cured, the cohesive strength within the glue line is so great, and the adhesion of the epoxy to other materials is so good, that failure under stress often occurs in one of the materials being bonded rather than in the epoxy or at the interface. This often happens with glass and aluminum as well as with weaker materials such as concrete and wood.

(3) 100 percent solids: The epoxies cure without releasing water or other condensation by-products. This makes it possible to bond the epoxies at only contact pressures, or with no pressure at all. Also, since there is no water to remove, the epoxies are convenient for the assembly-line bonding of impervious surfaces such as metals and glass.

(4) Low shrinkage: The epoxies cure with only a fraction of the shrinkage of vinyl-type adhesives such as the polyesters. Consequently, less strain is built into the glue line, and the bond is stronger. Also, the epoxies do not pull away from glass fibers as polyesters do. The shrinkage can be reduced to

a minimum, about a small fraction of one per cent by the incorporation of silica, aluminum, and other inorganic fillers.

(5) Low creep: The cured epoxies, like other thermoset resins, maintain their shape under prolonged stress better than thermoplastics such as polyvinyl acetate.

(6) Resistance to Moisture and Solvents: Unlike proteins, starches, gums, the epoxies are insensitive to moisture. Their resistance to solvents is also outstanding, and accounts for their rapid advance in the coatings field. They are very effective barriers to heat and electric current. (12)

#### APPLYING THE ADHESIVE

For highest bond strength, the surfaces to be bonded must be chemically clean. Films of loosely adhering metal oxide, grease, mold release agent, etc., must be removed. A drop of water should actually spread to form a thin film. If plastics have been molded with silicone or other release agents, the surface should be sanded or buffed before bonding. Sometimes solvents are used to remove the film. Glass is cleaned with conventional detergents. Rubber may be etched with concentrated sulphuric acid at room temperature.

If surfaces are irregular, a layer of glass cloth will serve as a carrier, building up the glue line. Where no carrier is used, bonding pressure should be minimal to avoid squeezing out too much resin. The adhesive may be applied to the surfaces to be bonded by brush, roller, or spray gun. (12)

## EPOXY RESINS IN SURFACE COATINGS

Surface coatings are expected to protect substrata from the weather, the action of inorganic and organic solutions, physical abrasion, and corrosion, as well as to decorate and maintain the appearance. The paint manufacturer has available today a number of resins to assist him in attaining these qualities. These include:

(1) Phenolic resins: good in chemical resistance and hardness; limited in adhesion, flexibility, and color.

(2) Alkyd resins: good in durability, color and versatility; limited in alkali resistance and adhesion.

(3) Vinyl resins: good in chemical and water resistance, toughness; limited in thermoplasticity, softness, gloss and solubility.

(4) Epoxy resins: possess all of the desirable qualities mentioned above, with a minimum amount of the limiting qualities. (12)

Where mild corrosive conditions are involved, epoxy primers are used. This is common in industrial plant maintenance. White epoxy coatings are receiving increasing attention in refinery and petrochemical storage areas. A combination of good metal protection, effective heat reflection and good appearance make these coatings very desirable in this type of application.

Coating formulations may be of three types: (a) 100 per cent solids coatings, (b) nonesterified solution coatings and (c) esterified solution coatings. (2)

(a) 100 per cent solids coatings: Coatings designated as 100 per cent solids coatings contain no volatiles which must be

driven off during cure. Such coatings are based on the low-viscosity liquid epoxy resins, and the resin itself thus serves as a wetting agent for the pigmenting agents which may be required.

The 100 per cent solids coatings provide for thick build-ups in a single application, and since cure is accomplished without the release of solvents, there are no minute pinholes and passageways present in the film to admit contaminants to the protected components. The coatings can be applied to heat- or solvent-sensitive surfaces, and they are particularly convenient for coating small areas exposed to extremes of environment and for protection of in-place structural members.

However the disadvantages of the 100 per cent solids coatings have militated against their widespread use. These can be summarized - (1) brittleness, (2) poor resistance to higher temperatures and thermal cycling, (3) comparatively high cost, and (4) short pot life.

(b) Non-ester containing solution coatings: Non-ester containing epoxy-resin films are extremely tough, hard, and chemically resistant. Electric properties and moisture resistance are outstanding. In spite of the toughness of the cured film, it can be bent or flexed as much as 180 degrees without cracking. This flexibility along with the color properties of the films are good and in most cases, white and pastel shades may be achieved easily. Resistance to weathering is generally good. The adhesion, like the chemical resistance, is extremely high, and the coatings can, therefore be applied without the use of

time-consuming primers.

(c) Epoxy Resin Esters: Approximately 50 percent of all solid epoxy resins go into the production of epoxy esters for coatings. Epoxy esters are used in air-dry formulations (for which a small amount of conventional catalyst, is added) or they may be used with ureas or melamines.

The over-all properties of the epoxy-ester films are, however, inferior to the properties of the nonesterified films. They possess the overriding advantage of lower cost, arising from the reduced epoxy content and the feasible use of inexpensive solvents. The coatings provide indefinite shelf life without requiring extra containers.

In concluding this matter of epoxies in coatings, I might mention that although it is possible to formulate 100 percent solids coatings based on the liquid epoxy resins, solution coatings are used almost exclusively for coating work. (2, 12)

The solution coatings may be considered to be of two types; those containing no ester linkages and those which do contain them. Both these, as mentioned earlier, exhibit characteristics superior to most conventional coating materials.

By far the largest volume of epoxy resin production is assigned to the coating industry for use in tough, flexible, chemically resistant films.

Over 50% of the epoxy resins produced in the U.S.A. were consumed in the coatings industry on an annual basis. This quantity is still rising although the annual percent used in

resins is decreasing slightly. This is especially due to the increasing usage in the tooling industry. (2, 10, 12)

#### EPOXIES FOR ELECTRICAL EMBEDMENTS

Epoxies and other insulating resins constitute only a small fraction of electrical equipment, but their role is vital. When used for coating wire, spacing capacitor elements, and encapsulating transformers, their contribution is far out of proportion to their cost. (12, 16)

Several factors have helped push epoxies to the forefront. Electronic devices are being operated at higher frequencies and temperatures. At the same time, the armed services, preparing for the contingency of global space war, require good performance under arctic as well as in tropical conditions. Guided missiles and satellites are hurtled into space with delicate electronic mechanisms protected in epoxy. Miniature components are brought closer together, with less resin to insulate them: consequent, greater strength and better dielectric properties are demanded from a smaller amount of plastic.

Outstanding in adhesion, curing with low shrinkage, and 100 per cent reactive, the epoxies can be formulated to give satisfactory performance with regard to each of the characteristics desired. Fillers are incorporated to reduce shrinkage and thermal coefficient and improve thermal conductivity. Cost reduction is usually of secondary importance in electrical embedding. Powdered glass, sand and calcium carbonate are among the other fillers most popular for encapsulating. To preserve

electrical properties, they must be completely dry.

Temporary castings are made from paper, aluminum, vinyl plasticol. The plasticol technique has been successful for the potting of armatures. The positive is heated to 350° F, then dipped into plasticol, drained, and put back into the oven at 350° F to fuse the vinyl resin composition.

In the electrical industry, the epoxies are utilized in and around motors, transformers, rectifiers, potted circuits, printed circuits, amplifiers, torquemeters, capacitors and elsewhere. However due to the delicacy of such work, various problems arise. It is necessary to make sure that exotherm and cure temperatures do not damage the component. In addition, pressure-sensitive components such as rectifiers and vacuum tubes require flexible potting compounds.

At McCulloch Motors, the wires and split rings contacts of a large D. C. motor armature are held safely in place while the armature whirls around in an aircraft compressor at 8000 rpm.

An amplifier made by Minneapolis-Honeywell Regulator Company has been cradled in a flexible coating of RTV "Silastic" (Dow-corning Corp.), then encapsulated with epoxy as electrical insulation and protection against moisture, corrosion and fungi.

At General Motors, the precisely positioned electromagnetic sensing pickups of a torquemeter were embedded in epoxy for dimensional stability and protection from engine oil.

Larsen-Hogue Electric Company, uses these coatings for motor insulation. At General Electric, epoxies go into the stacks of laminations which form the magnetic portion of motors,



chokes and transformers. (12, 16)

#### MISCELLANEOUS STRUCTURAL EPOXIES

(1) Glass-Reinforced Epoxies: These epoxies have important uses in several fields besides toolings. Their good adhesion, low shrinkage and chemical resistance is combined with the high tensile strength characteristics of glass fiber to provide a structure that is strong, light and corrosion resistant. The reinforced epoxies are replacing metals for many piping and pressure vessel applications.

The petroleum and chemical process industries are the chief beneficiaries of the development of glass-reinforced epoxy pipe. Less than one-fourth the weight of stainless steel and only one-third the cost, epoxy line pipe and well tubing is indifferent to sour crudes, salt water, and concentrated mineral acids.

To realize optimum strength from the glass fiber, it must be used in the form of oriented filaments rather than glass cloth. Also, closer packing of the fibers permits a greater percentage of glass in the resin-bonded composition. Since glass fiber tensile strengths are in excess of 200,000 psi, while that of the cured epoxy resin is in the order of 10,000 psi, it is obvious that the resin content should be kept as low as possible, while still wetting the glass completely. In practice, resin content is 30 per cent or less.

While glass fiber has extraordinary tensile strength, it lacks chemical resistance. Perhaps the most important function of the epoxy resin is to shield the glass fiber from the chemical

environment. The low shrinkage of the resin during cure helps it to remain in contact with the glass surface. (12, 13)

(2) Pressure Spheres for Compressed Air: Compressed air is used in aircraft for the operation of many pneumatic devices. The air is commonly stored aboard planes at 3,000 psi, in spheres of 650 cu. in. vol. In the pre-epoxy era, wire-wound steel was the preferred material of construction. The purpose of the wire winding was to prevent shattering in case of rupture. The sphere weighed 20.5 lbs. The epoxy-bonded fiber glass sphere of 650 cu. in. capacity, one foot in outside diameter, weighs only 12.25 lbs. - a saving of more than eight pounds compared to the steel globe. If it is worth approximately \$400 to lighten the weight of a plane by one pound, then the reduction pays for the epoxy-glass spheres ten times over. In guided missiles, the weight saving is even more important. In addition, the glass-filament sphere retains the shatterproof characteristics of the wire-wound device. Bullets penetrate the sphere but do not cause it to fly apart. (12)

(3) Springs: Helical springs of reinforced plastic have been developed to replace steel in many end uses on the basis of its nonmagnetic, dielectric, heat insulation and corrosion-resistant characteristics. While the steel spring, made by winding around a mandrel, is dimensionally unstable because of residual stress, the plastic spring can be molded to close tolerance without appreciable internal stress. High strength-to-weight ratio and easy colorability are additional advantages of glass-plastics.

On the disadvantage side, the plastic combinations are more temperature sensitive than metals, have greater tendency to creep, and have lower moduli. (12)

(4) Vacuum Forming Molds: In the vacuum forming process, a flat thermoplastic sheet is given a three-dimensional contour by heating it and drawing it against a mold, with the aid of a vacuum. The mold is punctured with numerous tiny holes perpendicular to its base, through which the vacuum is pulled. Many mold materials preceded the epoxies, but all had drawbacks: aluminum castings are expensive and lack precision; sprayed metal is even more expensive; wood chars; cast phenolics are difficult to make, and not durable; plaster is even less permanent.

For runs of more than 1000 pieces, an aluminum-filled epoxy composition is ideal. (12)

(5) In the Radiation Laboratory: Epoxy castings containing 90 per cent lead are employed as radiation shields. The easy fashioning of complex shapes, as well as their ability to bind lead, make the epoxy resins very useful preparative materials. (12)

(6) Television receivers: Major design advances in television receivers have occurred as a result of a newly developed TV picture tube relying heavily on epoxy resin for its unusual construction. Conventional tubes consisted of just a large glass bulb. Generally a separate implosion glass is installed in the cabinet, as a rule an inch or so in front of the picture tube. In the new constructions, an implosion panel, contoured to the

shape of the tube face with an epoxy resin. About 1 lb. of resin is used per tube. Major firms as National Video, RCA, Sylvania, and Westinghouse are presently using these resins for their tubes. (12)

(7) Propeller Cover Plates: Glass-reinforced epoxy has replaced aluminum in a Curtiss-Wright propeller component, on the basis of the plastic's superior resistance to high frequency vibration. Reinforced epoxy has been found to stand up at least 12 times as long as the aluminum. The glass-epoxy part is considerably lighter than the old aluminum cover, partly because of its lower gravity - 1.8 compared to 2.77 for aluminum - and in addition, because the thickness is varied across the piece, in contrast to the uniform thickness of the stamped sheet metal. At the edge, where high rigidity is needed, 14 layers of glass cloth are used; across the flat surface, the thickness is cut down to 6 layers for greater flexibility. (12)

(8) Safe roads that last: Long service life and improved safety are the two major contributions epoxies bring to the road construction. In this application the dual purpose of the resin is to render concrete road surfaces water proof and skid-resistant. Longterm testing by resin suppliers has confirmed that epoxy coatings, if properly cured, perform so well on highways and bridges that the higher cost of road building is fully offset by savings in repairs. Indirect savings resulting from reduced driving hazards on epoxy-surfaced roads are incalculable. Epoxy road surfaces are impervious to water, de-icing

salts, and freeze-thaw cycles. They are highly resistant to oils and other solvents, and possess good wearing properties.

The cost of typical epoxy compounds for this application is usually between 50 cents to \$1.00 per square foot. (9, 12, 17)

## FUTURE OF EPOXIES

The future of the United States plastics is very bright. According to most authorities, it is independent of any ebbs and flows of the national economy. This prediction is based not only on the past history of the industry, which followed an upward production curve through several recessions, but also upon several new developments. These include a greatly increased use of plastics in building and construction. (6, 7)

In 1965, epoxies are estimated to supply 0.10 per cent of the total plastics used in building and construction. This would mean almost 2 million pounds of epoxies. The average 1965 car consumed almost 35 pounds of plastics. On the assumption that 8,000,000 cars would be produced, the total would be 280,000,000 pounds of plastics and almost 1.5 percent of this would be epoxies.

Hence, it can be stated that there will, indeed be a future for epoxy resins. It is likely that the price of epoxy resins will not decline very much within the next five years. Whether there will be a marked decline, thereafter, will depend strictly on technological break-throughs which will provide a more economical way for inserting an epoxy group into organic compounds.

There are other factors in addition to lower price, however, which may expand epoxy resins usage. Again, most of these factors are based on technological break-through. Thus, procedures for improving the weatherability and yellowing characteristics of the epoxy resins are sorely needed. Procedures for improving the water resistance of epoxy resins are needed.

Improved resins for the formulation of solventless coatings; resins which are water dispersible; resins which make possible one-component systems with room temperature cure; and new procedures for applying two-component systems are all technological break-through which will help to expand the market.

Particular emphasis must be placed on this area of providing new devices which will make possible the ready application of two-component epoxy compositions for glass laminations, for coatings and for other applications. This is extremely important for a large potential market for epoxy resins in highway construction where the virtues of the sand filled compositions have already been mentioned. Similar devices are necessary to expand the use of epoxy resins in the building industry in general.

Basically, then, the growth of the epoxy resin market can be projected not only on the basis of lower prices but also on technological break-throughs in mechanical equipment for applying two-component systems.

## BIBLIOGRAPHY

1. Lamberg, L. J., "A Materials Engineer Looks at Plastics." Metal Progress, April 1964.
2. Lee, Henry, Kris Neville. Epoxy Resins - Their Applications and Technology, 1957.
3. Liepens, Raimond. Doctor of Philosophy Thesis, Kansas State University, 1960.
4. Materials in Design Engineering, Reinhold Publishing Corporation, New York
5. Modern Plastics Encyclopedia
6. Morgan, Philip M.A., Progress in Plastics - 1957. New York Philosophical Library, 1957.
7. Plastics World. Cleworth Publishing Company, Inc., Conn.
8. Ren Plastics, Inc., Michigan. Epoxy Plastic Tooling Materials.
9. Shell Chemical Company, New York. Everybody Needs Epoxies.
10. Simonds, H.R. A Concise Guide to Plastics. Reinhold Publishing Corporation, New York, 1957.
11. Simonds, H.R., J. M. Church. A Concise Guide to Plastics. Reinhold Publishing Corporation, New York, 1963.
12. Skeist, Irving. Epoxy Resins. Reinhold Publishing Corporation, New York, 1958.
13. Sonneburn, R.H. Fiberglas Reinforced Plastics. Reinhold Publishing Corporation, New York, 1954.
14. Statistical Abstract of the United States - 1964. U. S. Department of Commerce, Washington, D. C., July 1964.
15. The Dow Chemical Company, Michigan. Dow Liquid Epoxy Resins.
16. Union Carbide Plastics Company, New York. New Developments in Epoxy Resins, 1960 - 1961.
17. Union Carbide Plastics Company, New York. The Use of Epoxies For Industrial Maintenance.
18. Wittecoff, Harold. Epoxy Resins. American Paint Journal, August 1961, September 1961.



## ACKNOWLEDGEMENT

I would like to express sincere appreciation to my advisor, Dr. A. E. Hostetter, for the advice, guidance and patience during the completion of this work. He painstakingly read the entire report and his excellent suggestions have been incorporated into the final form.

It is a pleasure to take this opportunity to express my profound gratitude to Dr. G. F. Schrader, Head of the Department of Industrial Engineering for his great interest, personal as well as professional.

I would like to take this opportunity to thank the various faculty and staff members of the Kansas State University for all their encouragement and valuable guidance in my graduate studies.

It would be a folly to neglect to mention my wonderful friends who inspired me throughout my work.

All the U. S. Companies that I corresponded with were most helpful. I would like to express my deep gratitude to Union Carbide Corp., N. J. the Dow Chemical Company, Michigan, General Mills, Inc., Illinois, Shell Chemical Company, N. Y., Ciba Products Company, N. J. for all their valuable information. B. C. MacDonald and Company of Kansas City and Wichita, agents for Ren Plastics, Inc., Michigan were very kind in supplying me with information and useful solutions.

My parents, Mrs. Hassi Ramchandani and Mr. Murli Ramchandani, have not only encouraged me but have made many sacrifices, and through their devotion, have anticipated my needs, thereby removing impediments which would have diverted my attention from my studies. To them I am profusely indebted.

## LAMINATED PLASTIC TOOLS



A laminated master duplication for an aircraft cabin section.



Prototype skin panels for automotive parts. These are used to set up conveyer lines - brackets, clearances, etc.

## LAMINATED PLASTIC TOOLS



Prototype parts - portable TV cabinet. Parts were made from regular dies.



Prototype skin panel of automotive floor pan.

## LAMINATED PLASTIC TOOLS



Aircraft drill jig and scribe template.



Laminated plastic body stack for an automobile. All the body sections are fitted to a master cube. The frame structure of the cube and each body section is made of plastic tubing.

## SURFACE CAST TOOLS



Surface casting on stretch block for an aircraft leading edge wing skin. The above female mold is laminated material, using welded steel framework.



Aircraft leading edge stretch block. A kirksite core with plastic surface cast.

## SURFACE CAST TOOLS



Aircraft form blocks for inter-wing de-icer skins. The surface cast on kirksite cors.

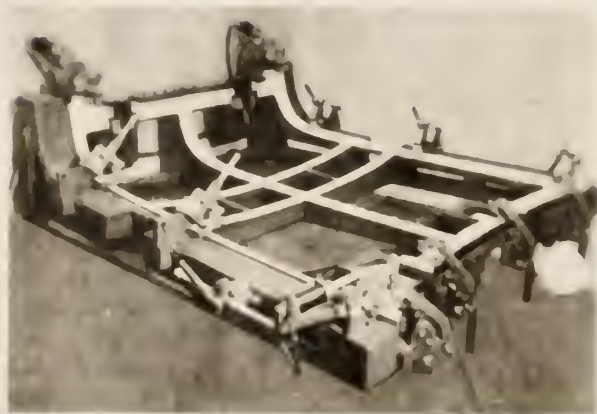


Master model of an automobile deck lid. The edges of the templates have been surface cast against a matching set of female templates.

## SURFACE CAST TOOLS



Aluminum cast frames, surface  
cast with plastic material.  
Tools used for checking fixtures.



Cast iron frame with plastic  
surface cast face.



## MASS CASTINGS



A good example of mass casting is this door hemming fixture for a hand flanging automobile door. The thin laminate shell is filled with epoxy resin mixed with sand and gravel.

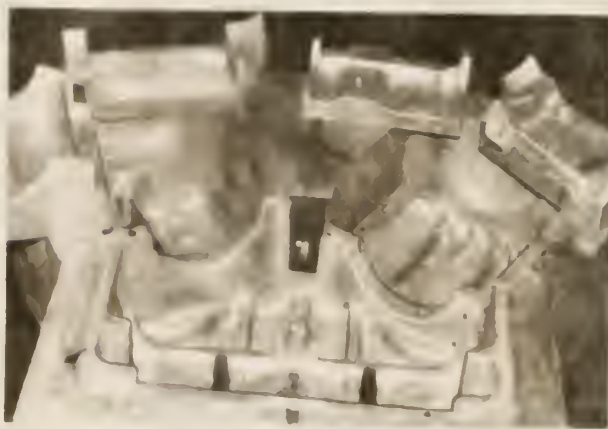


This aircraft stretch block is a solid cast comprising of epoxy resin mixed with sand and gravel.

## MASS CASTINGS



Vacuum holding fixtures are often cast with epoxy resins. The above fixture is used for machining thin aluminum aircraft forgings. The entire surface was machined on an end mill.



Plastic core box for aircraft engine. The laminated facing was done on a mass cast core.

## PASTE PLASTIC TOOLS



Master model of an automobile roof panel.



View showing spline model in photo above, while under construction.

## PASTE PLASTIC TOOLS



Master model of an aircraft gun turret. Metal forming tools are made from an accurate spline master model in order to provide precise fits of compound contoured parts.



Large spline master model made of an aircraft canopy.

EPOXIES  
THEIR RECENT APPLICATIONS  
IN AMERICAN INDUSTRY

by

MITHOO RAMCHANDANI

B.S., University of Poona, India, 1962

---

AN ABSTRACT OF A REPORT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Industrial Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

.1965

## ABSTRACT

Success is a habit with plastics. New materials, new processes, new end uses keep the industry flourishing. Hardly known a decade and a half ago, the achievement of the epoxies is outstanding. They have been established as unique materials for coatings, adhesives, tooling and low pressure molding and as stabilizer-plasticizers for other resins.

The epoxy resin is a viscous liquid or brittle solid, of no use until reacted and hardened with other materials. The commercial exploration of epoxy resins was begun by I. G. Farbenindustrie in the thirties. Since then the epoxy industry has grown and changed rapidly during growth. The early emphasis (1950) was on coatings. Nowadays they are used for tooling, road and building constructions and television tubes.

The future of the epoxies is very bright. Though the price is not expected to decline, the usage will increase primarily because of anticipated technological break-throughs.