MODIFICATION OF THE PROPERTIES OF AN EPOXY POLYMER ADHESIVE WITH BLENDING OR REINFORCING AND AN APPLICATION TO A SOLAR HEAT STORAGE MODULE

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ABSTRACT

Modification of the Properties of an Epoxy Polymer Adhesive with blending or reinforcing, and an application to a solar heat storage module.

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A study of the properties of a commercial epoxy polymer (EP) and of a modified epoxy polymer (MEP) by blending or reinforcing and the application of EP in producing a solar heat storage module was undertaken at the Centre for Building Studies (Concordia University, Montreal, Quebec).

The EP used (Araldite CA-1200) supplied by CIBA-GEIGY, proved to be effective for bonding sheet molding compounds (SMC) using a new EP riveting technique, and was found superior to joining with the conventional metal bolts technique. When cured, EP has good chemical resistance to water and benzene, it has low stability to methanol, but deteriorates in dimethyl formamide (DMF), acetone and aqueous solutions of sodium and calcium chloride.

Modification of EP by blending with poly-(vinyl chloride) (PVC), poly-(vinyl alcohol) (PVA) and dibutyl phthalate (DBP) in small concentrations (up to 4% of DBP) does not improve the tensile strength of bonded aluminum substrates, or the weatherability of the product when exposed to Canadian winter climate; however, improvement in the tensile strength and in

weatherability was found for the EP blend containing a higher concentration of DBP (6%). Incorporation of DBP into EP causes a marked reduction in heat distortion temperature (HDT), whereas addition of PVC has only a moderate effect; GF increases the HDT. Modification of EP with PU, DBP and PVC in concentrations of 7, 8, 15% respectively increases significantly the shear strength of aluminum bonds. The compressive strength of EP decreases when blended with DBP and PU, while the flammability increases.

The solar heat storage module studied here*, made from an EP shell and fatty acid esters mixture core, can be produced by different methods. The melting points of the fatty acid esters mixture are about 17°C for a minor part and about 22°C for the major part, which makes the module applicable for heating and cooling purposes. The high mechanical strength of the module makes it applicable for heat storage, partition wall or even as structural wall. Its low thermal conductivity makes it a good insulator in winter when stacked up infront of a south glazing.

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*This study was done to demonstrate an application of epoxy polymer in modern technology.

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TABLE OF CONTENTS

LIST OF FIGURES

Fig. LIST OF FIGURES Page

LIST OF TABLES

LIST OF SYMBOLS

ASTM	American Standard for Testing and Materials
DBP	Dibutyl-Phalate
DMF	Dimethyl-formamide
DPP	Diphenylol propane
DSC	Differential Scanning Calorimetry
DTA	Diethylene triamine
ECH	Epichlorohydrin
EP	Epoxy polymer
GF	Glass fibres
HDT	Heat distortion temperature
I.R.	Infrared
MEP	Modified epoxy polymer
N.W.	Natural weathering
PCM	Phase change material
PU	polyurethane
PVA	Poly-(vinyl alcohol)
PVC	Poly-(vinyl chloride)
R.T.	Room temperature
R, R', R''	Alkyl or aryl group
SMC	Sheet molding Compound
T_g	Glass transition temperature

CHAPTER I

INTRODUCTION

Since their conception, epoxy polymers have effected the building industry. Due to their introduction, many materials have been changed and new ideas have surfaced in building engineering. This has resulted in building installations which are more economical, more effective and which require less energy.

Epoxy polymers have a wide application to conventional and modern building materials to their versatility. Proper selection of resin, crosslinking agents and modifiers allows a wide choice of properties for the cured products ranging from soft, flexible material, to hard, tough and chemically resistant products with curing times ranging from virtually instantaneous to those requiring several hours.

Epoxy polymers can also be used in solar energy storage applications as a building component containing phase change material (PCM) for heating and cooling systems for residential and commercial buildings. The advantages of using epoxy over other similar building components are many. First, it has good mechanical properties which allows its use for both wall partitions and structural walls. Also, its cohesion, impermeability and adhesion to many substrates make it a good candidate for use in forming a tight container for phase change materials.

This thesis covers the preliminary stages of the experimental research program being conducted to study some applications of epoxy polymer and modified epoxy polymer. It has been divided into three parts.

Part I (Chapters II and III) is a general review on epoxy polymers, their curing agents and modifiers as well as their basic characteristics and applications for building and civil engineering.

Part II (Chapter IV) comprises the actual research study performed on the application of an epoxy polymer, before and after modification, as an adhesive. This research was conducted to improve bonding sheet molding compound using a new EP riveting technique and to check the chemical stability of EP. Also, the effect of modification of EP adhesive by blending or reinforcing was tested, using building materials, for tensile and compressive strength after the adhesive was exposed to Canadian winter climate. Tests were conducted to observe the changes in HDT, Tg, flammability and the peak exothermic temperature for the MEP.

Part III (Chapters V and VI) covers the second part of the study which deals with the application of epoxy polymer as one of the basic materials for a solar heat storage module. The EP was used in the module to get good mechanical properties within the temperature range of its application as a short term heat storage (usually 20°C to 50°C) and to achieve low thermal conductivity in preventing the heat loss when the modules are stacked infront of a south glazing. The flammability of the module was considered in the study.

The conclusions and recommendations are reserved until the end, Chapter VII.

PART I

CHAPTER II

EPOXY POLYMER - A GENERAL REVIEW

2.1 HISTORICAL REVIEW

Epoxy resins were first synthesized by P. Schlack, the inventor of nylon-6, in 1934 (1). The important curing reactions with polyfunctional amines and anhydrides were discovered by P. Castan in Switzerland in 1946, and the products were introduced by Ciba A.G. of Basel (now CIBA-Geigy) (2). Epoxy resins were initially developed as structural adhesives, then at the Swiss Industries Fair in 1946, Ciba Company demonstrated the use of an epoxide resin adhesive, Araldite Type I, to bond light alloys, and at the same time offered samples of an epoxide casting resin to four Swiss electrical companies. This introduction of the resins to industry can be considered as the beginning of the commercial exploitation of these remarkable materials.

Parallel with this European activity, the paint company Devoe and Reynolds had been working with Shell Chemical Corporation in the U.S.A. to develop epoxide resins suitable for the surface coating industry (3).

In the late 1950's and early 1960's other types of resin began to appear in the market, including epoxidised novolacs and other polyfunctional epoxy resins, resins derived from halogenated diphenylolpropane (DPP) for flame retardancy and resins to impart flexibility to castings (3).

The period from the mid-1960's to the late 1970's saw the continued development of new types of epoxy resins and curing agents. Increased interest was shown in the various types of cycloaliphatic resins, especially in view of their good anti-racking properties and resistance to ultra-violet light.

Undoubtedly, the future remains bright for epoxy resins. Since the 1930's and 1940's, this industry has expanded enormously and this trend will certainly continue since the demand for these materials is continuously increasing.

2.2 EPOXY POLYMER

The word "epoxy" comes from the Greek prefix meaning "over" or "between" and the English suffix for oxygen. The polymers are compounds which contain, on the average, more than one epoxide group per molecule, Fig. (1).

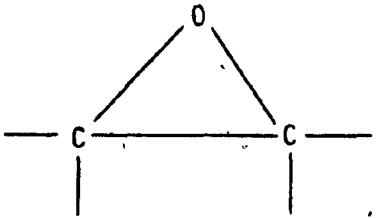
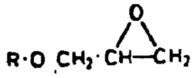
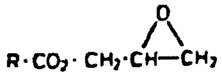


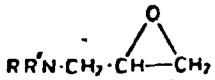
Fig. 1: Epoxide Group

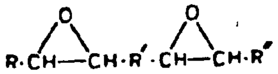
Those uncured resins, which range from free-flowing liquids to high melting solids, are not useful in this state, as they lack adequate molecular size. Once polymerized through these epoxide groups, using a cross-linking agent (also called a curing agent or hardener), they form a tough three dimensional network.

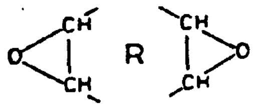
The parent resins can be broadly classified into the following five chemical groups (4).

(i) Glycidyl ethers 
$R\cdot O\,CH_2\cdot CH-CH_2$

(ii) Glycidyl esters 
$R\cdot CO_2\cdot CH_2\cdot CH-CH_2$

(iii) Glycidyl amines 
$RR'N\cdot CH_2\cdot CH-CH_2$

(iv) Linear aliphatic 
$R\cdot CH-CH\cdot R'\cdot CH-CH\cdot R''$

(v) Cycloaliphatic 

The epoxides in (i)-(iii) are usually prepared through a condensation reaction between the appropriate diol, dibasic acid, or diamine and epichlorohydrin (ECH) with the elimination of a simple molecule, hydrogen chloride. Epoxidised olefins (group (iv) and (v)), on the other hand, are formed by an addition reaction.

The most important group of commercial resins are made from glycidyl ethers of dihydroxy compounds; and 95% of all epoxide resins are made by the interaction of (ECH) and (DPP). Their general formula is given below (4).

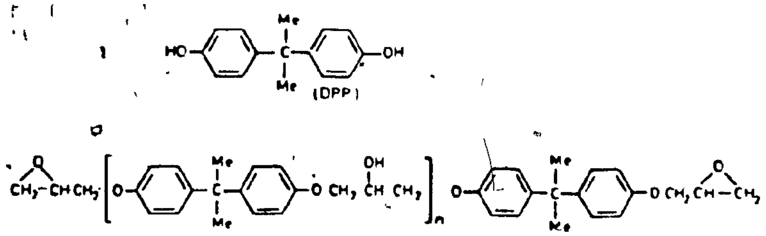


Fig. 2: Epoxide Resin

From the above figure, it is shown that resins with different degree of polymerisation (i.e. different values of n) are possible. The resin corresponding to n = o in the formula is a low-melting solid which can exist as a supercooled liquid. At values of n > 1 the resins are solids of increasing melting point.

These resins will, in general, react with compounds containing active hydrogen atoms such as phenols, alcohols, thiols, primary and secondary amines and carboxyls.

2.2.1 Epoxy Curing

Epoxy polymer can be transformed from a liquid or thermoplastic state to a hard thermosetting solid. This process is accomplished by the addition of a chemically active reagent known as a curing agent or hardener.

In the last twenty three years a number of compounds have been screened for their stability as curing agent. Many compounds used in the early years of the epoxy resin technology have now been replaced by more sophisticated materials, though some still keep their popularity and even, occasionally, enhance it (3). Table (1) shows some commercial curing agents and their characteristics (1).

The choice of curing agent to be used with an epoxy resin will depend on:

- The temperature required, the cure and post-cure time.
- The required handling characteristics in the uncured system, such as viscosity at working temperature, pot life, exothermic reaction and toxicity.
- The properties (physical, mechanical, electrical and chemical) required of the cured agent.
- The cost of curing agent.

The correct choice of curing agent can therefore be as important as the choice of the resin itself, both playing a part in determining the extent and nature of the intermolecular cross-linking, table (2) shows some more characteristics of curing agents (5).

Table 1. Commercial curing agents (1)

Materials	*Amount used parts per 100 resin*	*Pot life*	*Comments*	*Uses*
Diethylenetriamine (DTA)	8–11	45 min at 20°C	Liquid, volatile, and toxic. The amount used is also very critical	General-purpose room-temperature curing agent
Triethylene tetramine (TETA)	Very similar to diethylenetriamine			
Pipiridine	6	90 h at 40°C	Liquid, toxic, and volatile	Longer pot life and is used for castings
Triethylamine	10	7 h at 20°C	Catalytic	Adhesives
m-phenylenediamine (MPDA)	14	2½ h at 50°C	Solid with low toxicity	Chemical and heat resistant laminates
p,p' diaminodiphenyl methane (DDM)	27	8 h at 20°C	Solid-toxic	General purpose laminates
p,p' diaminodiphenyl sulfone	30	2 h at 20°C	Solid	Produces a cured resin with high heat distortion, point
BF_3 monoethylamine	5	3 weeks at 20°C	Solid—has a delayed action effect	Heat resistant resins
Phthalic anhydride	30–45	14 h at 100°C	Solid—produces a low exotherm	Coatings
Hexahydrophthalic anhydride (HHPA)	80	ditto	Solid	Castings
Chlorendic anhydride (HET ACID)	100	½ h at 110°C	Flame resistant	Flame resistant laminates

(a) Amines. Each amine group is difunctional and the following reactions are therefore possible.

Table 2. Characteristics of curing agents(5)

Curing Agent	Recommended Conc. Range with Standard Resin (phr)	Curing Temp. Range (°C)	Remarks
Diethylenetriamine (DETA)	8–10	R.T.–150	Fast cure, short pot-life
Triethylenetetramine (TETA)	10–13	R.T.–150	Fast cure, short pot-life
Diethylaminopropylamine (DEAPA)	4–8	R.T.–150	Requires moderate heat cure, longer pot-life
Aminoethylpiperazine (AEP)	20–23	R.T.–150	Requires moderate heat cure
Adduct of epoxy resin and DETA (Epon Curing Agent U)			Fast cure, short pot-life, low toxicity
m-Phenylenediamine (MPDA)	13–14	60–200	Requires heat cure, excellent High temp properties
Methylenedianiline (MDA)	28–30	60–200	Requires heat cure, excellent High temp properties
Diaminodiphenyl sulfone (DDS)	20–30	115–150	Requires heat cure, excellent High temp properties
Dicyandiamide (Dicy)	4–6	150–175	Long R.T. storage life
BF_3-monoethylamine (BF_3-MEA)	2–4	150–175	Long R.T. storage life
Polyamides (Versamid 100 series)	50–100	R.T.–100	Less toxicity, less volatility than polyamines
Amidoamines (Lancast A)	30–70	R.T.–100	Low viscosity
Polysulfides (Thiokol LP3)	50–100	R.T.–100	Flexibilizers, used with amines.
Polymercaptan (Dion 3–800LC)	50–100	R.T.–75	Used with amines or polyamides, fast cure

Curing agents have been considered in the following categories:

(1) Amines: These are the most commonly used hardeners in epoxy resin technology.

The primary and secondary aliphatic polyamines are a group of unmodified room-temperature curing agents which can be regarded as having low viscosity and low cost. The aromatic amines are essentially hot-curing systems, offering improved heat, chemical resistance and better strength properties than the aliphatic polyamines (4).

(2) Anhydrides: These compounds form one of the most important groups of curing agents and were mentioned by Castan in his early work (3).

When used with glycidyl ether resins, anhydrides provide cured systems that are light in color and have good mechanical and electrical properties and better high temperature stability than the amine-cured systems.

The resin-anhydride mixture has a low viscosity, long pot life and low volatility. It is non dermatitic, although the breakdown products formed during the cure of the mixtures may be irritating or even toxic (4). During cure, there is only little shrinkage and low exothermic heat evolution.

(3) Catalytic curing agents: All of the curing agents so far described have achieved curing primarily by a polyaddition reaction. The curing agents are compounds that have labile hydrogen atoms which react on a 1:1

basis with the epoxide group. The resulting cross-linked network has the curing agent built into it as the means of holding the resin molecules together.

Catalytic curing agents achieve cross-linking by initially opening the epoxide ring and causing homopolymerisation of the resin (1). The resin molecules react directly with each other and the cured polymer has essentially a polyether structure. Catalytic curing agents can be used in three ways: as a sole curing agent, as a co-curing agent in conjunction with a polyamine or polyamide or as an accelerator for anhydride systems.

2.2.2 Modifiers

Commercial epoxy polymers possess outstanding properties and can satisfy many applications without modification. Sometimes a certain change in a property or properties is required and this can be achieved selectively by the addition of modifiers.

Some of the important modifiers are fillers, reinforcing agents, plasticizers and accelerators.

- Fillers

Some fillers are added to epoxy in their application as epoxy adhesives. Their primary role is to reduce shrinkage. Since they do not shrink themselves and may occupy a significant volume of the total system, overall shrinkage is reduced. Fillers also reduce the coefficient of thermal expansion, aid thermal stability, including thermal shock resistance, increase thermal conductivity and lower the cost.

Some of the fillers used are: aluminium oxide, iron powder, copper powder and silica (table 3), (5).

- Reinforcing agents

Reinforcing agents can be added to epoxy polymers to improve some mechanical properties such as compression. Glass fibers of appropriate length are frequently used for this purpose (table 3).

- Plasticizers

The slight flexibility that is needed for shock or impact resistance can be readily achieved by minor variations such as decreasing the crosslink density. This is done by adding a higher molecular weight resin, by increasing aliphatic amine concentration or by decreasing anhydride concentration.

- Accelerators

Some accelerating agents can be added to epoxy to improve the speed of curing at room temperature. This is done by chemically leading the attack on the involved reaction groups in the resin or hardener.

Table 3 lists some fillers, reinforcements and additives that would result in modifying of epoxy polymer.

Table 3. Fillers, refinforcements and additives (5)

Property Improved	Filler, Reinforcement or Additive
Mechanical strength	Asbestos, glass fibers, alumina, silica
Specific strength or modulus (higher)	Graphite fiber, boron fiber
Specific gravity (lower)	Hollow microspheres
Shrinkage and coefficient of thermal expansion (lower)	Alumina, silica, quartz, calcium carbonate
Heat-resistance (higher)	Asbestos, mica, glass flakes, silica
Thermal conductivity (higher)	Metal powder, quartz, alumina
Electrical conductivity (higher)	Copper or silver powder, graphite
Arc resistance and dielectric strength (higher)	Mica, hydrated alumina, silica
Cost (lower)	Sand, calcium carbonate, many others
Fire retardance	Antimony oxide
Thixotropy	Colloidal silica, modified clays
Adhesion	Silane coupling agents

2.3 BASIC CHARACTERISTICS OF EPOXY RESINS

The popularity of the epoxy resins is a result of the following important characteristics:

1. Adhesion: Because of the epoxide-hydroxyl, amine and other polar groups, the epoxies have high specific adhesion to metals, glass, ceramics, plastic and mortar. They can be formulated to give mixes of low viscosity with improved wetting, spreading and penetrating action. The variety of functional groups also provides good affinity between metals and plastics.

2. Cohesion: When the resin is properly cured, the cohesion strength within the glue line is so great and adhesion of the epoxy to other materials so effective, that failure under stress often occurs in one of the adherents rather than in the epoxy or at the interface. This happens with glass and plastic as well as with weak adherents such as concrete, wood and glass.

3. Low Shrinkage: The epoxies cure with only a fraction of the shrinkage of vinyl-type adhesives such as polyesters and acrylics. 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 fraction of 1% by incorporation of silica, aluminum and other inorganic fillers.

4. Low Creep: The cured epoxies, like other thermosetting resins, maintain their shape under prolonged stress better than thermoplastics.

5. Resistance to Moisture and Solvent: Unlike proteins, starches and dextrins, the epoxies are insensitive to moisture. Their resistance to most chemicals is also outstanding and accounts for their rapid advance in the coatings field. They are effective barriers to heat and electric current. Their chemical inertness is enhanced by a dense, closely packed structure of the resinous mass, which is extremely resistant to solvent action.

6. Cure at Ambient Temperature: Expoxies can be cured within one minute at room or lower temperatures, depending on the curing agent.

7. Resistance to Wide Temperature Range: Epoxies can be formulated for use in cryogenic applications or for continuous service in high temperature environments.

8. Versatility: Numerous curing agents for the epoxies are available and the epoxies are compatible with a wide variety of modifiers. Hence, the properties of the cured epoxy-polymer system can be engineered to widely diverse specifications.

2.4 APPLICATIONS FOR BUILDING AND CIVIL ENGINEERING

Epoxy resins possess many outstanding and versatile characteristics including extreme toughness, low shrinkage on cure due to the absence of volatiles, also, an excellent resistance to chemicals, thermal change, solvents and water. They can, however, be modified with flexibilizers or reinforcing agents to improve their properties further and widen their applications, as mentioned earlier.

Epoxy resins are widely used in industry, especially for building engineering purposes when engineers are in need of durable, strong products which require little servicing and which have a long life expectancy.

Some of the many applications of epoxy polymers for Building and Civil Engineering are as follows:

- flooring
- road and bridge coatings
- bonding and repairing of building materials
- polymer concrete composites
- soil consolidation
- laminates
- castings
- Miscellaneous uses (repairing of statues, parking lots, foundations, etc.)

FLOORING

Floors based on conventional materials such as concrete break down very rapidly under certain conditions, resulting in severe problems. Chemical spillage, heavy wear by pedestrians and vehicles or vigorous cleaning are all factors that can lead to the disintegration of a floor. These conditions exist particularly in chemical plants, refineries, food factories, plating and pickling shops, canneries, breweries and warehouses.

Epoxide resin floors consist essentially of the binder resin, curing agent, any other ancillary chemicals in the formulation and the aggregate (i.e. filler) and pigments, if required. They are usually applied to concrete, metal or wood substrates.

A range of colours, surface finishes and thicknesses are possible. Important characteristics of these floors are:

- Excellent adhesion to a variety of surfaces
- Outstanding chemical resistance
- High tensile, compressive, impact and flexural strength
- Easy application and rapid cure
- Light weight compared with concrete
- Jointless, dust-free, skid-resistant and readily cleaned.

I. Screeded Epoxide Flooring

In this system, the resin binder is usually filled with graded silica sand or calcined bauxite in proportion of about 85% filler. The bauxite confers a wear resistance several times greater than that of Portland cement screeds. Typical formulations for trowelled application are as follows (6):

- Binder	Parts by Wt.	Parts by Wt.
Liquid diglycidyl ether resin	100	100
Pine oil (plasticizer)	27	20
Phenol (cure accelerator)	5	5
Diethylene triamine (DTA)	3	17
Coal tar (extender)	-	110

- Aggregate

Silica sand or calcined bauxite at an aggregate-to-binder ratio of 7:1.

Typical mechanical properties of trowelled epoxide resin floors compared with concrete are:

Property	Epoxide System	Concrete
Ultimate tensile strength, KPa	7-13790	1379-3448
Ultimate compressive strength, KPa	55-82740	20-41370
Impact resistance, N-m	146-292	160
Ultimate flexural strength, KPa	7-27580	6895
Specific gravity	1.9-2.1	-

Attractive epoxide resin terrazzo floors are also possible in both tile and jointless forms where the resin replaces the conventional cement binder.

II. Self-Levelling Epoxide Flooring

This system has a low viscosity and filler content, both ensuring a free-flowing mixture. It is poured onto concrete or other rigid substrates and spread out with a plastic comb, or broom, to a thickness of about 1.6 mm. The substrate must, therefore, be even enough to accept this thickness.

The self-levelling system has wear characteristics at least as good as the highest quality PVC or linoleum and has the added advantage of withstanding indentation by such things as stiletto heels (6). It is not suitable for areas where heavy abrasive wear is encountered, but is widely used for continuous floors in hospitals, schools, kitchens, light industrial factories and numerous other comparable situations.

ROAD AND BRIDGE COATINGS

Epoxide resin systems were first used in the U.S.A. as a protective membrane to prevent the spalling of concrete road and bridge surfaces and to overcome the ingress of water via cracks in the concrete of bridge decking which subsequently corrodes the steel structure underneath. In addition, the epoxide surface can be given non-skid properties by using an appropriate filler. These thin surfacings also give protection to the concrete from attack by de-icing salt, fuels and lubricants. An assessment of epoxide resin systems for road and bridge surfacings has been made by James (8) who classified the possible applications as:

(a) thin coating for concrete roads that are scaling
(b) thin coating for asphalt or concrete surfaces which have become slippery but are still sound.
(c) surfacing for sites where fuel spillage is a problem
(d) road marking material
(e) thin lightweight surfacings for bridge decks

(f) coloured surfacing

(g) additions to conventional bituminous surfacings to improve the performance.

BONDING AND REPAIR OF BUILDING MATERIALS

In 1944, epoxy resin adhesives were recognized as the first cast-in-place adhesives capable of reacting without the evolution of volatiles, often without heat or pressure and curing with low shrinkage.

Epoxide resins, which have good adhesion and good mechanical strength properties, are ideal for the bonding and repair of cracks in concrete (dams, columns, piers, roads), wood, brick, metal and many other materials. An important feature is their ability to form strong bonds between wet alkaline materials such as concrete.

For grouting or crack repair, filled adhesive is poured, brushed or even injected under pressure when the crack is very fine. The strength and slight flexibility of the epoxide binder are sufficient to resist load and temperature stresses. They also prevent progressive concrete failure that would otherwise occur at the cracks. Epoxide grouting mixtures have the following properties that can be utilized to advantage:

- low-shrinkage
- room temperature curing
- excellent dimensional stability and mechanical strength when cured
- excellent adhesion to metal and concrete
- good chemical resistance
- vibration damping effect.

Bonding is very useful for precast concrete structures. By this technology, epoxies were used to assemble huge structures on site. A recent structure assembled with the aid of epoxy adhesives was the Olympic Stadium and Velodrome in Montreal. This project was described by a prominent Canadian Civil Engineer (7) as "the most sophisticated complex and largest precast, prestressed and cast in site concrete structures ever attempted by man - all in the shortest possible period of time. A task truly Olympian in imagination, challenge, strength and stamina!" In this project, with an average joint thickness of one millimeter, the epoxy adhesive consumption was around three tonnes.

POLYMER CONCRETE

In essence, polymer concrete is a generic term and refers to a type of concrete produced with no cement or water in its make-up: The binder consists of synthetic polymers (epoxy). The most dramatic result of this switch is the very impressive strength properties of polymer concrete: 103 MPa in compression compared to 34 MPa for high quality precast concrete (9). This is in large part due to the inseparable bond the polymers form with aggregates and sand in the mixture. It is also the reason why, in tensile strength, polymer concrete is four to five times as strong as regular concrete. Polymer concrete can be used at one-quarter the thickness of regular concrete, yet exhibits superior qualities. Usually reinforcing steel is not needed.

SOIL CONSOLIDATION

An ingenious use for epoxide resins is in oil wells which are drilled in geological formations of loose sand. In cases of this kind, the sand can enter the well, cause blockages and hence reduce the output. This difficulty has been successfully overcome by using a solvent containing an amine-cured system to consolidate the sand around the well bore. The consolidated sand then becomes a filter, which prevents further movement of sand into the well itself. The process of consolidation first requires the use of an alcoholic solvent to remove water in a small area of the sand around the bottom of the well. The liquid resin system is then pumped into the pore space of the dry loose sand. As curing proceeds, a liquid polymer first separates out and spreads over the sand grain surfaces, concentrating at grain-to-grain contact points. This liquid phase then undergoes further curing to form the usual tough, cross-linked polymer which cements the grains firmly together.

LAMINATES

Epoxy resins are used to manufacture laminates at low and high pressure. The presence of reinforcing fibers lends added strength and stiffness to the final composite. A combination of high-strength fibers with the adhesive properties of epoxy yields physical properties unsurpassed by other similar building materials.

Epoxy resins cure without water of condensation. This makes them particularly suitable for this application since the absence of water in the curing process permits the development of great adhesion to the reinforcing fibers. When cured, the laminates exhibit outstanding mechanical, thermal, structural, electrical properties and good chemical resistance.

The market for laminates in building and Civil Engineering applications is limited now because of high price.

CASTINGS

Epoxy resin is used for casting some special building components when physical and chemical properties are needed.

For solar energy purposes, epoxy polymer can be used for macro-encapsulation of phase-change material because of the following properties:

- easy and fast handling
- good physical properties
- good dimensional stability
- low volumetric shrinkage on cure
- good chemical and heat resistant properties
- low coefficient of thermal expansion on curing
- sufficient low viscosity to be pourable.

This material was used for a heat storage brick module that was designed and will be explained in detail later on.

MISCELLANEOUS USES

Lightweight exterior cladding panels for buildings have been coated with an epoxide system which is followed by an aggregate to protect and enhance the appearance of the panelling. Epoxide resin mortars have been used as tile grouts with outstanding chemical resistance. Kitchen sinks and shower bases have been fabricated from epoxide moulding powders by a compression moulding technique. Reflecting studs for road use have been made from reflecting particles (small glass spheres) dispersed in the epoxide resin system, the stud being bonded to the road by an epoxide adhesive. Epoxide resin laminates have been used as shuttering for structural concrete and for the preparation of decorative concrete facing panels. Statues affected by weathering and aging are repaired by epoxy polymers.

There are numerous other examples of epoxide resin compositions being used in the construction industry but all of the aforementioned uses represent only a few of the many applications of these highly versatile resins in building and civil engineering industries.

CHAPTER III

EXPERIMENTAL RESEARCH

3.1 OBJECTIVES AND RESEARCH PROGRAM

The objectives of the research is: first, to study a commercial epoxy polymer adhesive and improve its properties by modifying it with plasticizer, polymers and a reinforcing agent. Second, to use this epoxy polymer as the basic material to produce a container for phase change thermal storage module.

Some tests were chosen to study the mechanical, physical and thermal properties of the EP, the MEP and the module.

- CHARACTERIZATION OF THE EPOXY AND MODIFIED EPOXY POLYMER

I. Mechanical Properties

A) Tension and shear test

a) Using conventional building materials: wood, mortar and aluminum as substrates, the adhesion of EP & MEP was measured in tension after the samples were exposed for a period of time to room temperature (R.T.) and natural weathering (N.W.) to evaluate the effect of the outdoor exposure to Canadian climate.

With aluminum substrates, EP and MEP were tested for shear strength using over lap joints with a new design of epoxy rivets.

b) Using a modern building material plastic reinforced composite, known as sheet moulding compound (SMC), the adhesion strength of EP and MEP using overlap joints with different arrangements of epoxy rivets was tested.

B) The compressive strength of EP and MEP was measured in accordance with ASTM methods after the samples were exposed to room temperature and artificial weathering. The artificial weathering consisted of 57 and 171 cycles respectively at 8 cycles/day between a temperature of $-40^{0}C$ to $+10^{0}C$.

C) The chemical stability of EP was characterized with a tensile test after being immersed in chemicals for four months.

II. Physical Properties

A) The flammability by oxygen index method was evaluated for EP and MEP.

III. Thermal Properties

A) The glass transition temperature (Tg) of EP and MEP was established by differential scanning analysis.

B) The heat distortion temperature (HDT) and relative degree of cross-linking was tested with ASTM (D648) method.

C) The peak exothermic temperature of EP and MEP was followed.

- APPLICATION OF EPOXY POLYMER FOR A HEAT STORAGE MODULE

I. Mechanical Properties

A) The compressive strength of the module was measured at $23^{0}C$ and $50^{0}C$.

II. Physical Properties

A) The flammability of EP (XP-1203) was established by ASTM D-2863, the oxygen index test.

III. Thermal Properties

A) The thermal conductivity of the module was measured in accordance with ASTM C518.

B) The heat distortion temperature for EP (XP-1203) and plastic material (plexiglass) was established by ASTM test D648.

C) Using the thermal analyzer, the glass transition temperature of EP (XP-1203), the melting temperature and the heat of fusion of the phase change material (PCM) were determined.

3.2 MATERIALS

The epoxy polymer (control) was a commercial, thixotropic, structural adhesive grade (Araldite CA-1200) supplied by CIBA-GEIGY. It was cured with an aliphatic diamine, using the weight ratio of 100:11 (EP: amine). Table 4 shows its properties and, in some cases, those of similar commercial adhesives.

The other commercial modifiers used for EP are: a well known plasticizer for polymers, dibutyl phthalate (DBP) (J.T. Baker Chem. Co.), polymers such as poly-(vinyl alcohol) (PVA) (Anachemia), poly-(vinyl chloride) (PVC) (B.F. Goodrich), poly-(urethane) (PU) (Helmitin Canada Inc.).

In the case of the reinforced product, the reinforcement was provided with short glass fibers type E, (7 ηm ∓ 0.6) in diameter, and a length distribution in the range of 10-15 mm.

The building materials used as substrates were:

- Conventional materials: California red-wood, high early strength Portland Cement (type 30) and aluminum.
- Modern material: Sheet moulding compound, SMC-R65, supplied from Budd Company with the material code DSM-750 which comprises a thermosetting polyester, reinforced with glass fibers.

For the heat storage module, some additional materials were used: thixotropic structural adhesive (XP-1203), which have the same chemical structure as (CA-1200) but with lower viscosity, supplied by CIBA-GEIGY, cured with an aliphatic diamine hardener using the weight ratio of 100:11

EP: amine), shown in table 4, commercial plexiglass, 6.35 and 2.00 mm thick and a mixture of Fatty Acid Esters, commercially known as Emery 2204, supplied from Emery Industries Limited.

TABLE 4

PROPERTIES OF ADHESIVES

Adhesive	Basic Polymer	Color	Viscosity Mpa x sec x 10^{-3}	Density g/cm^3	Mix Ratio	Supplier
CA-1200 Hardener	Epoxy	White Black	1200 .05	1.64 0.91	100 11	Ciba-Geigy
Araldite AV I38M Hardener HV 998	Epoxy	Pale Beige Grey	500 380	1.60 1.70	100 40	Ciba-Geigy
Poliogrip 6000 Poliogrip	Polyurethane ----	Tan-Brown Green	30-10 8.5-1.5	1.22 1.03	100 25	Goodyear Chemicals
XP-1203 Hardener	Epoxy	Brown Clear	50-30 .05	1.70 0.87	100 11	Ciba-Geigy

PART II

CHAPTER IV

EPOXY AND MODIFIED EPOXY POLYMER ADHESIVE

4.1 INTRODUCTION

The outstanding characteristics of epoxy polymer as an adhesive are that they will form strong bonds to almost all surfaces. Modern adhesives technology has led to the development of many types of epoxy and modified epoxy-based adhesive systems. This modification of epoxy should lead to some improvements in its properties and broaden its application in building industry.

Only a few studies dealt with blends of epoxy polymers and other high polymers, including diallyl phthalate-epoxy interpenetrating polymer network (10), nylon-epoxy blends (11) and epoxy-modified polyethylene (12). Most studies discussed different aspects of rubber modified epoxies (13-19).

At the Centre for Building Studies*, previous studies (20,21) of some modified polyurethane were reported. A similar but more detailed study was subsequently carried out on an epoxy polymer modified by blending with DBP, PVC, PVA and by reinforcing with glass fibers. Some tests, previously listed, were chosen to study the mechanical, physical and thermal properties of the epoxy and the modified epoxy polymer.

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* Concordia University, Montreal, Quebec

4.2 MECHANICAL PROPERTIES

4.2.1 A) Tensile Strength (Conventional Building Material)

This experiment was done to study the adhesion of EP to conventional building materials and the effect of natural weathering (N.W.) on the properties of EP and the behaviour, under the same conditions, of its polyblends and mixtures with the reinforcing agent or plasticizer. Identical samples were subjected to two different types of weathering:

a) the first series was maintained 200 days at a temperature of 22°C and 20 - 50% relative humidity.

b) the second series was kept outside on the top of a building, in downtown Montreal, in a relatively highly polluted area for 100 days during the period of January - April. The lowest temperature recorded during that time was -26°C (January 26th) and the highest, 22°C (April 16th).

The specimen comprised essentially a bead (12.5 x 12.5 x 50 mm) of epoxy cast between two rectangular plates of substrates (13 x 25 x 76 mm).

Preparation of Specimens

a) Epoxy

The control specimens of EP were prepared by mixing epoxy resin (CA-1200) with the hardener for five minutes at room temperature in the ratio of 100:11, W:W. The samples were kept for 7 days at the same temperature for curing.

The modified epoxy specimens were prepared in two steps; in the first (5-10 min.) the resin was mixed (with a rod in a beaker) with the modifier (PVC, PVA, DBP or G.F.) and, in the second step (5 min.), the resultant mixture was blended with the hardener in the same ratio as in the control specimens (100:11, epoxy:hardener). It was then poured between the rectangular plates of the substrates.

b) Substrates

The substrates were made of aluminum, wood or Portland Cement. The preparation of the surface for casting the epoxy varies with the type of material. They were prepared as follows:

Aluminium: The substrates selected were free from scratches or any other defects. To remove any gross oil films, the substrates were immersed for five minutes at 75°C in an etching solution of chromic acid (sulphuric acid plus potassium bichromate). Then they were thoroughly washed with tap water for 10 minutes. Finally, they were then dried in an oven at 105°C for one hour before casting.

Mortar: The Portland cement mortar pieces were prepared by using one part of high early strength Portland cement and two parts by weight of clean, well graded fine aggregate (ASTM C33). After curing one day in moist conditions (90-95% R.H.) and 28 days in water at 23 $\mp$ 2°C the tested surface was polished by wet grinding using No.60 silicon carbide. The pieces were then oven dried to a constant weight at 105°C and cooled to 23 $\mp$ 2°C. The substrates were brushed with a clean natural bristle paint brush to remove any loose dust left on surface.

Wood: The wood pieces (California red wood) were brushed clean with a natural bristle paint brush to remove dust and dirt then kept at room temperature (23 + 2^{0}C, 35-50% R.H.) until the samples were prepared.

Casting Phase

This phase involves the casting procedure and comprises the following steps:

a) a piece of wax paper was placed in the wooden mold

b) the substrate bars were positioned on the wax paper in the mold with 12.5 x 12.5 x 12.5 mm end spacers which were placed between the substrate bars to provide uniform sizes of the polymer.

c) the epoxy-polymer or modified epoxy-polymer was poured into the 12.5 x 50 mm cavities. Care was taken to ensure that pouring was slow and even in order to avoid entrapping air which would weaken the bond.

Testing Equipment

An instron Model 1125 (fig. 3), Universal Testing machine with a direct plotter was used for all mechanical testing. Two new grips were designed (fig. 4) to accommodate and avoid the destruction of the samples before being tested.

Results and Discussion*

Effect of Additives on the Ultimate Tensile Strength

a) DBP: Blends of modified EP containing small amounts of DBP (2-4 Wt%) were found to have moderately lower ultimate tensile strength (7.8 - 8.3 MPa) than that (9.8 MPa) of the unmodified polymer. However, an increase in the concentration of DBP in the blend to 6% was found to result in

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* All results were taken as an average of at least five specimens.

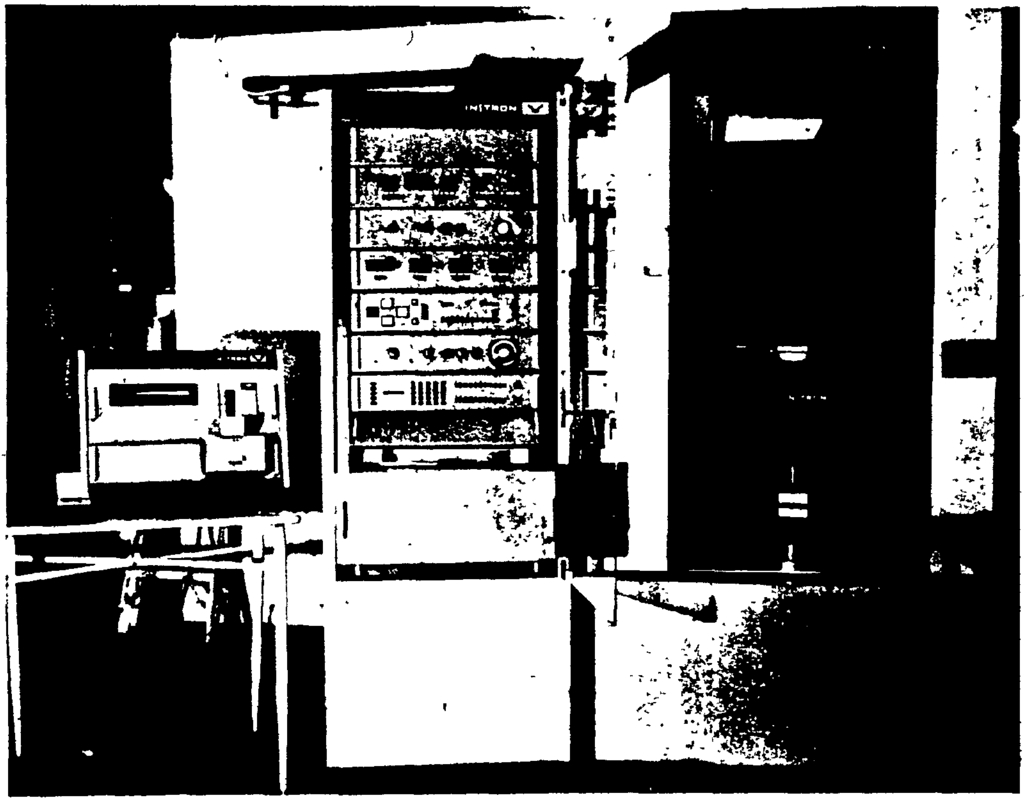

Fig. 3. The INSTRON Model 1125 mechanical-tester

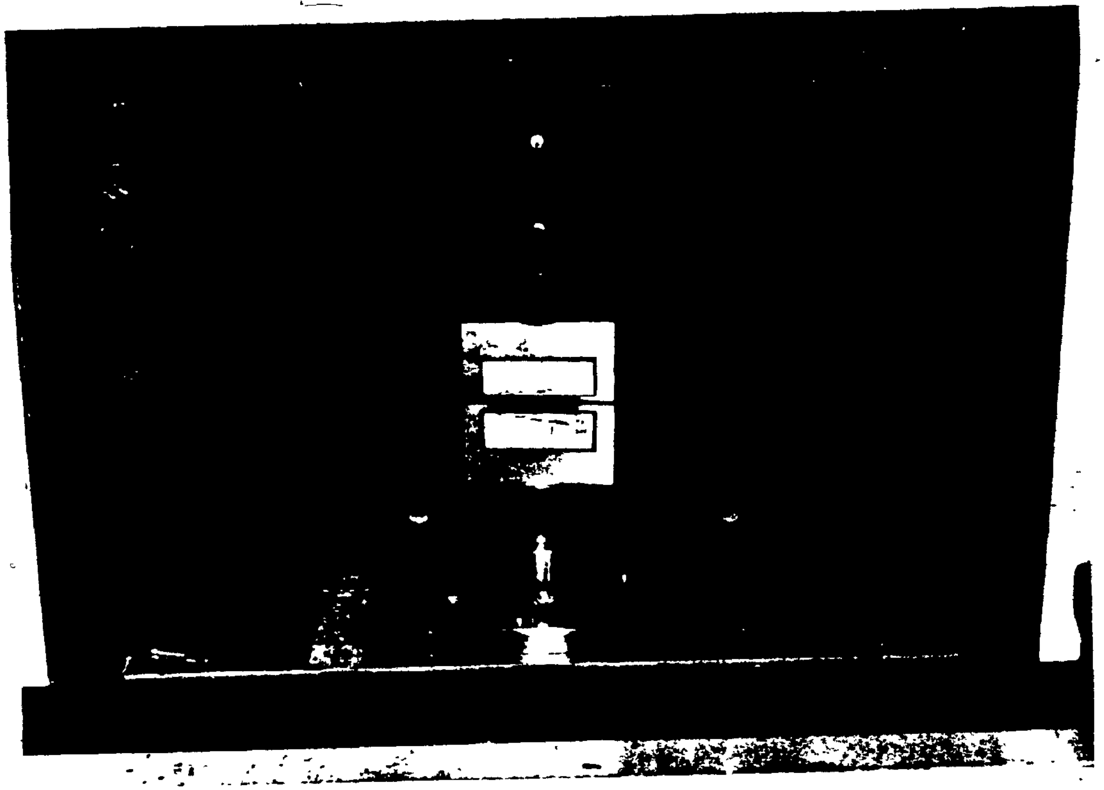

Fig. 4. Instron grips and tension test sameple, Aluminum substrate.

slightly higher value than that of the unmodified EP, for both the ultimate tensile strength (9.9 MPa) and strain (fig. 5).

The higher amount of DBP might have lead to higher value of intermolecular forces and higher mechanical properties. Both materials (EP and DBP) being polar, may reach dipol-dipol intermolecular bonds.

a) PVC: Incorporation of PVC into the cured EP has generally detrimental effect on the ultimate tensile strength of the corresponding blend (fig. 6). The tensile strength of blends containing 2-5% of PVC is only approximately 35-50% that of unmodified EP. A concentration of 6 to 10% of PVC in the EP-PVC blend causes a reduction of 10% in the ultimate tensile strength (fig. 6) because of a probable decrease of the degree of cross-linking of EP.

c) PVA: PVA has a greater effect than PVC in lowering the ultimate tensile strength of EP-PVA blends. A 10% concentration of PVA induces a reduction in ultimate tensile strength greater than 36% (fig. 6).

d) GF: Reinforcing with glass fibers (1 or 2%) caused a marked decrease in ultimate tensile strength and strain (fig. 7). For example, the ultimate tensile strength of blends containing 1 and 2% of glass fibers is only 50 and 30% respectively that of unreinforced EP. This decrease in strength can be caused by:

- decrease of the degree of crosslinking
- lack of a coupling agent between the fibres and EP.

Effect ~~of~~ Outdoor Exposure (N.W.) on the Ultimate Tensile Strength

The resistance of EP adhesive material (unmodified and modified) to outdoor exposure was assessed on sandwich specimens. Aluminum was used as

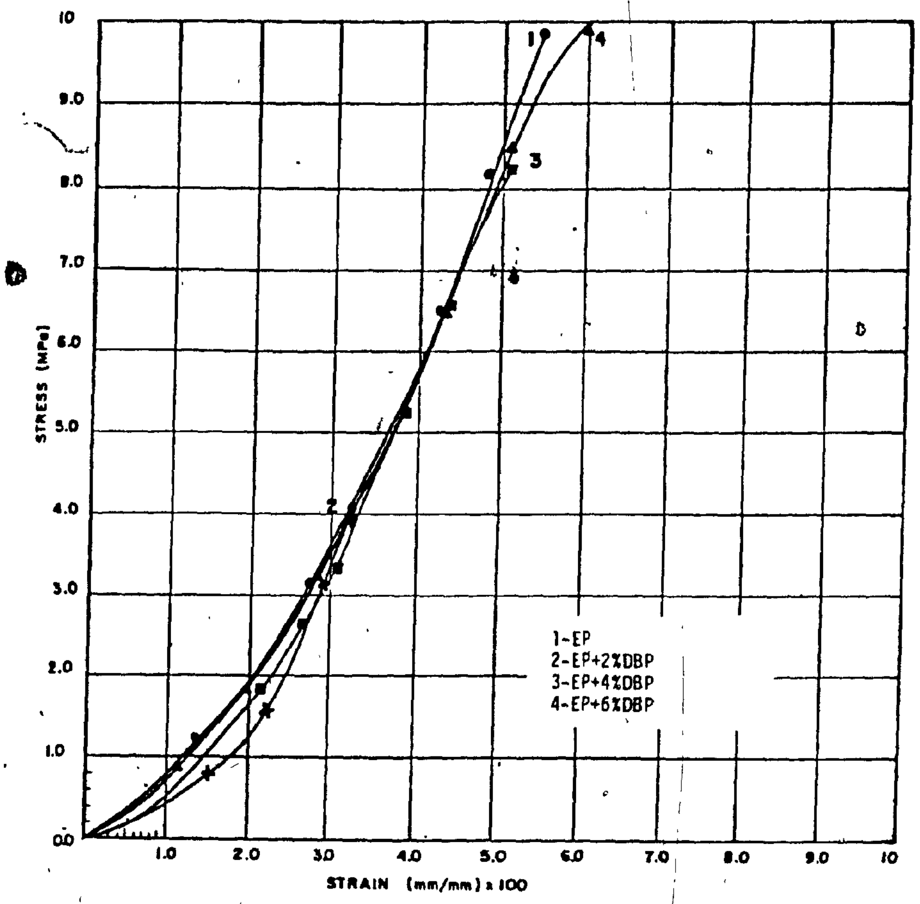

Fig. 5.Stress-Strain Curves Showing the Effect of DBP on the Ultimate Tensile Strength of Epoxy.

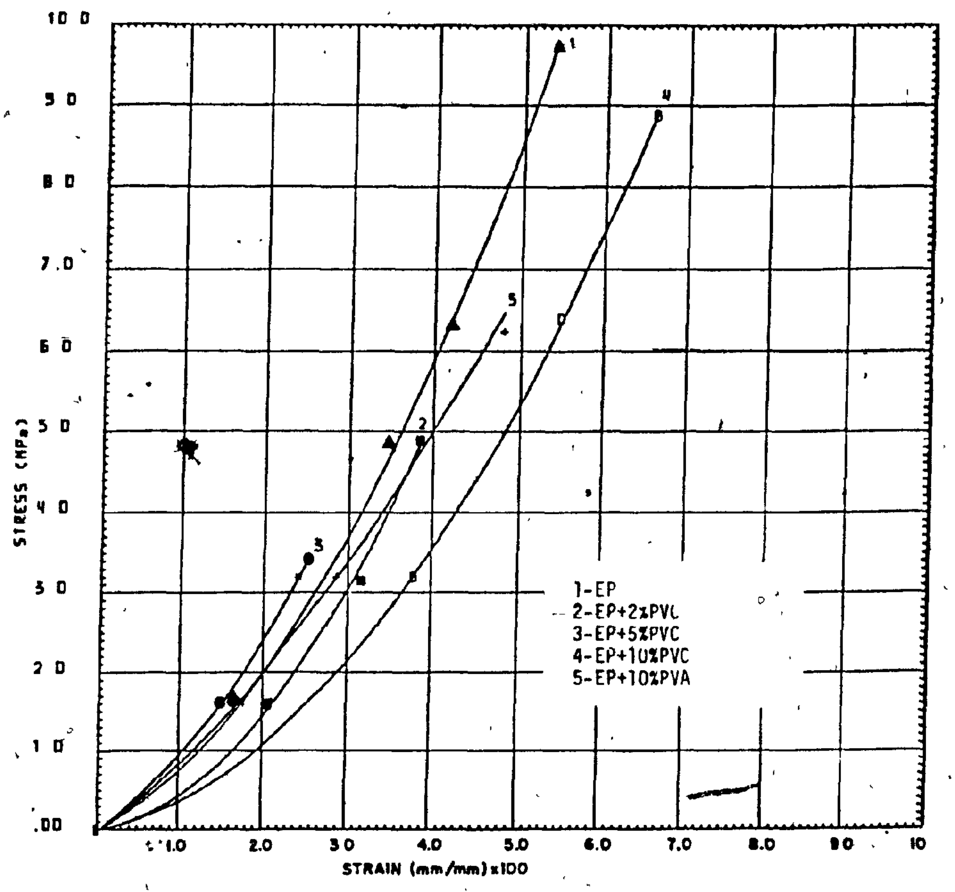

Fig. 6. Stress-Strain Curves Showing the Effect of PVC and PVA on the Ultimate Tensile Strength of EP-Based Blends.

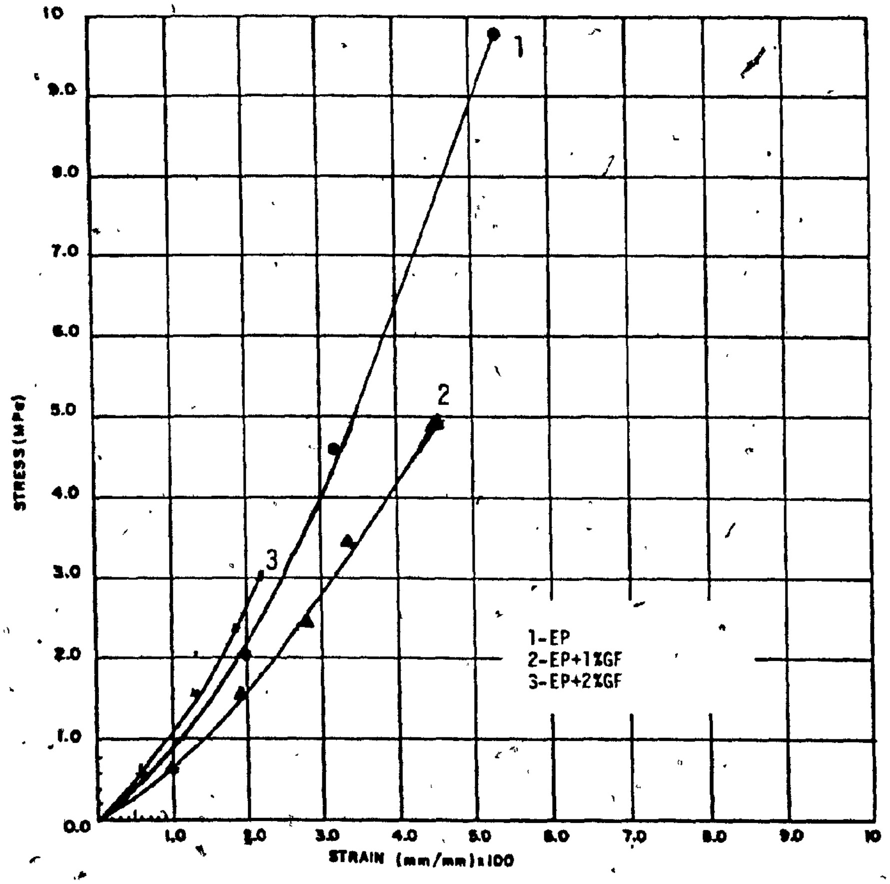

Fig.7. Stress-Strain Curves Showing the Effect of GF Reinforcement on the Ultimate Tensile Strength of EP.

substrates as aluminum was found to have a better adhesion to cured EP, also, with this substrate it allows a more accurate method to assess the adhesion properties. In many cases, the mortar or the wood failed without any failure of the adhesive.

At the end of 100 days of outdoor exposure the various specimens were tested for tensile strength to assess the change in bond strength. Results are presented in fig. 8.

Outdoor exposure for 100 days causes a considerable deterioration in the tensile strength of unmodified EP. The exposed specimens retain only approximately 43% (curve 2) of the ultimate tensile strength of the unexposed material (curve 1). It is believed that the deterioration is caused by a cryolitic process (mechano-chemical degradation as a result of freeze-thaw cycles) which occurred within the epoxy network in a manner similar to that of polyurethanes (22) which occurs very frequently in the Canadian climate during March and April. It is known that freeze-thaw cycling induces the formation of localized forces which cause the mechanical degradation of the polymer chain, resulting in a decrease of the molecular mass. For example, water which is liquid during the warmer period of the cycle, is converted into ice crystals at the freezing temperature and thus produces considerable localized stresses as a result of its volume increase. In addition to mechano-chemical degradation, EP resin may also undergo chemical degradation induced by chemical pollutants, that is, in an acidic atmosphere (SO_2, SO_3, CO_2, etc.) and in the presence of moisture we may have acidolysis of the main chains of EP.

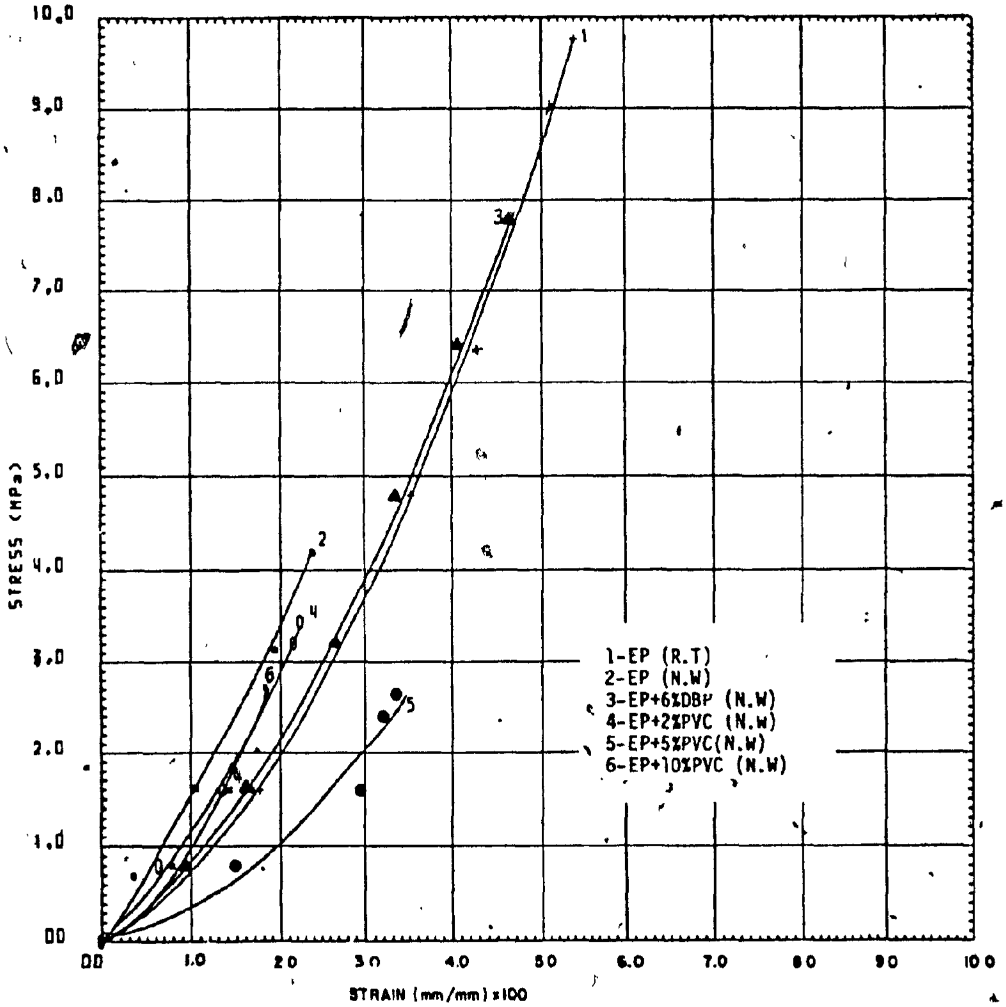

Fig. 8.Stress-Strain Curves Showing the Effect Of Outdoor Exposure on the Ultimate Tensile Strength of EP and MEP.

a) DBP: EP based blends containing 6% of DBP have better resistance to deterioration by freeze-thaw cycles in outdoor exposure than unmodified resin. For example, the ultimate tensile strength of the blend at the end of 100 days after outdoor exposure (fig. 8, curve 3) is 78% of that of an unexposed sample (control) and 1.8 times higher than that of the unmodified EP exposed outdoors under similar conditions (fig. 8, curve 1).

b) PVC: The PVC modified EP samples had slightly better resistance to outdoor exposure at low concentrations (2% of PVC) (fig. 8, curve 4) but they underwent a marked deterioration in ultimate tensile strength with increasing concentration. The tensile strength of EP blends containing 5 and 10% of PVC (fig. 8, curves 5 and 6) was only 28 and 25% respectively of the value of unexposed (control) blend.

c) G.F.: The G.F. modified EP samples experienced a reduction in tensile strength when exposed to the outdoor climate. A reduction of 30 and 10%, that of unexposed samples, for the 1 and 2% G.F. respectively (fig. 9, curves 4 and 5). This may be explained by a low adhesion (lack of coupling agent) between the glass fiber and epoxy adhesive. An improvement of this property may be expected by using a special treatment with a coupling agent for the fiber before mixing with the polymer.

d) PVA: All samples prepared with PVA modified EP failed at the end of exposure period and before they were tested.

Effect of Substrate on Adhesive Properties of EP

The effect of substrate on the adhesion strength of EP was hard to compare because, in the case of wood and mortar, the substrates broke, leaving behind an undamaged adhesion and cohesion bonds. Fig. 10 shows the adhesion strength of EP with aluminum and the strength of wood and mortar substrates.

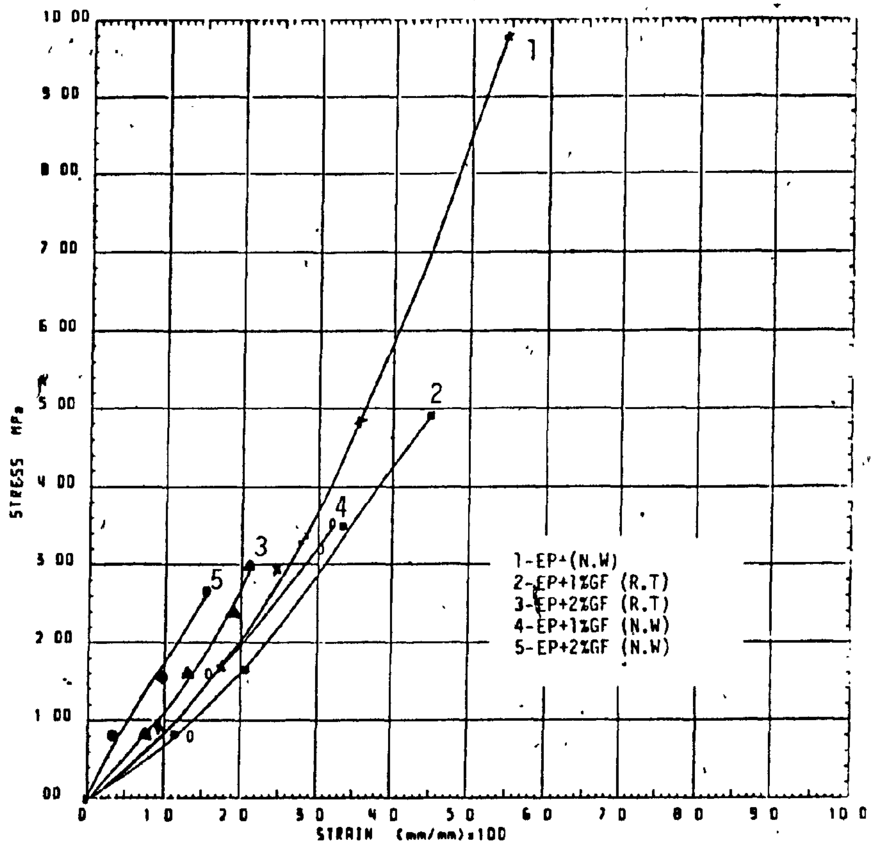

Fig. 9.Stress-Strain Curves Showing the Effect of GF Reinforcement on the Ultimate Tensile Strength of Exposed EP.

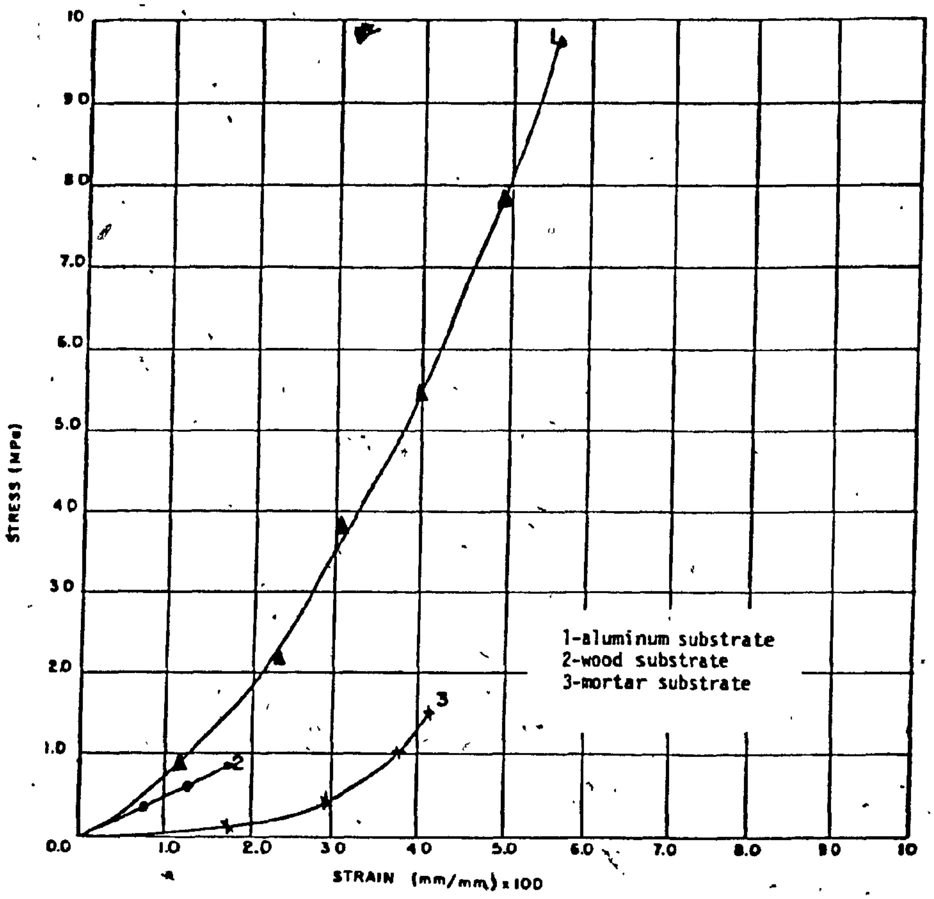

Fig. 10.Stress-Strain Curves Showing the Effect of Substrates on the Ultimate Tensile Strength of EP Bonds.

4.2.1 B) Shear Strength (Conventional Building Materials)

This test was conducted on a specimen made of aluminum substrates bonded together in an overlap form with EP and MEP. A new riveting technique was used.

The EP and MEP were prepared by the previously mentioned method; the modifiers were DBP, PVC and PU.

The size of the aluminum substrates was 25 x 100 x 1.5 mm. An etching solution of chromic acid was used in which the substrates were kept at 75^0C for five minutes. After this, they were washed thoroughly with tap water for 10 minutes, dried in the oven at a temperature of 105^0C until one hour before bonding.

The area of overlap was 25 x 25 mm with a hole at center (fig. 11). Two thin layers of EP or MEP were applied to the bond area, and two pieces of thread were laid to control the adhesive thickness. The samples were kept at room conditions for seven days before testing. The Instron machine was used at a cross head speed of 5.0 mm/min. and a chart speed of 50 mm/min. at room conditions (22^0C).

Results and Discussion*

In testing the control EP and MEP with aluminum substrates and using the new method of epoxy rivet, the following observations were made:

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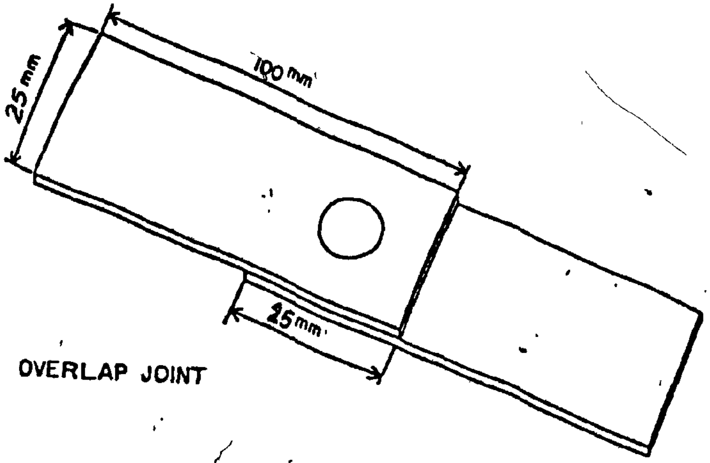
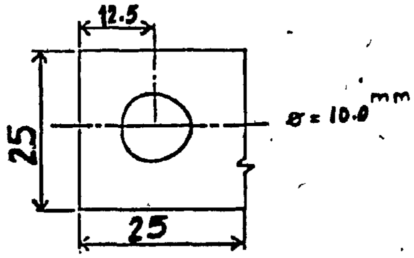
* All results were taken as an average of at least five specimens.



(a) OVERLAP JOINT



(b) BOND AREA

Fig. 11. Shear Strength Test Specimen with Riveting Technique, Aluminum Substrate.

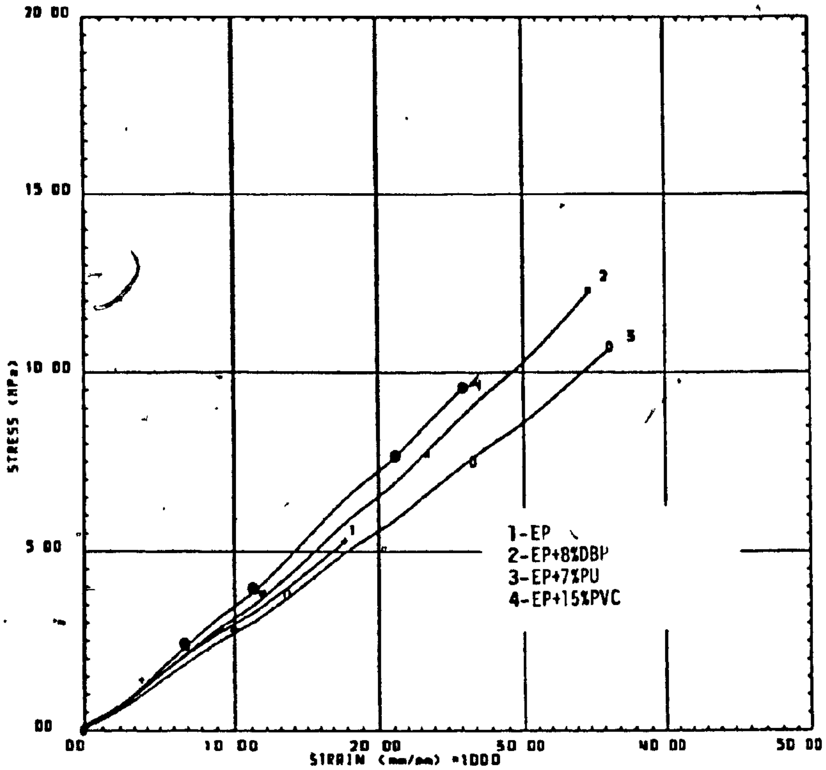


Fig. 12.Stress-Strain Curves Showing the Effect of Modified EP on the Ultimate Shear Strength of AluminumBonds Using Riveting Technique.

Table 5: Shear strength results, aluminum substrates

Epoxy Polymer	Additive	% Additive	Shear Strength MPa
CA-1200	———	———	5.0
CA-1200	DBP	6 8 14	11.5 12.5 8.0
CA-1200	PU	5 6 7 8	8.0 10.5 12.0 11.0
CA-1200	PVC	10 15 20	5.0 6.0 5.0

1. The DBP modified epoxy samples were found to develop an increase in shear strength,12.5MPa for 8% DBP compared with 5 MPa for control EP. This represents an increase of 160% (fig. 12, curves 1, 2), (table 5).
2. It was observed that PU modified epoxy shows an increase in shear strength, 12 MPa for 7% PU, that is, an increase in strength of about 140% that of the control EP (fig. 12, curves 1, 3).
3. Using PVC modified epoxy, it was noticed a very slight improvement in tensile strength of about 18%, that of EP, for 15% PVC (fig. 12, curves 1, 4).

4.2.2 Tensile and Shear Strength (Modern Building Materials)

EP bonding of sheet molding compound was tested using different types of overlap and butt joint arrangements. With overlap, different epoxy rivet arrangements were used to improve the classical bonding technique of metal bolts (fig.13, a). The control EP CA-1200 with two other adhesives, AV-138 and Poliogrip 6000, were used for bonding. The properties of these adhesives are listed in table 4.

The modern material (SMC-R65) was cut to a size of 100 x 38 mm, brushed and kept at room temperature until the epoxy was applied.

The Instron machine was used with a cross-head speed of 5.0 mm/min. and chart speed of 50 mm/min.

Joining Arrangements

Different joining arrangements are shown in fig. 13,

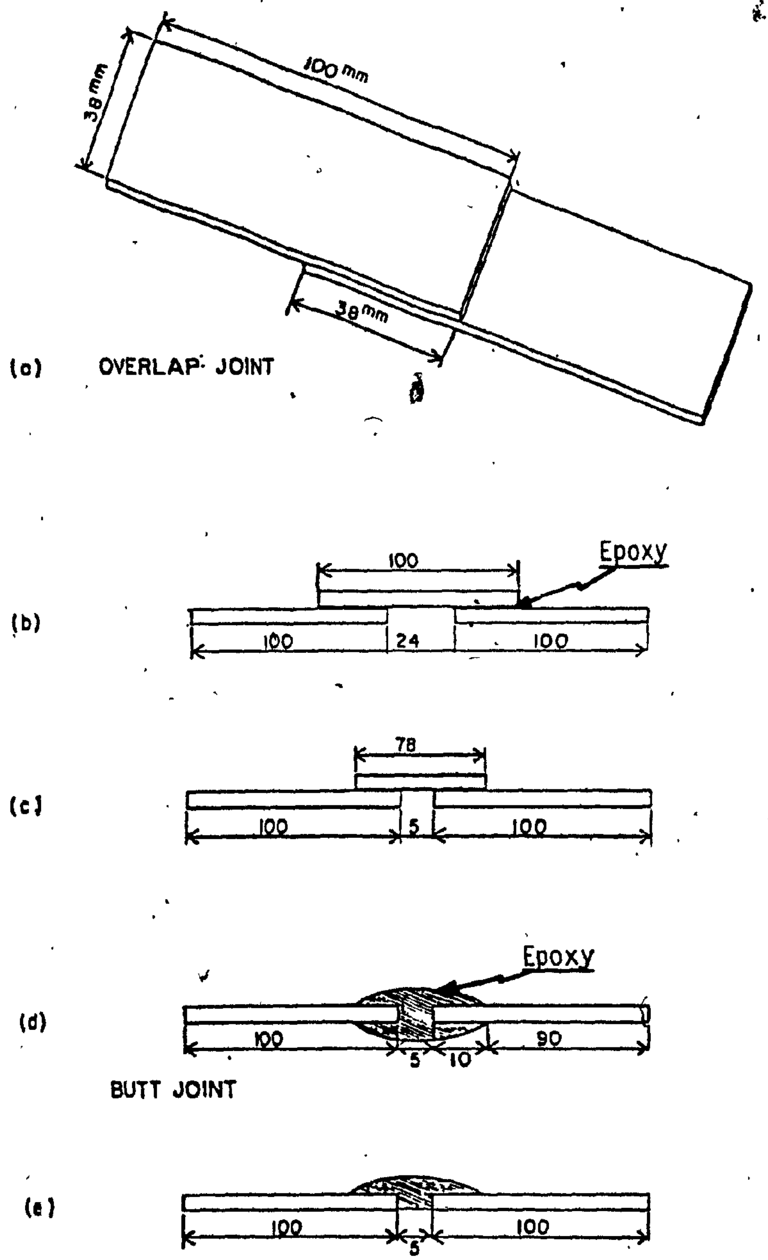


Fig. 13. Joining Arrangements for Modern Building Material

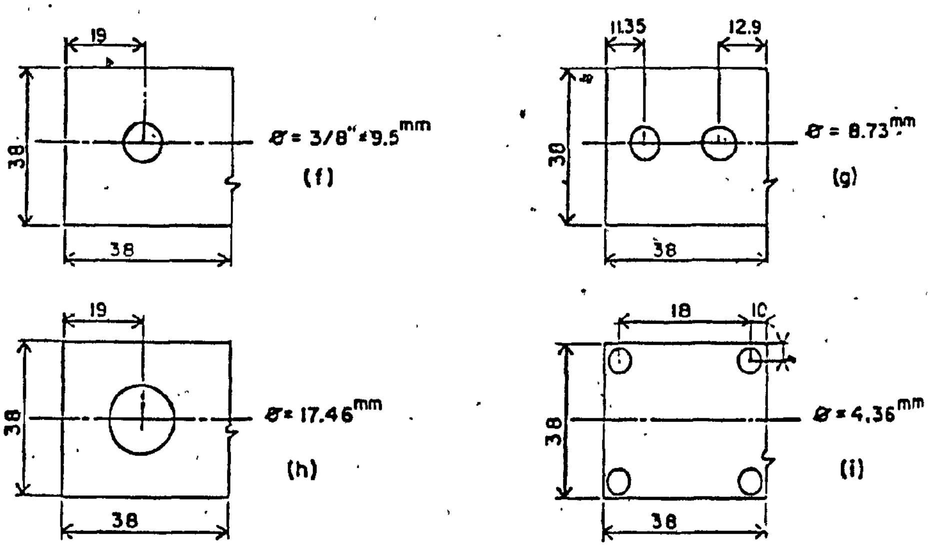


Fig. 13. Joining Arrangement for Modern Building Material, continued.

- a-c show the arrangement for lap joints
- d and e show the double butt joint and single butt joint respectively
- f shows the bolting arrangement using metallic bolts and adhesive bond
- h shows an arrangement similar to f except that adhesive bolts were used
- g and i show the bolting with adhesive bolts together with bonding

Bonding Phase and Condition

Overlap samples were prepared by applying a thin layer of adhesive and a thread spacer between substrates and filling the holes with adhesives after binding the two pieces. Butt joints were prepared by simply lining up the substrates on a table and applying the adhesive; another layer was applied on the second side after the first was cured.

The test was divided into two stages, in the first stage CA-1200 was tested with the different arrangements of butt and overlap joints. In the second stage the three adhesives were tested with the arrangements that gave the best results. In the second stage all samples were divided into two groups, each subjected to a different environmental treatment.

a) the first group of specimen was maintained at room temperature ($22^{0}C$) and 20-50% relative humidity for 30 days before testing.

b) the second group of specimen was cycled between $-30^{0}C$ and $+ 40^{0}C$ in a cooling chamber at a rate of 4 cycles/24 hrs, for different periods (50, 100 cycles).

To simulate the sun rays effect, the specimens were exposed to ultraviolet light supplied by a germicide lamp 930 T8 with 254 nm wave length. After 50 and 100 cycles, the specimens were removed from the chamber and tested.

Results and Discussion

For room temperature samples, it was found:

- Single overlap showed higher shear strength than double overlap joints (tables 6b, 6d)
- Arrangement (a + h) had the best shear strength when compared with other arrangements using only CA-1200
- Poliogrip 6000 had good shear strength for (a + h), (5.3 MPa), also, (CA-1200) (5.2 MPa) (tables 6b, 6c, 7a)
- Double butt joints gave better results than single joint, the best result was given by CA-1200 with an average normal stress of 23 MPa, (table 6a).

For the samples subjected to artificial weathering, it was found that:

- The joints using CA-1200 adhesive were stable when subjected to fluctuations in temperature and exposured to ultra violet light (table 7b, 7c)
- The joints using poliogrip 600 showed a decrease in strength after being subjected to artificial weathering, a decrease of shear stress from 5.3 MPa for room temperature to 4.2 MPa after 100 cycles in environmental chamber (tables 7a, 7c)
- The butt joint strength using AV-138 decreased when the samples were exposed to weathering, 17.2 MPa for room temperature samples and 11.9 MPa after 100 cycles in environmental chamber (tables 6a, 7c)
- CA-1200 had the best results between the three adhesives when exposed to fluctuation in temperature and ultra violet light.

It is important to mention here that bonding SMC material using the adhesive rivet technique resulted in higher shear strength than the

Table 6(a)-Joint Strength Of Butt Joints

SAMPLE I.D	SPECIMEN. No.	SMC THICKNESS (MM)	BOND CROSS SECTION (MM2)	FAILURE LOAD	NORMAL STRESS	AVERAGE (MPA)	FAILED IN
TYPE d	1	2.7/3.0	230	5000	22	23	BOND
	2	3.3/3.5	250	6500	27		BOND
	3	2.9/2.4	220	4800	22		BOND
	4	3.2/3.5	250	5700	23		BOND
	5	3.3/3.3	250	5100	21		BOND
TYPE e	1	3.4/3.0	170	2400	14.0	16.9	BOND
	2	2.7/3.1	85*	2400	28.8		PLASTIC
	3	3.3/3.1	180	3500	19.8		BOND

* CROSS SECTION OF SMC IS USED

** CA-1200 was used.

Table 6(b)-Joining Strength of Lap Joints,Using CA-1200

SAMPLE I.D.	SPECIMEN No.	SMC THICKNESS (MM)	BOND THICKNESS (MM)	BOND AREA (MM²)	FAILURE LOAD (N)	SHEAR STRESS (MPA)	AVERAGE SHEAR STRESS	FAILED IN	COMMENTS
TYPE a	1	*2.6/2.9	0.020	1400	4900	3.5	3.7	PLASTIC	
	2	3.1/2.7	0.026	1500	4600	3.1		PLASTIC	
	3	2.3/3.2	0.030	1400	5500	4.0		PLASTIC	
TYPE a+f	1	3.0/3.0	0.020	1400	5200	3.7	3.2	PLASTIC	
	2	3.0/3.0	0.019	1500	3600	2.4		PLASTIC	
	3	3.0/2.7	0.020	1500	5300	3.5		PLASTIC	
TYPE a+g	1	2.9/3.0	0.027	1460	5300	3.6	3.7	PLASTIC	
	2	2.8/2.9	0.025	1450	5300	3.6		PLASTIC	
	3	3.1/3.0	0.026	1440	5700	4.0		PLASTIC	

*CA-1200 was used.

Table 6(c)-Joining Strength of lap Joints ,using CA-1200,continued.

Sample I.D.	Specimen No.	SMC Thickness (mm)	Bond Thickness (mm)	Bond Area (mm)	Failure Load (N)	Shear Stress (MPa)	Average Shear Stress	Failed in	Comments
Type	1	3.0/3.1	0.020	1450	7400	5.1	5.2	Plastic	Peeling off
a+h	2	3.0/2.9	0.015	1300	6900	5.3		Plastic	
	3	2.8/2.0	0.018	1500	7400	4.9		Plastic	
	4	2.8/2.8	0.021	1400	7300	5.2		Plastic	
Type	1	2.8/2.9	0.016	1460	4800	3.3	3.3	Plastic	Peeling off
	2	2.9/3.0	0.016	1450	5800	4.0		Plastic	
a+i	3	3.0/3.2	0.015	1450	5900	4.1		Plastic	

* CA-1200 was used.

Table 6(d)-Joining Strength of Lap Joints Using EP CA-1200,continued.

SAMPLE I.D.	SPECIMEN No.	SMC THICKNESS (MM)	BOND THICKNESS (MM)	BOND AREA (MM).	FAILURE LOAD (N)	SHEAR STRESS (MPA)	AVERAGE SHEAR STRESS	FAILED IN	COMMENTS
TYPE b+h	1	3.0/2.9	0.015	1450	2200	1.5	2.1		PEELING OFF
	2	2.9/2.7	0.020	1450	3600	2.5			
	3	3.0/2.7	0.025	1450	2700	1.9			
	4	3.1/3.0	0.030	1450	4300	2.9			
	5	2.8/2.0	0.020	1450	2200	1.5			
TYPE b+g	1	3.0/3.1	0.020	1450	5200	3.6	3.6		PEELING OFF
	2	3.0/2.8	0.030	1450	5400	3.7			
	3	2.9/3.1	0.025	1440	4900	3.4			
	4	2.7/3.3	0.022	1440	5200	3.6			
	5	3.5/3.1	0.010	1460	5200	3.6			
TYPE c+h	1	3.0/2.7	0.020	1440	3700	2.6	2.7		PEELING OFF
	2	2.8/2.9	0.025	1450	3600	2.5			
	3	3.3/3.0	0.030	1445	4200	2.9			
TYPE c+g	1	2.8/3.1	0.010	1450	5200	3.6	3.4		
	2	3.2/3.1	0.015	1450	4900	3.4			
	3	2.9/2.7	0.020	1450	4500	3.1			

* CA-1200 was used.

Table 7(a)-Joint Strength of Room Temperature Samples.

Sample I.D.		Joint Type	Adhesives	SMC Thick-ness (mm)	Bond area (mm²)	Failure Load (N)	Shear Stress MPa	Normal Stress MPa	Average Shear	Average Normal	Comments
Type d	1	butt	AV138M	3.2/3.1	272	5100		18.7		17.2	Adhesive failed
	2			3.1/3.0	281	3400		12.1			
	3			3.2/3.1	249	4500		18.1			
	4			3.2/3.0	195	3300		16.9			
	5			3.2/3.1	196	4000		20.4			
Type a+h	1	overlap	goodyear	3.2/3.1	1528	8400	5.5		5.3		SMC & rivet failed
	2			3.9/3.1	1499	7200	4.1				
	3			3.0/3.2	1466	7900	5.4				
	4			3.1/3.2	1545	8650	5.6				
	5			3.2/3.1	1547	8300	5.4				
Type d	1	butt	goodyear	3.1/3.3	327	1650		5.0		4.9	Adhesive failed
	2			3.2/3.1	330	1750		5.3			
	3			3.0/3.0	338	1550		4.6			
	4			3.1/3.0	304	1500		4.9			
	5			3.2/3.1	314	1450		4.6			

Table 7(b)-Joint Strength of Samples Subjected to 50 Cycles in Environmental Chamber.

Sample I.D.	Joint Type	Adhesives	# cycles	Plastic Thick-ness(mm)	Bond Thick-ness(mm)	Bond Area (mm)	Failure Load (N)	Shear Stress	Normal Stress	Av. Shear	Av. Normal	Comments
Type d 1	butt	CA -1200	54.5	3.5/3.1		276	5200		18.8		19.7	Adhesive broken at connection line
Type d 2			54.5	3.4/3.1		245	6600		26.9			
Type d 3			54.5	3.6/3.3		342	4100		12.0			
Type d 4			54.5	3.2/3.2		341	5300		15.5			
Type d 5			54.5	3.2/3.3		245	6200		25.5			
Type a+h 1	Overlap	CA -1200	52.0	3.2/3.1	.005	1451	7060	4.8		5.0		Plastic & rivet broke during loading
Type a+h 2			52.0	3.2/3.3	.005	1376	6150	4.4				
Type a+h 3			52.0	3.5/3.2	.005	1413	7150	5.0				
Type a+h 4			52.0	3.2/3.3	.005	1406	6700	4.7				
Type a+h 5			52.0	3.6/3.1	.005	1477	8500	5.7				
Type d 1	butt	AV138M	54.5	3.3/3.1		280	5300		18.9		16.8	Adhesive failed at connection line
Type d 2			54.5	3.2/3.1		270	3900		14.4			
Type d 3			54.5	3.2/3.3		251	3800		15.1			
Type d 4			54.5	3.0/3.3		299	5500		18.4			
Type d 5			54.5	3.0/3.0		309	5300		17.1			
Type d 1	butt	Goodyear	60.0	3.3/3.1		356	1700		4.7		4.3	Adhesive failed at connection line
Type d 2			60.0	3.3/3.0		290	1500		5.1			
Type d 3			60.0	3.1/3.2		265	1250		4.7			
Type d 4			60.0	3.1/3.0		475	1600		3.3			
Type d 5			60.0	3.2/3.2		277	1150		4.1			
Type a+h 1	Overlap	Goodyear	60.0	3.2/3.1	.005	1521	6700	4.4		4.3		Plastic Failed
Type a+h 2			60.0	3.0/3.3	.005	1462	6300	4.3				Adhesive Failed
Type a+h 3			60.0	3.2/3.0	.005	1490	6700	4.5				"
Type a+h 4			60.0	3.3/3.1	.005	1446	6700	4.6				"
Type a+h 5			60.0	3.2/3.2	.005	1236	4450	3.6				"

Table 7(c)-Joint Strength of Samples Subjected to 100 Cycles in Environmental Chamber.

Sample I.D.	Joint Type	Adhesives	# Cycles	Plastic Thick-ness(mm)	Bond Thick-ness(mm)	Bond Area (mm²)	Failure Load N	Shear Stress MPa	Normal Shear MPa	Av. Shear Stress	Av Stress	Comments
Type a+h 1	Overlap	CA 1200	98	3.3/3.2	.005	1412	6700	4.7		4.9		Plastic & Adhesive Rivet Broke.
Type a+h 2			98	3.4/3.1	.005	1455	7550	5.2				
Type a+h 3			98	3.1/3.3	.005	1442	7700	5.3				
Type a+h 4			98	3.0/3.3	.005	1544	7300	1.7				
Type a+h 5			98	3.4/3.2	.005	1474	6900	4.7				
Type d 1	butt	CA 1200	102	3.3/3.2		291	6800		23.3		20.2	Adhesive broke at connection line.
Type d 2			102	3.3/3.0		291	6400		22.0			
Type d 3			102	3.1/3.2		302	4300		14.2			
Type d 4			102	3.0/3.1		219	5750		26.2			
Type d 5			102	3.2/3.2		278	4200		15.1			
Type d 1	butt	AV138M	102	3.1/3.2		296	2600		8.8		11.9	Adhesive broke at connection line.
Type d 2			102	3.1/3.3		299	3550		11.8			
Type d 3			102	3.0/3.1		253	3900		15.4			
Type d 4			102	3.2/3.1		304	2900		9.5			
Type d 5			102	3.2/3.3		290	4100		14.1			
Type a+h 1	overlap	good year	101	3.3/3.0		1462	5150	3.5		4.2		Cohesive force failed
Type a+h 2			101	3.1/3.1		1451	7050	4.8				
Type a+h 3			101	3.1/3.0		1346	5750	4.3				
Type a+h 4			101	3.3/3.2		1411	5450	3.9				
Type a+h 5			101	3.0/3.2		1539	6750	4.4				
Type d 1	butt	good year	101	3.2/3.0	.005	266	1200		4.5		4.6	Adhesive failed
Type d 2			101	3.3/3.1	.005	294	1400		4.8			
Type d 3			101	3.2/3.	.005	238	1000		4.2			
Type d 4			101	3.4/3.	.005	292	4450		4.9			
Type d 5			101	3.2/3.4	.005	315	1900		4.4			

conventional metal bolt joint; 5.3 MPa for poliogrip 600, 5.2 MPa for CA-1200 (both with adhesive bolt), and 2.0 MPa for the metal bolt joint (23). The poor shear strength of metal bolting is due to the stress concentration in the SMC around the metal bolt which creates failure in the composite material at low shear strength.

4.2.3 Compressive Strength

Compression tests provide information about the compressive strength of materials when employed under conditions similar to those under which the tests are made.

EP and MEP were used for this test using the ASTM D695 compression method. The samples were prepared and cured for 24 hours at room conditions, then divided into three equal parts and exposed to the following weathering:

1. The first group was kept for 30 days at room temperature of 22°C and 20-50% relative humidity.
2. The second group was kept in a cooling chamber with a temperature fluctuation between -40 to +10°C, eight cycles a day for 57 cycles.
3. The third group was also in a cooling chamber under the above mentioned conditions but for 171 cycles.

The Instron machine was used with a cross head speed of 1 mm/min. and a chart speed of 10 mm/min. The tests were done at room conditions.

Table 8, Compressive Strength of EP and MEP

Condition Epoxy	R.T.	57 Cycles	171 Cycles
CA- 1200	76.9 MPa	75.0 MPa	81.0 MPa
CA-1200 + 8% DBP	59.3 MPa	61.5 MPa	60.8 MPa
CA-1200 + 6% PU	58.6 MPa	57.9 MPa	58.0 MPa
XP-1203	119.3 MPa	133.3 MPa	133.7 MPa

Preparation of Specimens

Epoxy

The preparation of CA-1200 epoxy and additives (8% DBP, 6% PU) were mentioned in section 4.2.1. Another epoxy XP-1203 (Araldite*) was also tested for further application in solar energy conservation. The preparation and mixing of this epoxy is the same as the CA-1200.

Results and Discussion**

It was found that EP (CA-1200) have a better compressive strength than the EP modified (table 8). This strength improves with time even when subjected to severe thermal shocks (-40 to +10°C) produced by cycling every three hours. Mixing EP with 8% DBP or 6% PU decreases its compressive strength of 22% and 23.8% respectively at room temperature and this strength doesn't show any improvement or deterioration after 57 or 171 cycles. EP XP-1203 had the highest compression resistance and had improved after 57 cycles.

The improvement of the compressive strength of EP (CA-1200) and (XP-1203) with time can be explained by the higher crosslinking of the polymer with time, to a certain extent, even when exposed to thermal shocks.

4.2.4 Chemical Stability and Tensile Strength

This test was performed to establish the chemical stability of CA-1200 when exposed to chemicals for a long duration. A tension test was

* Properties are listed in table 4.

** Results were taken as an average of at least five specimens.

done to compare the change in bond strength in relation to control samples after exposure.

The specimen is essentially comprised of a bead of adhesive cast between two rectangular plates of aluminum of 13 x 25 x 76 mm each. The samples prepared were kept immersed for four months at room temperature in different media such as:

- dimethyl formamide (DMF)
- acetone
- aqueous solution of sodium chloride
- aqueous solution of calcium chloride
- water
- benzene
- methanol
- air

Afterwards, the adhesive specimens were removed from the solution and kept for two weeks at room conditions for the removal of the organic solvent or aqueous solution excess. The percent weight loss and tensile strength were determined.

Results and Discussion*

As shown in table 9, cured EP has good resistance to tap water and benzene but it is very susceptible to deterioration by DMF, acetone, aqueous solutions, sodium and calcium chlorides. EP used in DMF or acetone,

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* All results were taken as an average of at least five specimens.

decomposed after only 14 days. Immersion of similar EP specimens in aqueous solutions of either sodium chloride or calcium chloride resulted in the weakening of the adhesive bond so that it broke under its own weight. Although long contact (120 days) with methanol is less detrimental than the other chemicals, the EP adhesion specimens had only 50% of the ultimate tensile strength of the unimmersed (control) specimens (table 9).

TABLE 9.- DATA ON THE CHEMICAL STABILITY OF EP[a]

Chemical	Ultimate Tensile Strength, MPa
Water	5.28
Air	5.12
Benzene	5.12
Acetone[b]	-
DMF[b]	-
NaCl[c] (Aqueous solution)	-
CaCl$_2$[c] (Aqueous solution)	-
Methanol	2.56

a. Specimens similar to those used for tensile testing were immersed for 120 days at room temperature.
b. Samples decomposed after 7 days (in DMF) and 14 days (in acetone).
c. Adhesive bond has broken under its own weight.

4.3 PHYSICAL PROPERTIES

4.3.1 Flammability (Oxygen Index)*

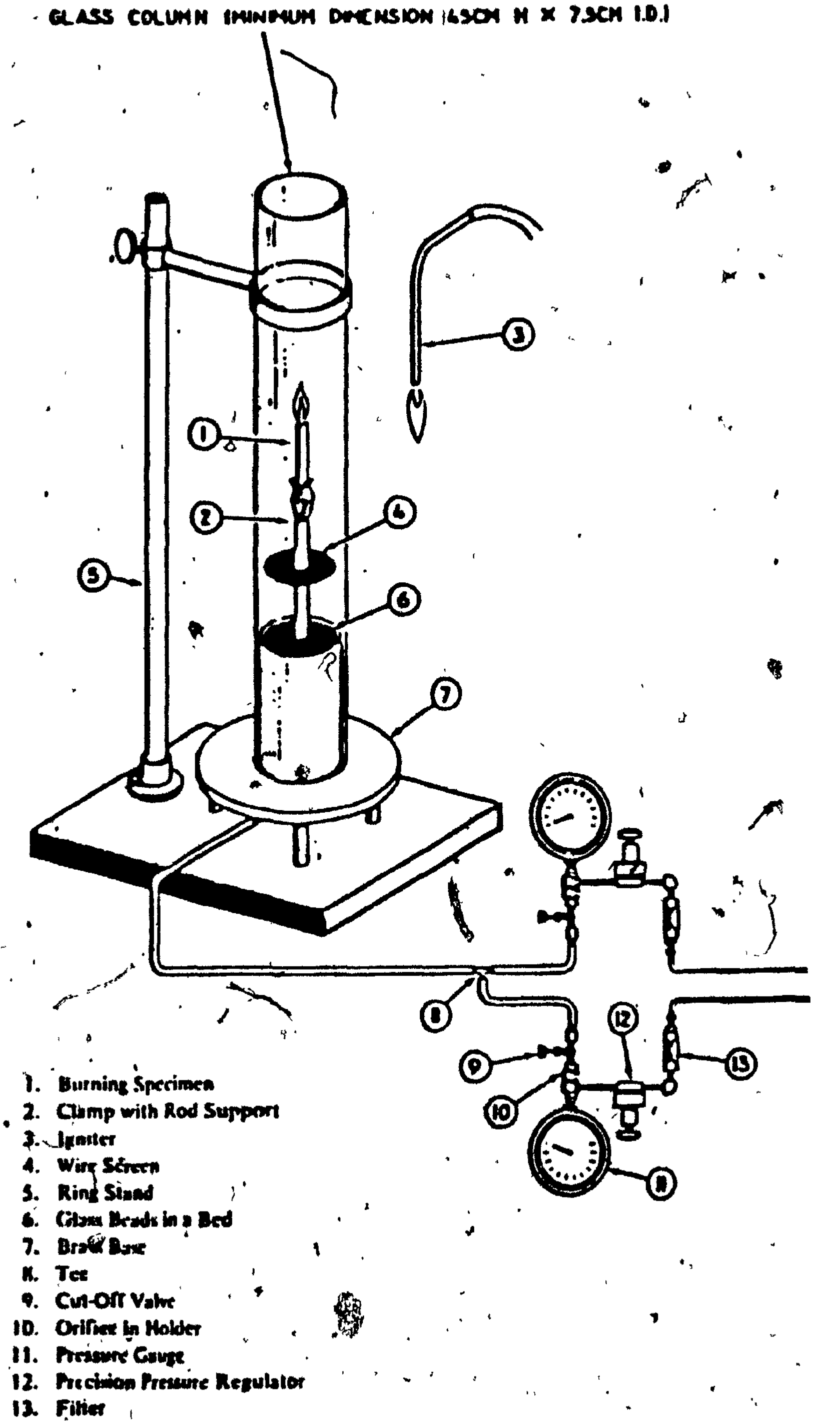
One of the tests which has been of considerable value in flammability study is the Oxygen Index. This test determines the relative flammability of plastics by measuring the minimum concentration of oxygen expressed as volume percentage in a mixture of oxygen and nitrogen that will just support flaming combustion of a material under the conditions of the test method (ASTM D2863); thus, higher oxygen index indicates lower flammability. Figure 14 shows the oxygen index apparatus.

Material and Method

Two types of adhesives were used, reference (EP) (CA-1200), and its modification (MEP) with (DBP and PU). The polymers were moulded then cut to a dimension of (6.5 x 3.0 x 12.7 mm) ∓ 0.5 mm, specified dimension for physically self supporting samples. They were kept at room conditions till testing.

The measurements were the minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that will just support combustion under equilibrium conditions of candle-like burning. The equilibrium is established by the relation between the heat generated from the combustion of the specimen and the heat lost to the surroundings as

* This test was performed at the NRC Laboratories, Ottawa, Ontario



1. Burning Specimen
2. Clamp with Rod Support
3. Igniter
4. Wire Screen
5. Ring Stand
6. Glass Beads in a Bed
7. Brass Base
8. Tee
9. Cut-Off Valve
10. Orifice in Holder
11. Pressure Gauge
12. Precision Pressure Regulator
13. Filter

Fig. 14. The Oxygen Index Apparatus.

measured by one or the other of two arbitrary criteria, namely a time of burning or a length of specimen burned. This point is approached from both sides of the critical oxygen concentration in order to establish the oxygen index.

Results and Discussion

The results obtained are presented in Table 10. The best behaviour is that of EP (CA-1200). The addition of DBP or PU to EP (CA-1200) doesn't improve its flammability probably because of a higher amount of carbon of this additive. A real improvement of the flammability might be obtained with halogenation (bromination) of epoxy which may constitute a basic polymer for a new group of epoxy adhesives.

Table 10 - Oxygen indices of EP and MEP

Epoxy Polymer	OI (% O2)
(CA-1200)	21.1
(CA-1200) + 8% DBP	19.0
(CA-1200) + 6% PU	19.3

Comparing EP and MEP in terms the oxygen indices (OI) of other plastics; table 11 shows that polystyrene has a lower OI than EP and MEP, while Birch wood is better than MEP but has a higher flammability than EP. Nylon 66 and poly (vinyl chloride) are less flammable than EP and MEP with OI of 24.3% and 40.3% respectively.

Table 11 - Oxygen indices of wood and various plastics (24)

Plastics	OI (% 02)
Birch wood	20.5
Nylon 66	24.3
Poly (vinyl chloride)	40.3
Polystyrene	17.8

4.4 THERMAL PROPERTIES

4.4.1 Differential Scanning Calorimetry (DSC)

DSC analysis is an effective thermo analytical technique to determine the transformation in physical or chemical states occurring during the heating and cooling of a material. It follows and measures both the temperature and heat associated with transitions in materials. The measurements lead to the glass transition temperature (Tg) and both endothermic and exothermic peaks (25).

As the temperature of a polymer is raised through its glass transition point, its change in physical condition from hard, glassy and brittle to a softer and more flexible rubbery state. This is frequently accompanied by quite dramatic changes in properties such as thermal conductivity, mechanical stiffness, moduli heat capacity and the volume expansion coefficient. The DSC was used to follow the changes in the (EP) before and after being modified.

The analysis system consists of a DuPont 1090 thermal analyzer, a 1091 Disc Memory and a 910 DSC (fig. 15).

The DSC cell uses a constantan (thermo-electric) disc as a primary heat transfer element. A selected sample and an inert reference were placed in small pans which sit on raised portions of the disc. Heat was transferred through the constantan disc to both the sample and the reference pans. Differential heat flow to the sample and reference was recorded on the memory disc.

Fig.15 . The DuPont 1090 thermal analyzer and the DuPont 910 differential scanning Calorimeter.

The analysis programs used were devised to calculate the heat of fusion, heat capacities and to extrapolate the onset and the peak temperatures. The experimental peak width varies with the heating rate and thus the location of the onset temperature may be shifted at high heating rates.

The reproduction of the thermograms performed in different laboratories is very difficult due to a number of factors, for example: size, shape and type of sample holder, diameter and positioning of the thermocouples, heating rate and sensitivity of the recording system. It may also be due to the condition and size of the sample.

The polymers tested were EP (CA-1200) and MEP, modified with (DBP, PVC, PU, GF), prepared by the previously mentioned procedure and kept to cure at room temperature for seven days.

Results and Discussion

For the unmodified EP (CA-1200) a Tg of about 59.6°C was found (fig. 16). At this Tg temperature (fig. 16), the slope of the base line started to change indicating a change in the physical condition of the epoxy from hard (glassy state) to flexible state, at about 64°C, the slope changed from negative to positive indicating the EP is totally flexible. With the addition of different additives, the Tg may be modified according to the need. Increasing the amount of PVC may increase the initial value of Tg in the case of natural weathering (100 days, -26 to +22°C) (fig. 17, curve 1) or room temperature conditions (curve 2). The higher values for N.W. specimens may result from a higher degree of crosslinking due to the combined influence of light, heat, oxygen and pollutants.

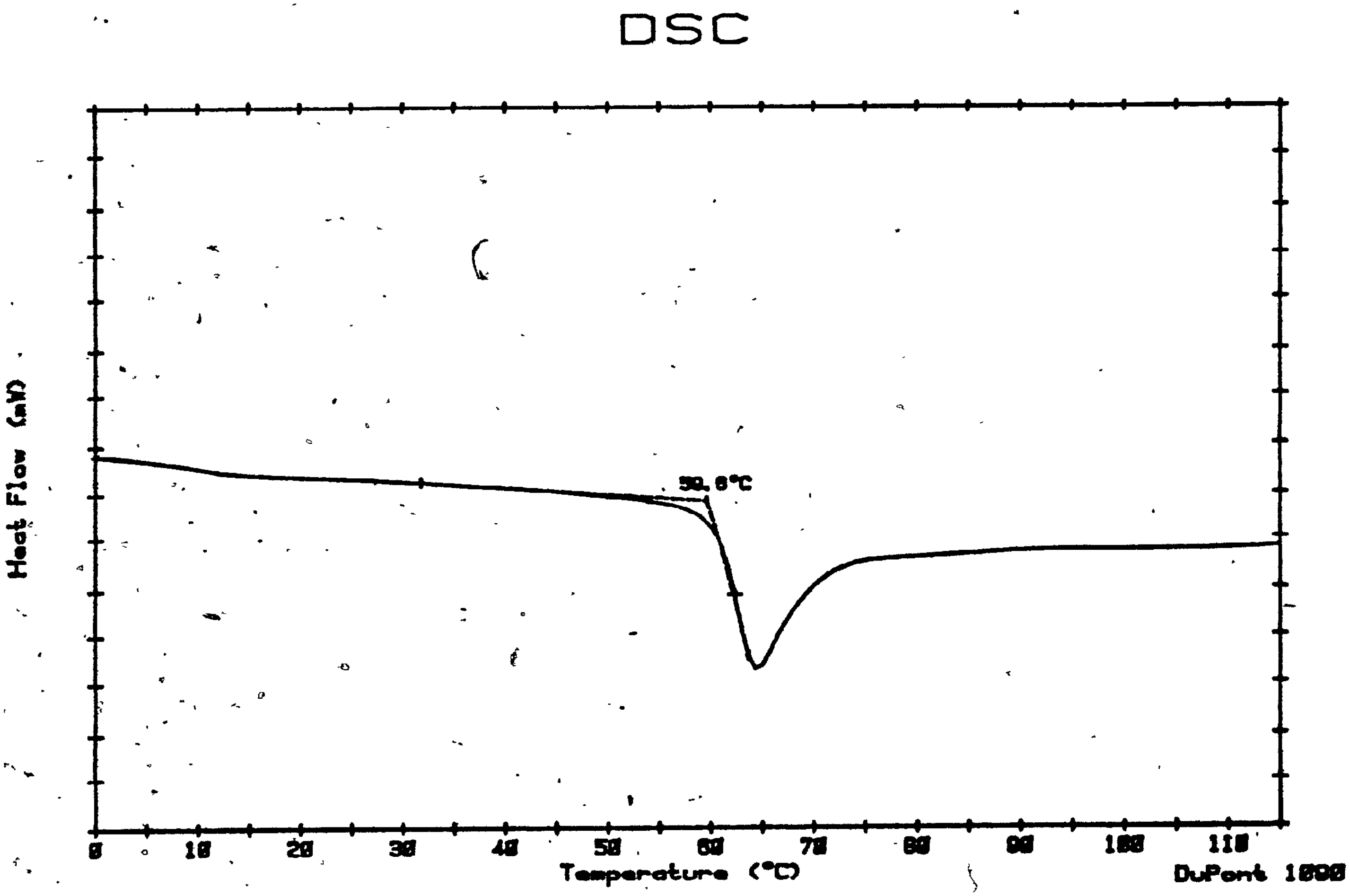


Fig.16 . Thermograph of EP (CA-1200).

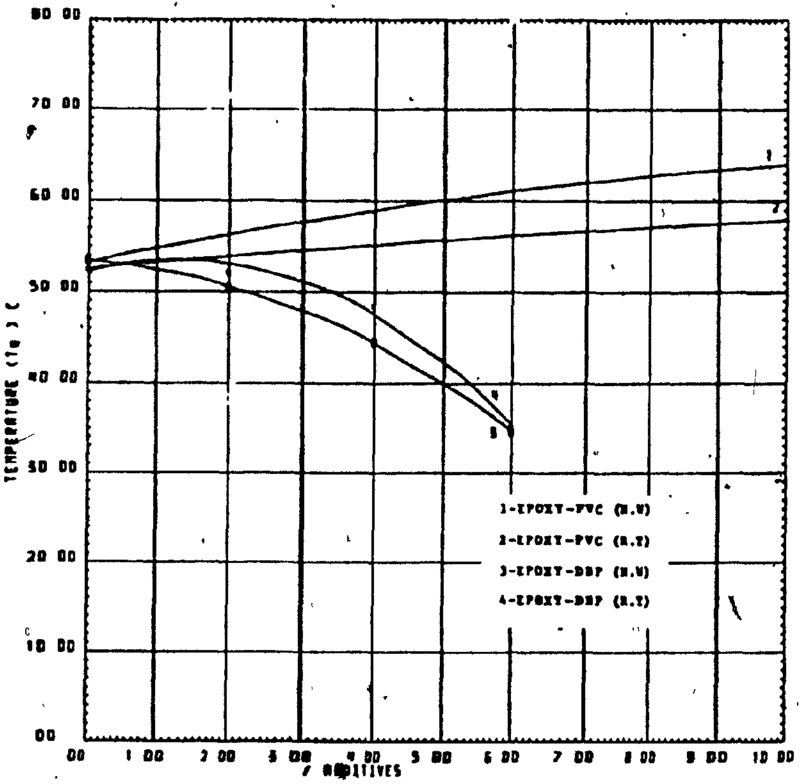


Fig. 17 . Effect of additives (PVC, DBP) and weathering on Tg of EP.

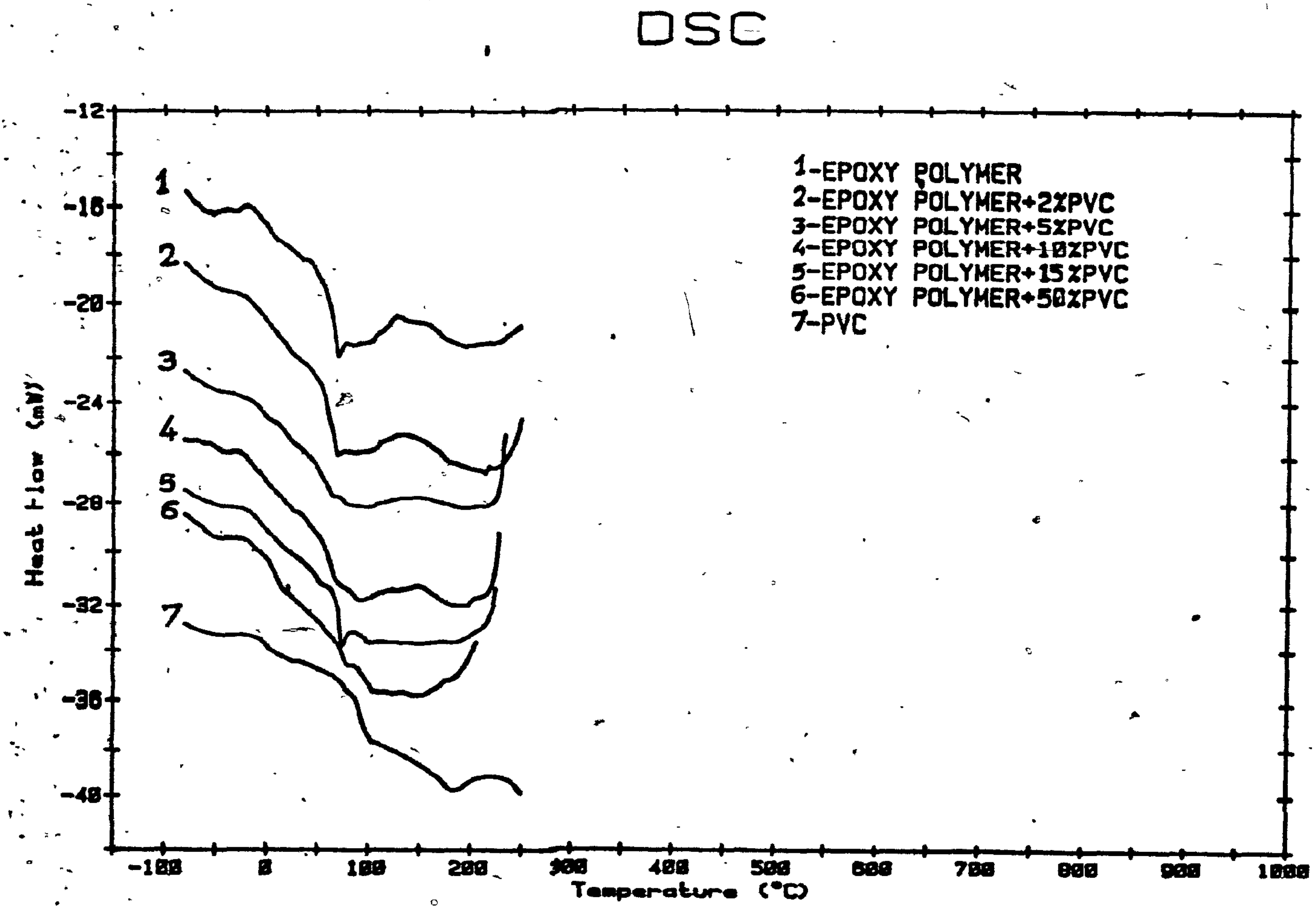


Fig.18 . Effect of PVC (2, 5, 10, 15 and 50%) on the Tg of EP-PVC Blend.

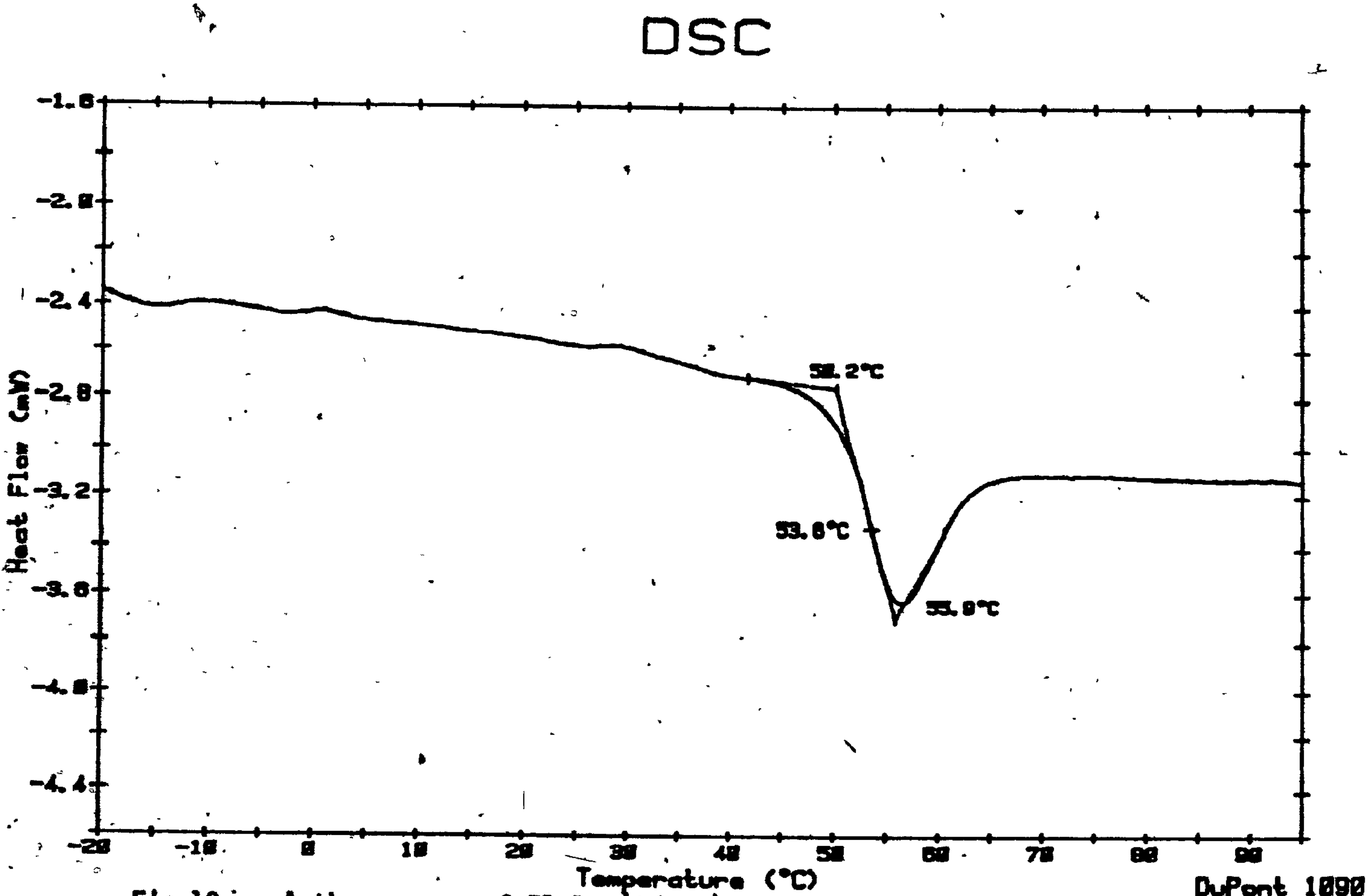


Fig.19 . A thermogram of EP-Pu (2% PU)

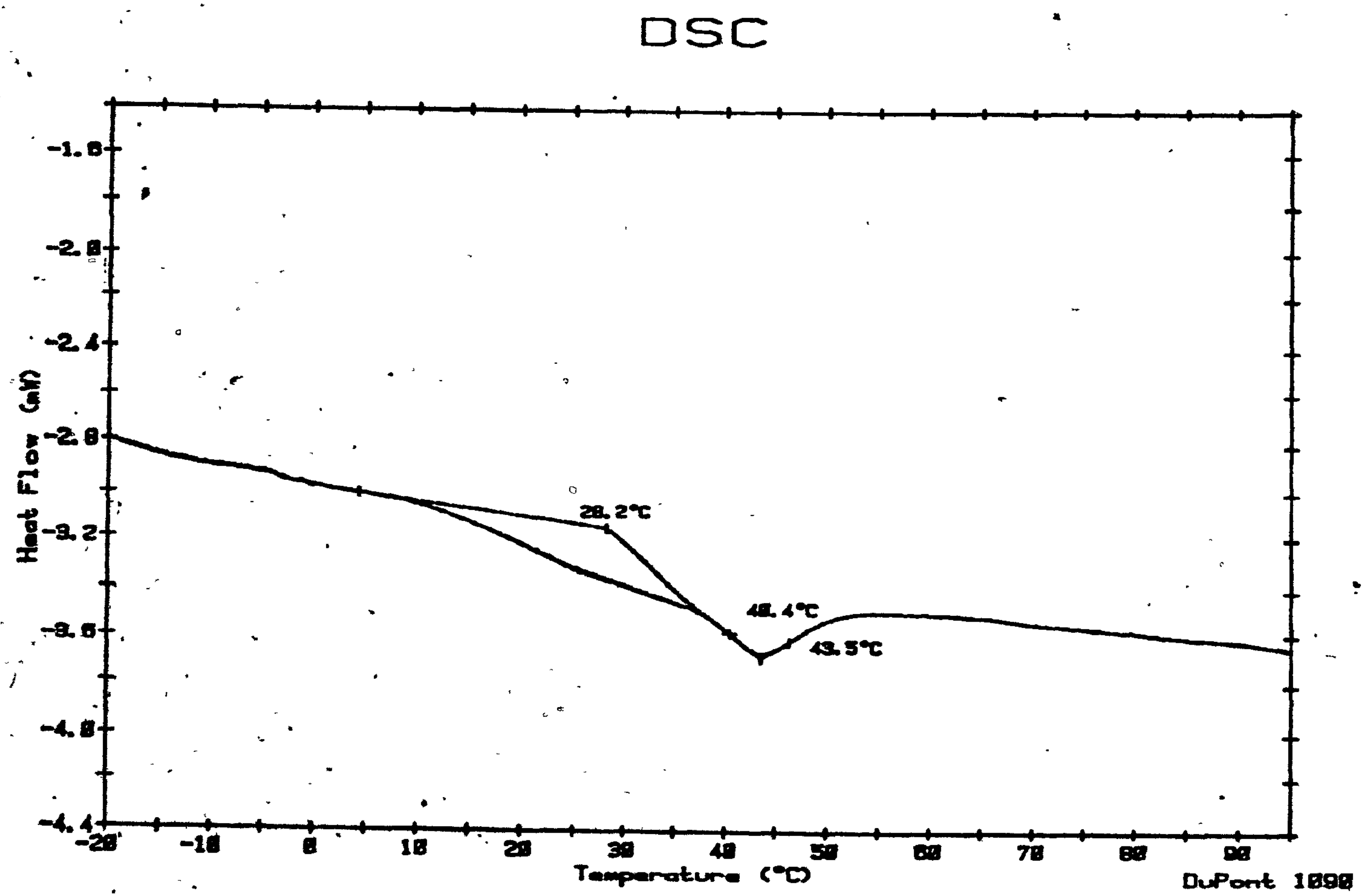


Fig.20 . A thermogram of EP-Pu (5% PU).

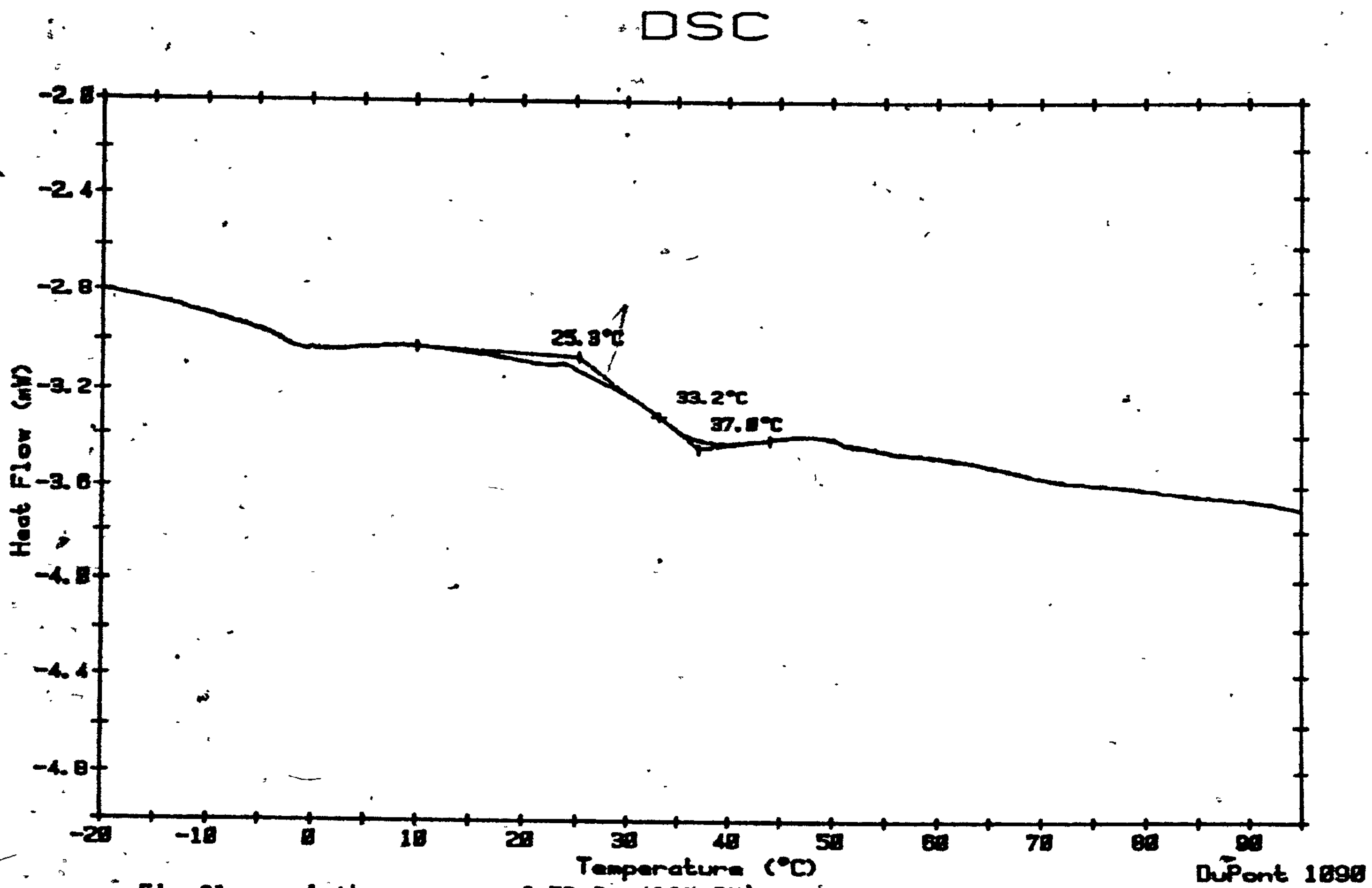


Fig.21 . A thermogram of EP-Pu (10% PU)

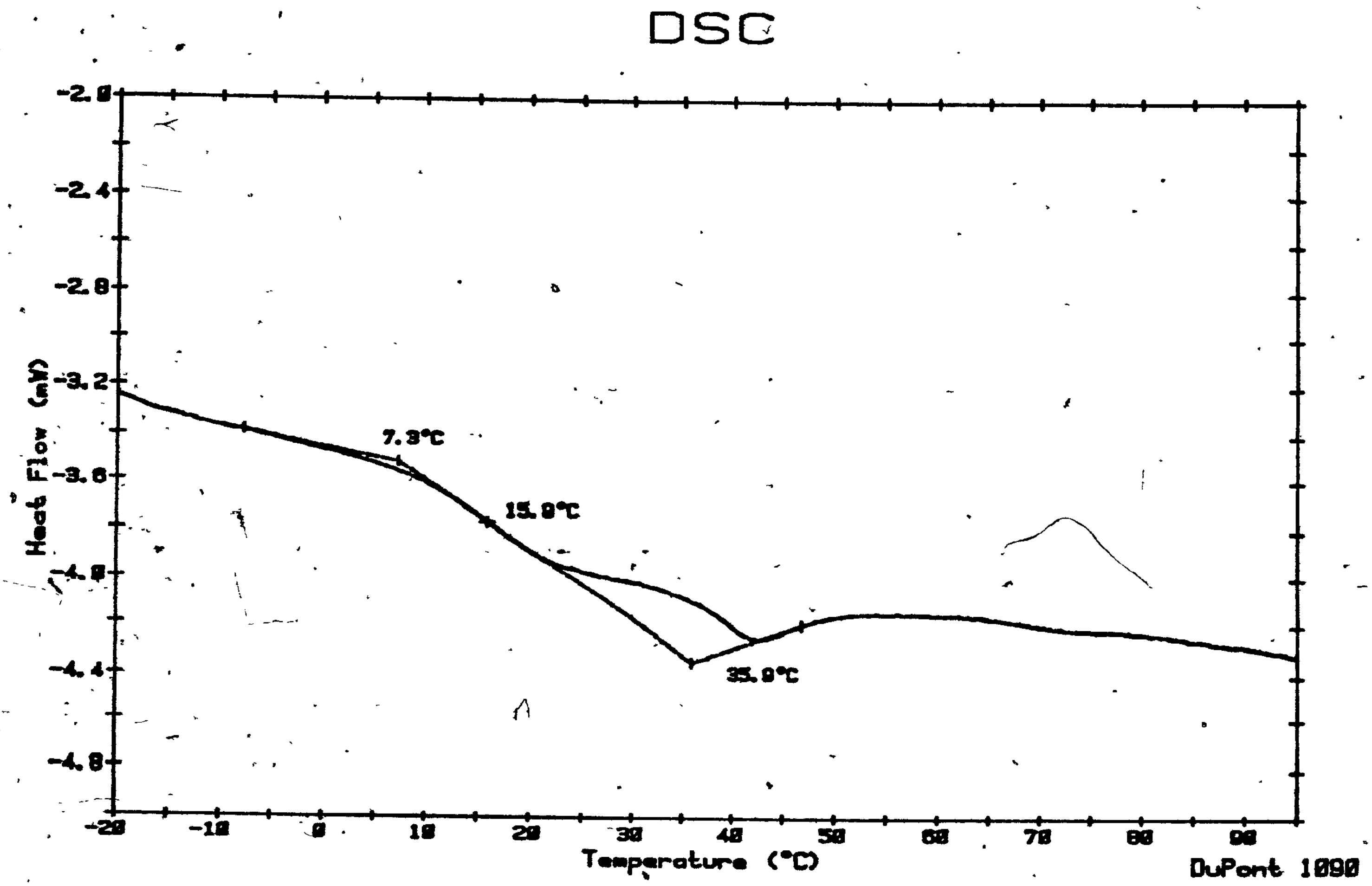


Fig.-22. A thermogram of EP-PU (15% PU).

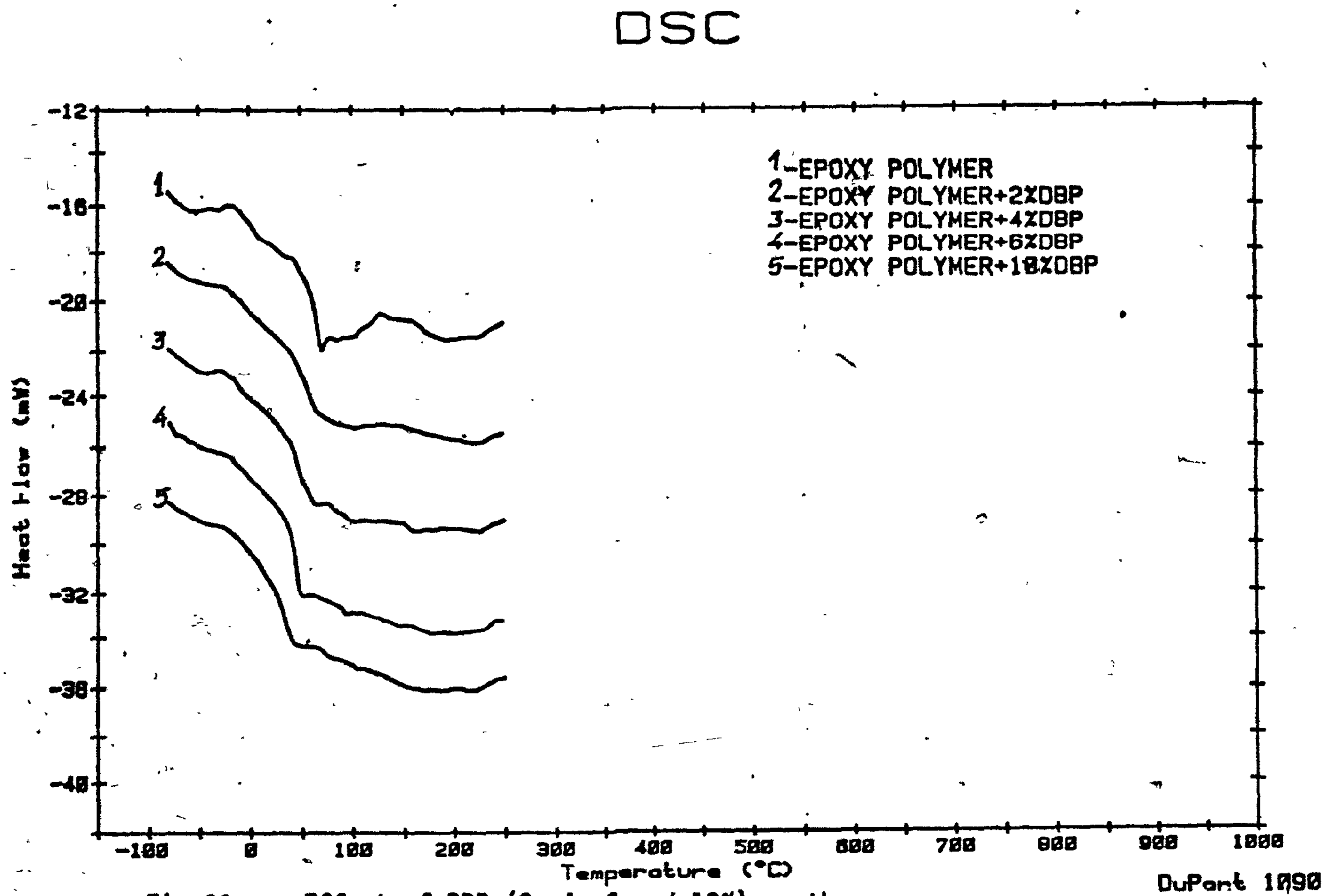


Fig.23 . Effect of DBP (2, 4, 6 and 10%) on the Tg of EP-DBP blend.

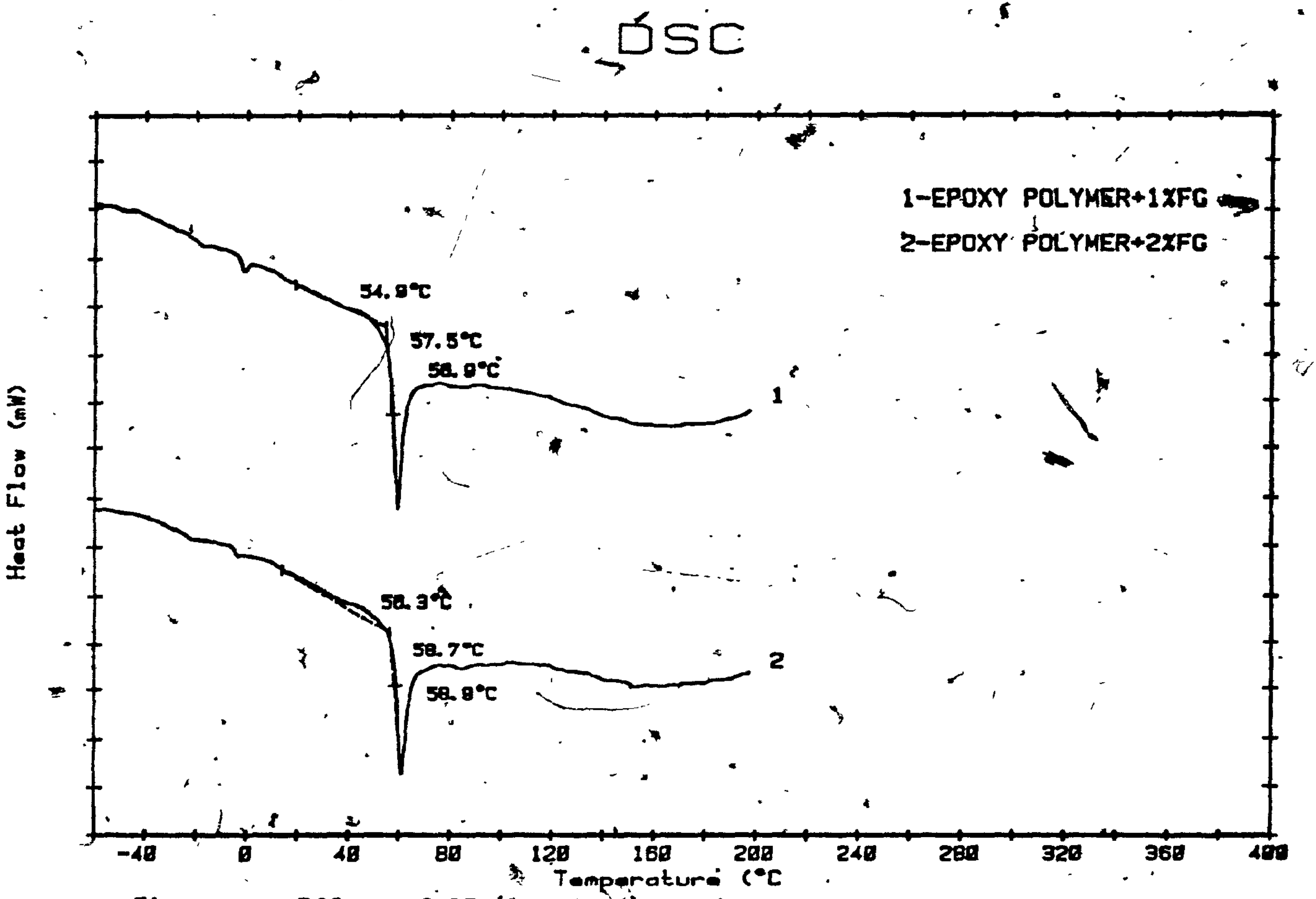


Fig. 24. Effect of GF (1 and 2%) on the Tg of EP-GF mixture.

As was expected, the addition of a plasticizer (DBP) decreases the (Tg) value (curves 3, 4, fig. 17). At 6% DBP a dramatic decrease up to about 35^{0}C was recorded.

Figure 18 shows the increase of Tg with the increase of PVC in EP-PVC polyblends up to 50% PVC. Depending on molecular mass, PVC has a Tg 80^{0}C. Other than increasing the Tg, PVC may also bring an important decrease in flammability of the blend.

PU, as a plasticizer, decreased the Tg as shown in figures 19 to 22. This decrease is dramatic between 2% PU (Tg = 50.2^{0}C) and 5% PU (Tg = 28.2^{0}C). For EP-PU (15% PU) the Tg is 7.3^{0}C (fig. 22).

The decrease of the Tg for the EP-DBP mixtures is recorded on Fig. 23.

Reinforcing of the EP adhesive leads also to an increase of the Tg as we may see from figure 24.

4.4.2 Heat Distortion Temperature (HDT)

Measurement of the heat distortion temperature of a cured resin is one of the most widely used methods of determining the degree of cure. The method used was outlined by ASTM (D648). This method determines the temperature at which an arbitrary deformation occurs when specimens are subjected to an arbitrary set of testing conditions. Data obtained this way may only be used to predict behaviour of the test loading and fiber stress are similar to those in the test. The EP and

The modified EP were tested to examine the effect of additives on the Heat Distortion Temperature.

The polymers tested were EP (CA-1200) and MEP modified with (DBP, PVC, PU and GF). Bars size 13 x 13 x 127 mm were casted in a silicone rubber mold for 48 hours before testing. A wallace HDT apparatus (fig. 25) was used where the samples were supported at either end and loaded in the middle to produce an uniform stress of 18.56 Kg/cm^2. The samples were immersed in an oil bath with a deflection gauge mounted on the specimen. The temperature of the bath was raised at a rate of $2^{O}C/min$. The HDT was recorded when the deflection of the bars reached 0.254 mm.

Results and Discussion*

In figures 34 to 36 are shown plots of heat distortion temperature (HDT) versus concentration of DBP, PVC and PU of EP - based blends. Incorporation of DBP into EP causes a marked reduction in HDT. For example, the value of HDT decreases from approximately $55^{O}C$ for unmodified EP to about $24^{O}C$ for a blend containing 15% of DBP (fig. 26, curve 2). The rate of decrease in HDT of EP - PVC blends is greater at lower than at higher PVC concentrations (fig. 26, curve 1 and fig. 27). Adding G.F. increases HDT significantly. For example, 1% G.F. increases temperature to $63^{O}C$ and with 5% G.F., the HDT was greater than $150^{O}C$ and, therefore, too high for the equipment to measure.

Figure 28 shows the decrease in HDT with the increase of PU in an EP-PU blend.

* Results were taken as an average of three specimens.

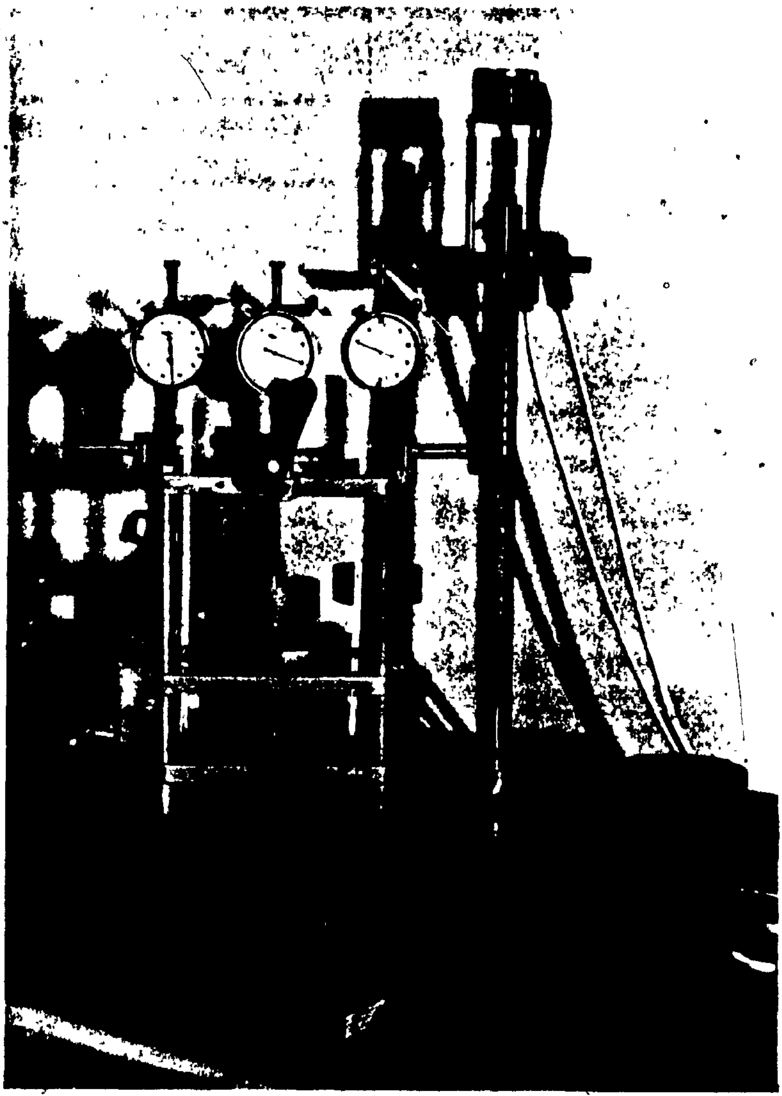


Fig. 25 . The Wallace apparatus for the H.D.T.

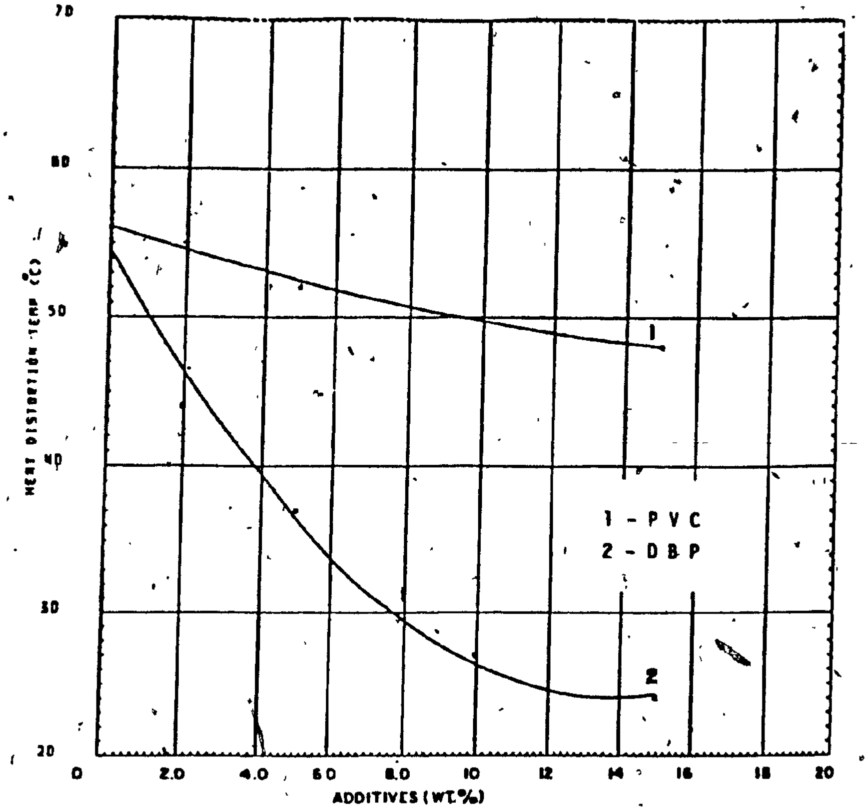


Fig.26 . Effect of additives (PVC, DBP) on the HDT of EP.

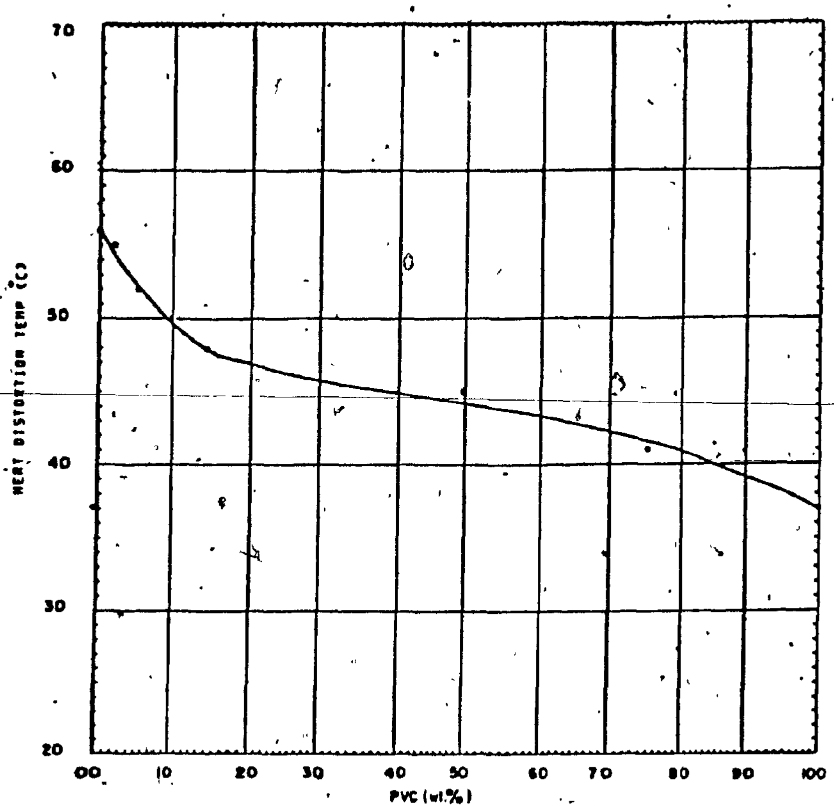


Fig.27 . Effect of PVC (0 to 100%) on the HDT of EP.

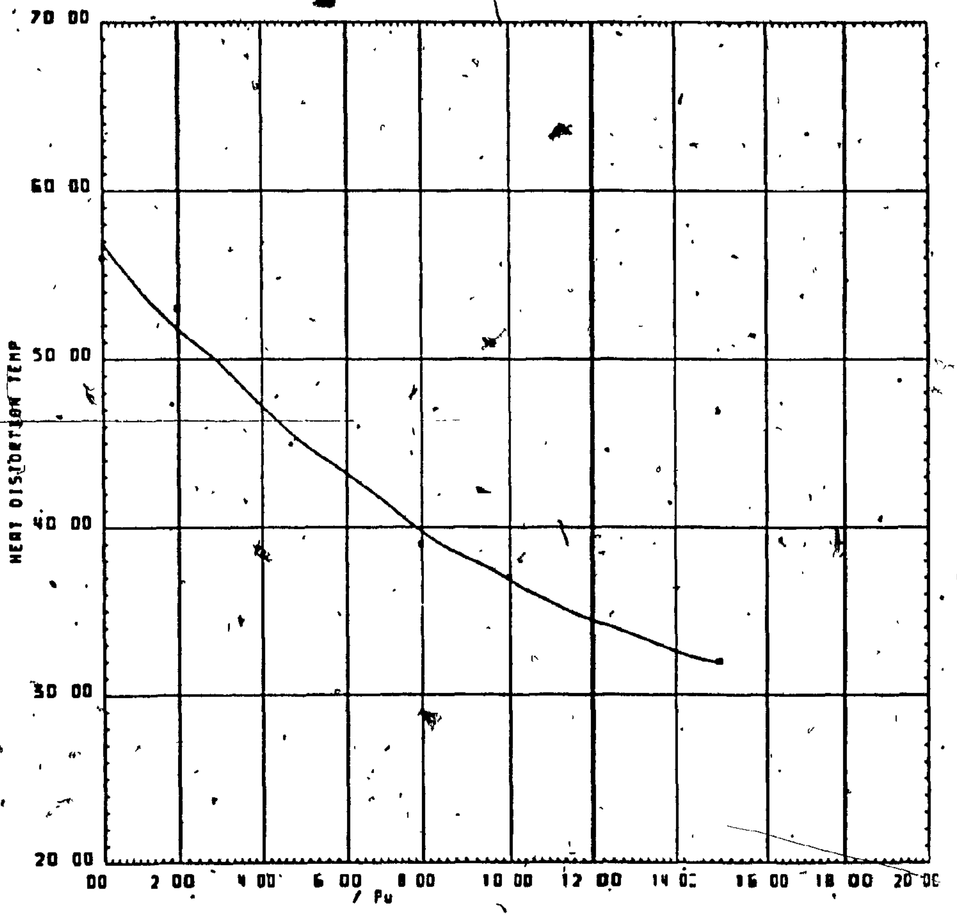


Fig. 28. Effect of Pu (0 to 15%) on the HDT of EP.

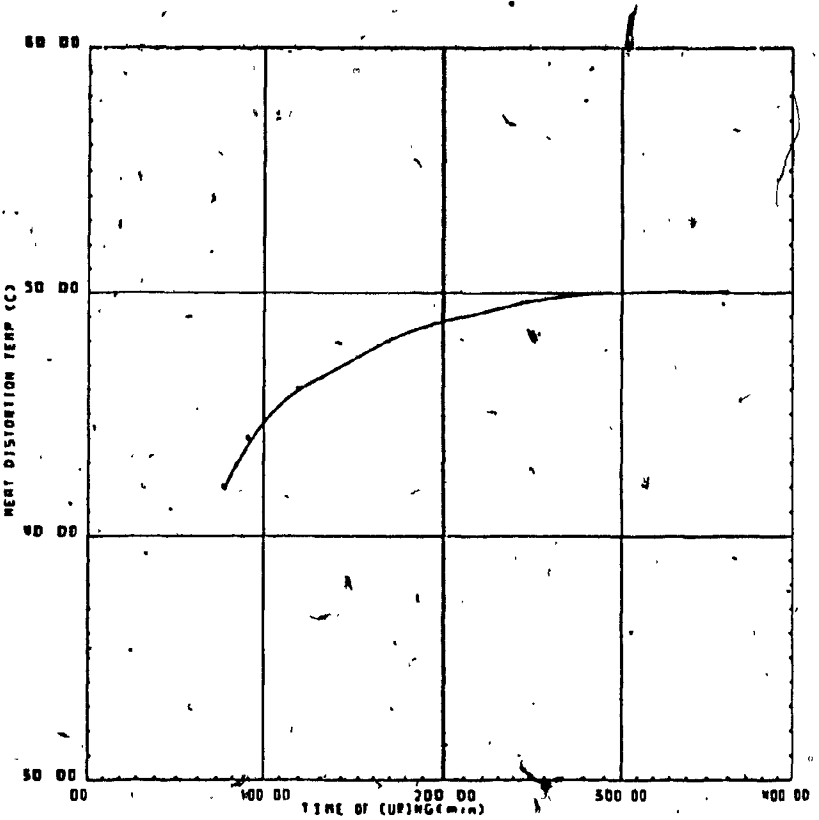


Fig.29 . Effect of crosslinking EP on the HDT.

It is well known in the field of adhesives that HDT increases with time due to the increase of crosslinking.

Following the curing process of (CA-1200) (fig. 29), it will be seen that the first stage of curing takes place up to a duration of 200 min. Above this, a platform is reached where the increase of HDT is not very fast and noticeable. A second stage of curing may occur after hours due to external conditions for example, temperature.

4.4.3 Peak Exothermic Temperature

When working with epoxy polymer, it is important to know the maximum temperature reached by a thermosetting plastic composition, as well as the period from initial mixing to the time when the peak exothermic temperature is reached.

Peak exothermic temperature of EP (CA-1200) and MEP modified with PVC, DBP, GF and PU) was found by having all items at room temperature, then mixing the EP or MEP for three minutes and putting a 100g in a (150 ml) tin container, with a thermal couple immersed in the center. The temperature was recorded every minute till the peak exothermic temperature was reached and the sample started to cool.

Results and Discussion

The effect of various additives (plasticizer, polymers and reinforcement) on the temperature evolution during curing (crosslinking reaction) is

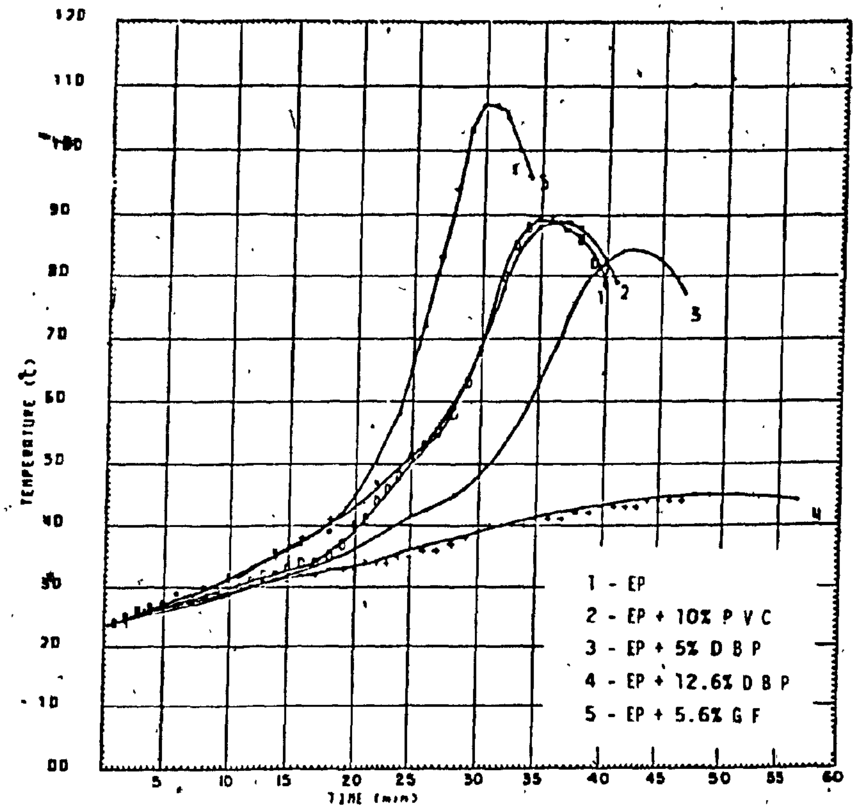


Fig.30 . Peak exothermic temperature of EP and MEP.

illustrated in figure 30. The temperature during crosslinking reaction of the unmodified epoxy polymer reaches a maximum (peak exotherm) at 90°C after 35 minutes (curve 1). Addition of 10% of PVC to EP polymer does not have any significant effect on the temperature maximum attained (curve 2).

However, incorporation of only 5.6% of glass reinforcement causes the maximum temperature to reach 108°C at a faster rate than in the unmodified EP (curve 5), probably due to low thermal conductivity of the reinforcement than that of the polymer ($K = 0.036\ w/m^{0}K$ vs. $K = 0.271$) and which acts as a thermal insulator. Addition of DBP to EP in low concentration (5%) results in diminished rates of temperature rise (curve 3). At higher concentrations of DBP (12.6%), the temperature rise of the blends is very gradual throughout the curing (curve 4).

PART III

CHAPTER V

SOLAR HEAT STORAGE

5.1 INTRODUCTION

Solar energy is a renewable energy source that can be used as an alternative in several applications. Space heating and cooling, which consume large amounts of electricity or fuel which are expensive and in limited supply, can be achieved with solar energy, moreover this energy can either be used directly or can be stored by various means for use later.

Various methods, employing different materials, have been used to store heat and concrete, rocks and water were among the first to be used for this purpose. More recently various latent heat materials, such as hydrated salts or organic materials, employed with building materials have been studied and evaluated for this purpose (26, 27, 28, 29, 30, 31 & 32). These materials (PCM) which involve the phase change heat storage process have a number of advantages:

a) room air temperature fluctuations are reduced because the energy exchange takes place at nearly constant temperature.
b) the mass and volume required by space storage due to the large heat material is reduced.

Forming part of this research, an epoxy polymer (EP) was applied in making storage module for passive solar energy heating and cooling in which a mixture of fatty acid esters was used to achieve the heat storage characteristics.

5.2 SOLAR ENERGY - HISTORICAL REVIEW

After the fifth century B.C. when wood and charcoal became very scarce, the Greeks developed basic principles of solar architecture heating and cooling buildings. They pointed out that the main rooms of a house should face south and the north side of the building should be sheltered from the cold winds. To minimize solar heat during the summer, caves were built on the south side to provide shade.

Archimedes also used solar energy to set fire to an attacking Roman fleet at Syracuse in 212 B.C.. He did this by means of a focused array of small square mirrors moving upon hinges (33). By 1700 diamonds had been melted by solar energy and by the early 1800's heat engines were operating with energy supplied by the sun.

In the last century, the solar architecture was neglected or deemed not very effective because of the effectiveness of recently developed central heating and cooling systems and the still more recent availability of external convenient forms of energy: electricity, gas and oil. The rapid depletion and escalation costs of fossil fuels caused people to reconsider the use of solar energy.

The availability of solar energy can be affected by the day-night cycle and atmospheric changes. Its effective use for heating purposes can be established only by incorporating thermal storage facilities in the solar heating and cooling systems. This feature is necessary for the maintenance of temperature variations within comfortable limits.

5.3 SOLAR HEATNG AND COOLING

Two distinct but complementary systems are used for solar space heating and cooling: active and passive. An active system is one in which all the mass flow is achieved by forced means such as pumps or fans which are used to convey heat between the solar collector, the heat store and the space to be heated. Passive systems do not use mechanical power and distribute heat by means of radiation, conduction or natural convection.

Passive systems have several advantages compared to active systems. They are less prone to breakdown, they require no special installation skills and their maintenance costs are lower.

It is important to mention that the inside air temperature for comfort in slab heated spaces is usually lower than in a space heated by conventional blower or radiators. This is because the vertical temperature gradients are also reduced, thus allowing the comfort level to be attained at a lower temperature and resulting in lower heating cost (28).

In passive solar systems, two basic elements are considered:

a) south facing glass or transparent medium for solar energy introduction

b) thermal mass for heat absorption and storage.

5.4 THERMAL ENERGY STORAGE

Thermal energy in the form of "hotness" or "coldness" can be stored in various media as sensible heat (temperature change), as latent heat (isothermal phase change), or by a combination of the two.

5.4.1 Sensible Heat Storage

The sensible heat ΔQ gained or lost by a material in changing temperature from T_1 to T_2 is:

$$Q = \int_{T_1}^{T_2} M \, cp. \, dt \approx M \, cp. \, \Delta T$$

where, Q = quantity of stored heat, KJ;

Cp = specific heat of storage medium, KJ/Kg.C;

M = mass of stored medium, Kg; and

ΔT = change in temperature, ^{o}C.

The specific heat, Cp, varies with temperature and phase change but its value is assumed constant over the range of temperaturs suitable for house heating applications.

5.4.1 A) Heat Storage in Solid Media

This type of heat storage is effected in accordance with the packed bid principle, that is, the storage unit is packed with solid bodies in direct contact with a heat-transfer medium which fills the space between the bodies. Heat storing building elements such as Trombe wall, long-duration underground storage in undisturbed rock and dry earth can also be used. Table 12 shows some readily available and economically competitive solid materials for sensible-heat storage.

TABLE 12. Solid Media for Sensible-Heat Storage [34].

Storage medium	Density ρ, kg/m^3 (lb$_m$/ft^3)	Heat capacity c_p, J/kg · °C (Btu/lb$_m$ · °F)	Thermal conductivity k, W/m · °C (Btu/h · ft · °F)	ρc_p, MJ/m^3 · °C (Btu/ft^3 · °F)	Remarks (see footnotes)
Concrete (sand and gravel)	2240 (140)	1130 (0.27)	0.9–1.3 (0.5–0.75)	2.53 (37.8)	4
Rocks (granite)	2640 (165)	880 (0.21)	1.7–4.0 (1–2.3)	2.32 (34.7)	1, 4
Cast-iron brick	7900 (494)	837 (0.20)	29.3 (16.9)	6.62 (98.6)	2, 3, 4
Magnesia brick	3000 (187)	1130 (0.27)	5.07 (2.93)	3.39 (50.5)	3, 4, 5, 6

1. Typical values for 0 to 100°C, various sources
2. Requires dry, nonoxidizing containment
3. Mean values for 550 to 816°C range, from
4. No allowance for voids,
5. Dusting problem with gas turbines
6. Carbon steel OK, but requires internal insulation for temperatures > 300°C.

5.4.1 B) Heat Storage in Liquid Media

Water is the only liquid used for storage temperatures below 100^{0}C. Water sometimes remains economically competitive at higher temperatures despite the need for pressure containment, especially when stored in aquifers, its specific heat is 80 cal/g. Water has some disadvantages: a high vapour pressure at increased temperatures and a tendency to contribute to corrosion in metallic containers in the presence of oxygen and/or salts in solution. Table 13 lists some liquids which can be used for sensible-heat storage applications.

TABLE 13. Liquid Media for Sensible-Heat Storage [34]

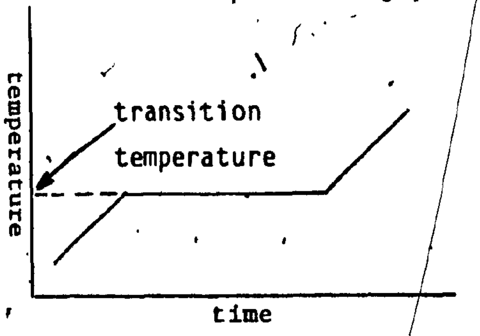
Media	Temperature: Melting point °C (°F)	Temperature: Maximum @ 1 atm, °C (°F)	ρ @ maximum temperature, kg/m³ (lbm/ft³)	c_p J/kg · °C (Btu/lbm · °F)	k, W/m · °C (Btu/h · ft · °F)	ρc_p MJ/m³ · °C (Btu/ft³ · °F)	Remarks (see Notes below where indicated by letters)
Water	0 (32)	100 (212)	960 (60.0)	4200 (1.0)	38°C 0.63 (100°F) (0.363)	4 (60)	(a) 120°C(248°F) at 2 atm 134°C(273°F) at 3 atm
Therminol 66*	−27* (−18)*	343 (650)	750 (46.8)	343°C 2740 (650°F) (0.655)	343°C 0.106 (650°F) (0.0613)	2.06 (30.7)	Modified terphenyl *Monsanto *Pour point (b), (d)
Dowtherm A*	12 (54)	260 (500)	867 (54.1)	2200 (0.526)	260°C 0.112 (500°F) (0.0645)	1.91 (28.6)	73.5 diphenyl oxide 26.5 diphenyl *Dow (a), (d) 288°C(551°F) at 2 atm 317°C(603°F) at 3 atm
Hitec*	142 (288)	540 1000	1680 (105)	540°C 1560 (1000°F) (0.37)	0.61 (0.35)	2.62 (39.0)	40 NaNO2, 7 NaNO3, 53 KNO3 *Dupont Also called HTS (b), (d).
Draw salt	220 (428)	540 1000	1733 (108)	1550* (0.37)*	0.57 (0.33)	2.70 (40.3)	46 NaNO3, 54 KNO3 *Assumed same as Hitec (b), (d).
Sodium	98 (208)	760 (1400)	960 (60)	1300 (0.30)	67.5 (39)	1.21 (18)	(c), (d)

Notes: (a) Carbon steel OK
(b) Carbon steel OK to about 315°C(600°F). Special alloys above
(c) Special alloy containment, nuclear technology
(d) Requires inert atmosphere blanket

5.4.2 Latent Heat Storage

A material can gain or lose heat by isothermal changes which occur between the solid and liquid phases (heat of fusion hf) between the liquid and vapour phases (heat of vaporization hv) and between solid crystalline phases (heat of solid-solid transition hs):

Figure 31: Time-temperature curve and phase change, with constant power input.



Usually transitions from the solid to the liquid state are used, not only in pure melting processes but also in eutectic and peritectic transitions as well as in solvation processes.

In melting process, the heat of fusion, ΔHf, is equal to:

$$\Delta hf = Tf . \Delta Sf \text{, in J/mole}$$

where Tf = melting temperature, in K; and

ΔSf = entropy change at the melting point in J/(mole. K).

The majority of substances at the melting point have a ΔSf-value which varies between 7 and 25 J/(mole. K). Table 14 presents some properties of a few phase change materials.

5.4.2 A) Characteristics of Latent Heat Storage Material

The choice of a material for latent heat storage should be based on an appropriate trade-off between the following characteristics (28):

1. an appropriate melting temperature with a small melting range;
2. similar melting and freezing curves that should repeat even after many cycles;
3. a large heat of fusion;
4. small volume change accompanying phase change;
5. a small degree of supercooling; with supercooling the heat will be produced at a variable temperature lower than the melting point;
6. thermal and chemical stability after many freeze-thaw cycles;
7. no reaction between the phase-change material and the container;
8. the rates of thermal expansion in the solid and liquid phases should not be very different to prevent pressure on encapsulators.
9. the phase-change material should not be toxic, flammable, explosive or corrosive;

Table 14. Properties of a Few Phase Change Material (28).

Material	Chemical formula	Group	Melting temp., C	Heat of fusion, KJ/Kg	Heat storage density, MJ/m³.	Density, Kg/m³		Thermal conductivity, W/m C		Specific heat KJ/(Kg.C)		Thermal diffusivity, x10⁻⁶ m²/s.
						solid	liquid	solid	liquid	solid	liquid	
Sodium sulfate decahydrate	$Na_2SO_4.10H_2O$	hydrated salt	31-32.4	215-253	300-372	1458-1460	1330-1460	2.25		1.76-1.78	3.30-3.31	0.87
Sodium thiosulfate pentahydrate	$Na_2S_2O_3.5H_2O$	"	48-50	200-209	335-346	1650-1730	1660	0.463-0.570		1.47	2.39	
Calcium chloride hexahydrate	$CaCl_2.6H_2O$	"	27-39	170-190	285-323	1634-1800	1560	1.09-1.10	0.54	1.44-1.46	2.13-2.37	0.44
Disodium phosphate dodecahydrate	$Na_2HPO_4.12H_2O$	"	34.6-36.5	264- 281	403-427	1520-1522	1520	0.512		1.55-1.70	3.18	0.21
Barium hydroxide octahydrate	$Ba(OH)_2.8H_2O$	"	78-82	263-300	657	2180				1.17		
Sodium carbonate decahydrate	$Na_2CO_3.10H_2O$	"	32-36	247-251	-	1440-1442				1.88	3.35	
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	"	117-120	165.6-172	250	1560-1570	1442			1.59-1.72	2.24-2.85	
Mixed calcium & magnesium hydrated chlorides	$CaCl_2/MgCl_2/H_2O$*	"	25	175								
Mixed sodium & magnesium fluorides	NaF/MgF_2**	Fluorides	832	615-625	1290-1370	2570	2090	4.2-8.4	4.65	1.42	1.38	1.72
Glauber's salt*** (eutectic)		-	13	146	215	1470				1.42	2.68	
Sodium hydroxide	$NaOH$	base	318-320	159-315	284-555	2030	1760	0.92	0.92	2.00	2.09	0.23
Ice	H_2O	-	0	334	305.8-308	917-920	998-1000	0.62	2.26	2.09-5.27	4.18-4.22	0.13
Cross-linked, high density polyethylene		polymer	132	230	207	960	900	0.36	0.36	2.30	2.30	0.15
Octadecane	$C_{18}H_{38}$	paraffin	28	244	188		756		0.15	1.45	1.70	
eicosane	$C_{20}H_{42}$	"	37		192				0.15			
eicosene	$C_{20}H_{40}$	olefin	27									
Paraffin wax	mixture of 23,24&25 C-atoms paraffins	paraffin	50-52		167	840	770	0.20		1.67		0.14
Lauric acid	$CH_3(CH_2)_{10}COOH$	fatty acid	44-47	178-183	155		870	0.151	0.111-0.147	1.60		
Stearic acid	$CH_3(CH_2)_{16}COOH$	"	69-69.6	199-240.8					0.160-0.172			
Pressed stearic acid (EMERY E400)		"	56.5	146	119	949	823	0.19		1.81	2.38	0.11
Paraffin wax(Sunoco P-116)		paraffin	47	209	161	820	770	0.14		2.89	2.51	0.06

* 41/10/49 (% by weight)

** 67/33 (% by weight)

*** composition (% by weight): $Na_2SO_4.10H_2O$(74.5%), NaCl(6.7%), NH_4Cl(6.2%), borax nucleator(2.6%), thickener(7.9%), boric acid(1.8%), and tetra-sodium phosphate(0.3%).

10. available and low cost
11. high thermal conductivity.

5.4.2 B) Examples of Latent Heat Storage Materials

A. Salt Hydrates

Salt hydrates are salts with water of crystallization, which usually melt below 100°C even if the melting point of the anhydrous salts are much higher (table 15). Partly incongruent melting in water occurs when some salt remains undissolved above the melting point or even at some higher temperature which results in phase separation and a decrease in heat storage capacity with thermal cycling.

When salt hydrates are heated in closed container above their melting points and are subsequently cooled, they may supercool considerably below their melting points (30). Tables 15 (a, b) (34) show some properties of salt hydrates.

A commonly used salt hydrate is briefly discussed below:

1. Sodium sulfate decahydrate ($Na_2 \cdot SO_4 \cdot 10H_2O$ - Glauber's salt

This salt hydrate is a byproduct of the potash production process. It has a high heat of fusion (215-253 KJ/Kg), and a melting temperature of 31-32.4°C which allows it to be used in a central storage.

Table 15(a) *Properties of Salt-Hydrates* (34)

Compound	H_2O Change	Density	Anhyd. Salt %	Solub. > mp %	Specific Heat Solid	Specific Heat Liquid
$Ba(OH)_2$	8-0	2.18	54.5	50	0.28	
$CaCl_2$	6-2	1.68	50.5	56	0.345	0.55
$Ca(NO_3)_2$	4-2	1.82	69.5	74	0.35	
$Cd(NO_3)_2$	4-3	2.45	76.5	73	0.26	0.38
$Co(NO_3)_2$	6-4	1,87	63	64	0.37	0.50
$CoSO_4$	7-1	1.95	.55	45		
$Cu(NO_3)_2$	6-4	2.07	63.5	62	0.33	0.48
$FeCl_3$	6-0		60	76		
$LiNO_3$	3-0		56	61		
$Mg(NO_3)_2$	6-4	1.46	58	65	0.54	0.88
$MgSO_4$	7-1	1.64	49	39	0.36	
$MgCl_2$	6-4	1.56	47	50	0.38	0.68
$MnCl_2$	4-2	2.01	63.5	52		
$Mn(NO_3)_2$	3-2		77	v.s.	0.34	0.41
$Mn(NO_3)_2$	6-4	1.82	62.5	67		
$NaC_2H_3O_2$	3-0	1.45	60.5	60	0.47	0.80
NaOH	1-0		69	75		
Na_2CO_3	10-1	1.44	37	34	0.45	0.80
Na_2CrO_4	10-4	1.48	47	48		
Na_2HPO_4	12-2	1.52	40	44	0.37	0.76
Na_3PO_4	12	1.64	43	44		
$Na_2S_2O_3$	5-0	1.69 s 1.66 l	6[illegible]	67	0.35	0.57
Na_2SO_4	10-0	1.46	44	34	0.425	0.79
$Ni(NO_3)_2$	6-4	2.05	63	64	0.38	0.74
$Zn(NO_3)_2$	6-4	2.07	64	67	0.32	0.54
PROP.-136°F		1.30	62	62	0.48	0.77
PROP.-190°F		1.64		78	0.36	0.80

Table 15(b) Properties of Salt-Hydrates (34)

Compound	H_2O Change	Melting Point °C	Observed Heat of Fusion cal/g	Btu/lb	Entropy of Fusion Obs	Calc	Calc/Obs
$Ba(OH)_2$	8-0	78	72	130	64.5	53.3	0.83
$CaCl_2$	6-2	29.5	40.7	73	29.4	31.6	1.07
$Ca(NO_3)_2$ α	4-2	42.6	33.5	60	25.0	25.5	1.02
β		39.7					
$Cd(NO_3)_2$	4-3	59.5	25.3	45	23.5	30.7	1.30
$Co(NO_3)_2$	6-4	57	30.4	55	26.7	36.0	1.34
$CoSO_4$	7-1	96	40.7	73	31.5	40.1	1.27
$Cu(NO_3)_2$	6-4	24	29.4	53	29.5	36.0	1.22
$FeCl_3$	6-0	37	54	97	47.1	46.8	0.99
$LiNO_3$	3-0	30	71	128	28.7	29.0	1.01
$Mg(NO_3)_2$	6-4	90	38.2	68	27.0	36.0	1.33
$MgSO_4$	7-1	48	48.2	87	37.5	40.1	1.07
$MgCl_2$	6-4	117	41.2	74	21.6	21.7	1.01
$MnCl_2$	4-2	58	42.5	76	25.5	21.7	0.85
$Mn(NO_3)_2$	3-2	35.5	28.8	52	21.0	30.7	1.46
$Mn(NO_3)_2$	6-4	26	33.5	60	32.1	36.0	1.12
$NaC_2H_3O_2$	3-0	58	43.0	77	21.0	26.1	1.24
$NaOH$	1-0	64	65	117	11.2	11.4	1.02
Na_2CO_3	10-1	34	60	108	56.6	64.5	1.14
Na_2CrO_4	10-4	20	39	270	46	53.1	1.15
Na_2HPO_4	12-2	36.5	63	114	66	71.3	1.08
Na_3PO_4	12-2	70	52.5	94	58	71.9	1.24
$Na_2S_2O_3$	5-0	49			37	42.3	1.14
Na_2SO_4	10-0	32.4	60	108	63.5	62.3	0.98
$Ni(NO_3)_2$	6-4	57	36.4	65	33.3	36.0	1.08
$Zn(NO_3)_2$	6-4	36.4	31	56	29.7	36.4	1.23
PROP.-136°F		58.0	63	113	25.6	26.1	1.02
PROP.-190°F		94	62	112	77	84.6	1.10

Incongruent melting, phase separation and decrease in heat storage which result from repeated thermal cycling are major problems associated with this salt hydrate which limits its application as an effective heat storage medium.

B. Fatty Acids

Fatty acids are organic compounds which can be used for heat-of-fusion storage from about 10°C, up to 70°C (35). They occur abundantly in vegetable and animal fats and the majority are straight-chain compounds (36). They may be also synthesized, usually through an oxidation of fatty alcohols.

A few examples of straight-chain saturated fatty acids are presented in table 16.

Table 16 - Properties of Common Straight-Chain Saturated Fatty Acids (28)

Systematic name	Common name	Formula Wt.	Density Kg/m^3	M.P. °C	B.P. °C
dodecanoic	lauric	200.31	883	44.2	298.9
hexadecanoic	palmitic	256.42	853	62.9-63.1	351.5
octadecanoic	stearic	284.47	847	69.6-70.1	376.1
eicosanoic	arachidic	312.52	-	75.3-76.1	204.0

Lauric, stearic and palmitic acids are the most widely distributed saturated fatty acids found in nature. Lauric acid (37, 38) and stearic acid (39) have been used in prototype solar systems.

These commonly used fatty acids are briefly discussed below:

1) Lauric Acid

Lauric (dodecanoic) acid is the most widely distributed saturated acid found in nature, with a chemical formula of $CH_3\ (CH_2)_{10}\ COOH$. Its name is derived from the plant "Lauraceae" in whose seeds it is found.

The heat of fusion of this acid is 178-183 KJ/Kg, melting temperature of 44-47^{0}C.

Lauric acid is practically insoluble in water (0.005g/100g water at 20^{0}C); freely soluble in diethyl ether, but less so in ethanol (1g/2ml) and propanol (1g/2.5ml) (35).

Lauric acid is usually obtained commercially from coconut oil. It was not affected after 130 thermal cycles and exhibits a negligible amount of supercooling (37, 40).

2) Stearic Acid

Stearic (octadecanoic) acid is the highest molecular weight fatty acid occurring abundantly in natural fats and oils. Its chemical formula is $CH_3\ (CH_2)_{16}\ COOH$. It usually occurs in smaller amounts than palmitic acid with which it is found in a number of plants and animals.

Stearic acid is a waxy crystalline solid which melts at 69-69.6^{0}C and has a heat of fusion of 199-240.8 KJ/Kg (table 13). It is practically insoluble in water (0.00029g/100g of water at 20^{0}C), is fairly soluble in chloroform (ca. 50g/100ml) and is decreasingly soluble in carbon disulfide, benzene, carbon tetrachloride, ethanol and acetone (37).

3) Palmitic Acid

Palmitic (hexadecanoic) acid (37) is present in almost every vegetable and animal fat. Its chemical formula is $CH_3\ (CH_2)_{14}\ COOH$. Despite its wide distribution in fats, it is generally not present in very large proportions.

Palmitic acid is an odorless waxy solid which melts at 62.9-63.1^{0}C. It is practically insoluble in water (0.00072/100g water at 20^{0}C). It is sparingly soluble in cold ethanol and petroleum naphtha, but freely soluble in hot ethanol and in diethyl ether, propanol and chloroform.

CHAPTER VI

EPOXY POLYMER FOR SOLAR HEAT STORAGE MODULE

6.1 INTRODUCTION

Building materials encapsulating phase-change materials can be used either as solar heat storage or as physical temperature regulators. These can be distributed as passive storages throughout residential, commercial and industrial buildings to absorb solar heat to warm the space and save on heating, or, to absorb excessive internal heat gains and reduce cooling costs. They can also be used in trombe walls to control overheating during the day and reduce night-time heat losses.

Experimental modules containing phase-change materials have presented several problems. The epoxy seal on thermocrete, for example, failed during aging tests and allowed phase-change material leakage (41). Also, in another research involving the encapsulation of fatty acid in concrete, the major problem has been that the mixture had a poor resistance to freeze-thaw cycling under humid conditions and a low compressive strength even at room temperature (28).

A production of heat storage module with epoxy polymer as a basic material was studied and tested in this research.

6.2 EPOXY POLYMER ENCAPSULATED PCM MODULE

The module produced, Fig. 32, was a container made from EP as a main structural component, the core was filled with heat storage material. The mechanism of heat storage was provided by the latent heat of melting of a mixture of saturated stearic, palmitic and myristic acids in the proportion of 69, 28 and 3% respectively. This mixture is called hydrogenated methyl tallowate, with the trade name of Emery 2204 and was supplied from Emery Industries Limited. Its convenient melting temperatures which are about 17°C and 22°C make it suitable for heating and cooling purposes.

The choice of this phase change material was based on the fact that, although salt-hydrates are low in cost, they suffer from incongruent melting, supercooling, gradual loss of heat storage capacity with thermal cycling and corrosion (42). On the other hand, the mixtures of fatty acid esters are thermally stable, do not corrode and are not affected by thermal cycling*, thus, they can be more expensive than the salt-hydrates.

The module may be produced with different sizes depending on the melting point of the chosen phase-change material, the amount of heat needed or the time desired to complete the melting of phase change mixture. A standard brick size of 65 x 120 x 122 mm was used in testing the mechanical and thermal properties of the brick module. Similar modules with other dimensions were also made.

* Dr. Shapiro, Concordia University, Montreal, Quebec

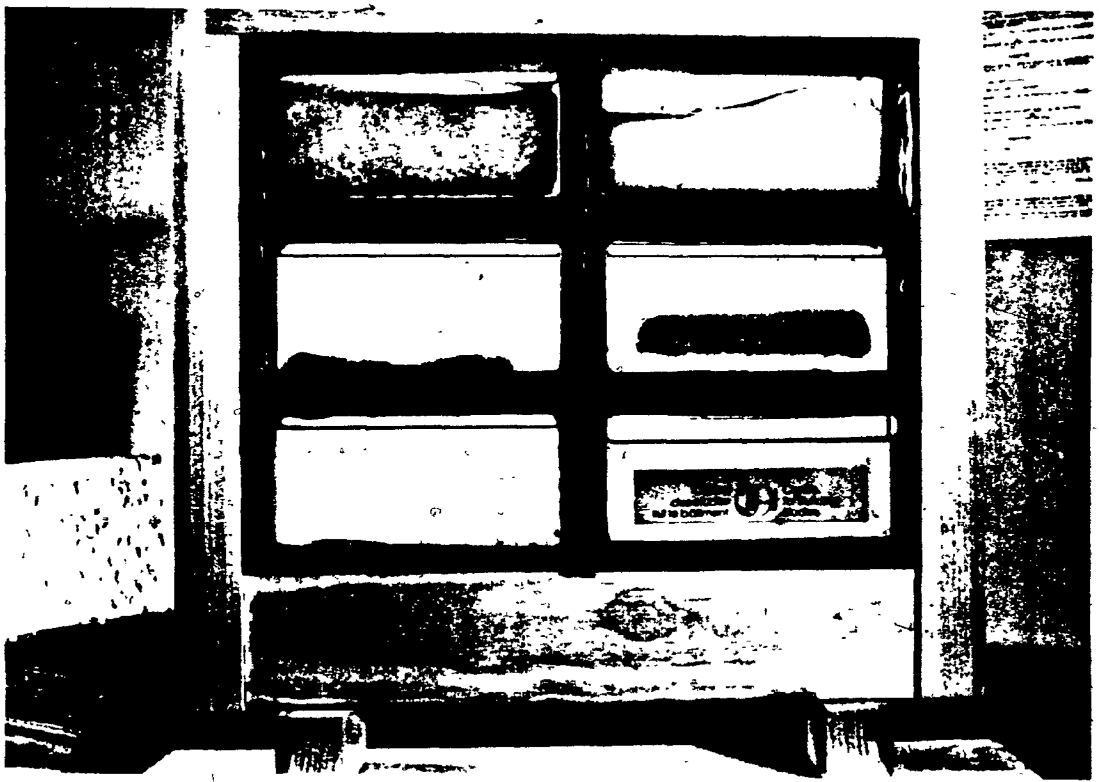


Fig.32.Six Framed Heat Storage Modules

6.3 MODULE DESCRIPTION

The brick lateral walls are made of a thermosetting two component polymer (XP-1203, CIBA-GEIGY). The composition of this epoxy polymer (EP) is based on that of the control EP (CA-1200, CIBA-GEIGY), (Section 3.3).

The large lateral faces (120 x 220 mm) are made of a transparent plastic, poly-methylmethacrylate (PMMA) known by its trade name as plexiglass (6.35 mm thickness), with the following light transmission characteristics:

1) ultra-violet cut-off below 2800-3000 A^0;

2) very low absorption of the visible spectrum but transmission of light incident normal to the surface of the sheet material suffers an 8% loss (4% reflection at each interface). The rapid increase in reflection above an incident angle of 60^0 results in an average transmission of daylight C.85%;

3) infrared cut-off above 23000 A^0.

The transparent plastic (PMMA) of the lateral large faces was used for the following reasons:

- since it is transparent, and when the acid is in liquid state, the bricks can be built into a south facing window to serve as a heat storage facility without losing much of the sunlight.
- It can withstand high temperature without changing its nature. Its heat distortion temperature is over 90^0C.
- It does not break when exposed to thermal shocks.

6.4 MODULE PREPARATION

The brick may be produced in various ways. Two approaches were tested:

a) The melted phase change mixture was poured into a six sided box of transparent polymer. The lateral large faces of which were 6.35 mm thick while the other four sides were about 2 mm in thickness (fig. 33). Subsequently, the filled transparent box was placed in a special mold in which all but the two largest faces were covered with an epoxy polymer to provide the necessary structural characteristics.

b) Two faces of the moulded solid phase change mixture were covered by the transparent polymer (fig. 34), these elements were placed in the mold as before to cover all but the two major faces with an epoxy polymer.

In executing the foregoing two procedures, the phase change material did not fill the brick cavity entirely, an empty space was left to reduce the pressure exerted by the expansion of the fatty acid mix when melted.

The EP XP-1203 composed the four later sides with a thickness of 10 mm. It was poured around the phase change mixture and left for six hours to cure before the brick was taken out of the mold.

Different thermal and mechanical tests were carried out to establish some properties of the module as a whole as well as those of the separate components. Further details of the procedures are given in Chapter IV.

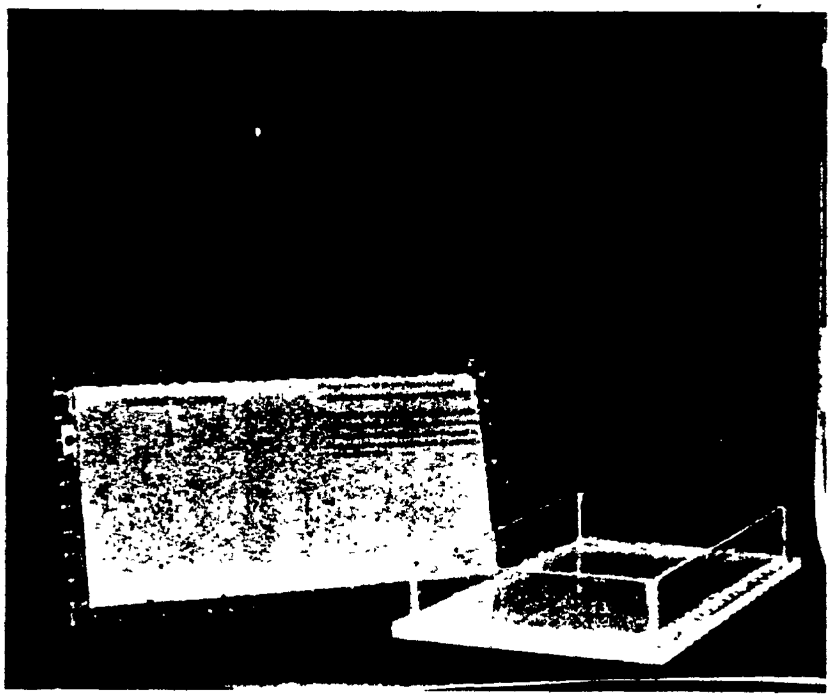


Fig. 33. Inner Plastic Container of the Heat Storage Module.

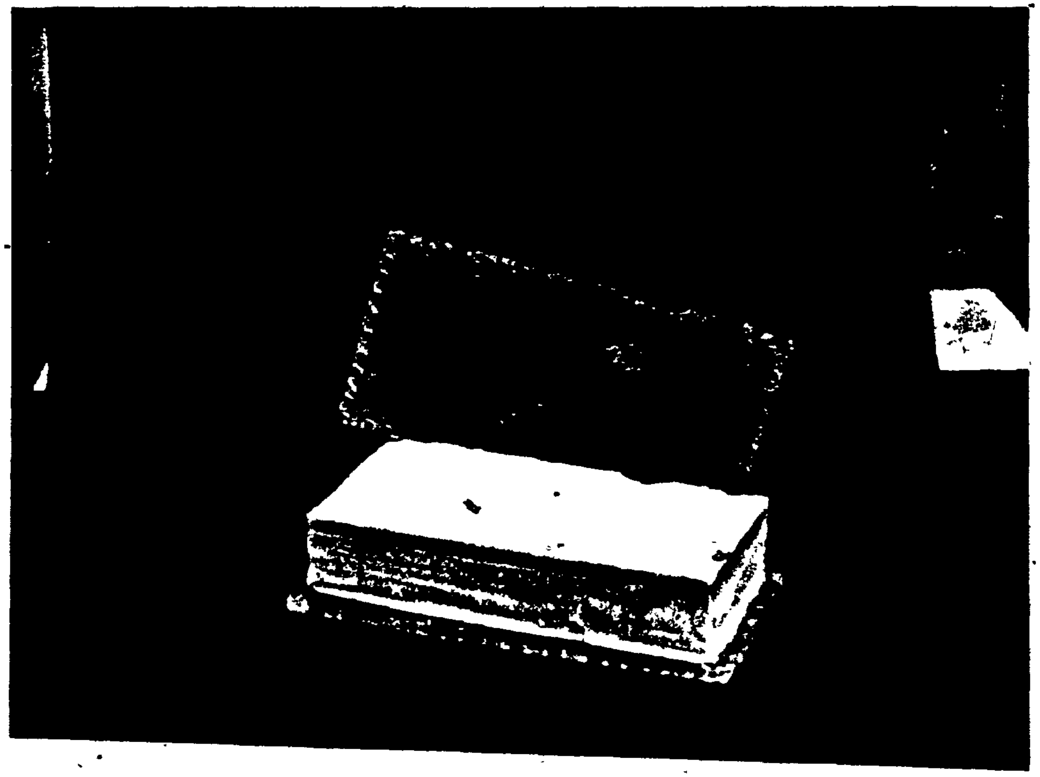


Fig. 34.Molded PCM with the Two Lateral Faces of the Module.

6.5 TESTS DONE ON THE MODULE

6.5.1 Compressive Strength

Using the Instron 1125 tester with a special thermal chamber, six standard bricks, with dimensions of 65 x 120 x 200 mm each, were tested for compressive strength under two conditions: three samples at room temperature (23^0C) and another three at elevated temperature (50^0C). The results were:

compressive strength at room temperature (R.T.) = 152 MPa

compressive strength at 50^0C = 57 MPa

compressive strength of standard clay brick (R.T.) = 35 MPa

6.5.2 Thermal Conductivity

The K-Value was established by using a thermal conductivity instrument model R-matic by Dynatech R/D company (fig. 35). This equipment conforms to ASTM-C518; thermal conductivity by means of a heat flow meter. Six modules were placed together in the machine after being kept at room temperature for 24 hours. During the test, the phase change mixture was in its solid state.

K-factor of bricks = 0.2 W/M.^{0}C

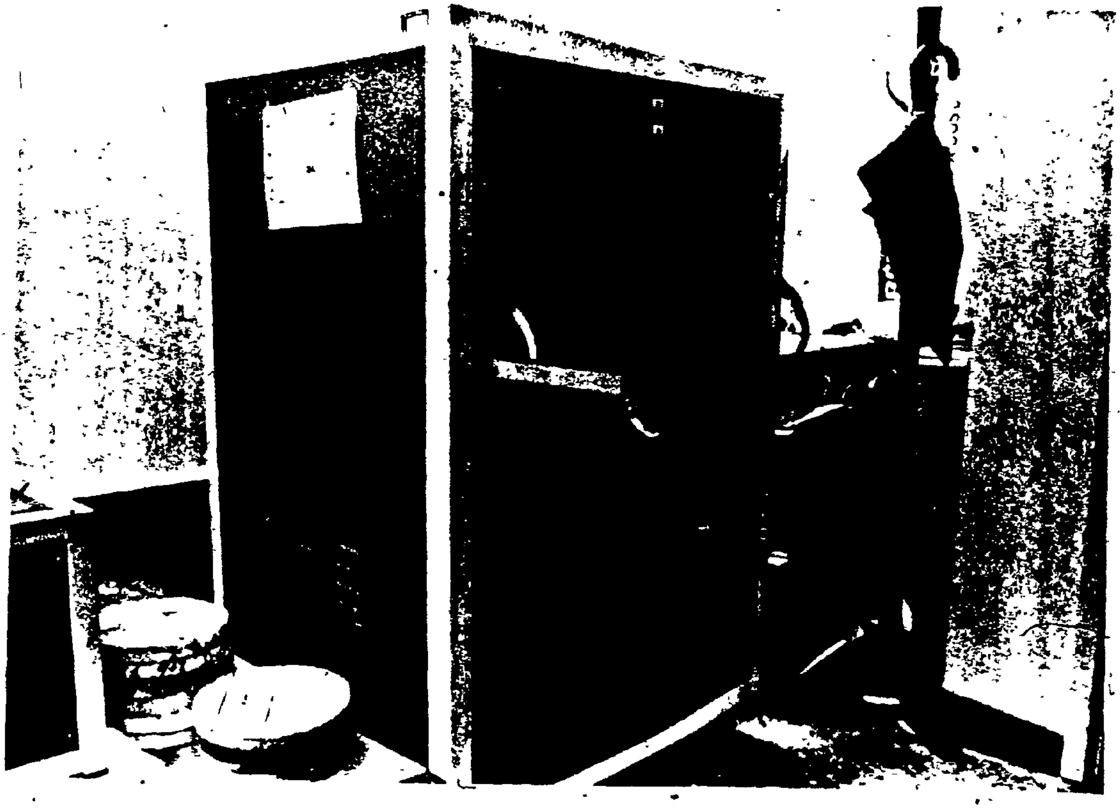


Fig.35 . The DYNATECH Model (R-Matic), thermal conductivity instrument.

6.6 TESTS DONE ON THE COMPONENTS

6.6.1 Heat Distortion Temperature

This test reflects the temperature at which the material deforms under flexural load, based on ASTM D648. Two main structural components of the module, plastic and epoxy polymer, were tested using a Wallace apparatus, the results were:

H.D.T. of plastic = 96°C
H.D.T. of cured EP (XP-1203) = 85°C

6.6.2 Flammability*

The flammability of EP (XP-1203) was evaluated by using the Oxygen Index method. This method measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen which will support flaming combustion. This was based on ASTM D2863. The polymer was moulded, then cut to a dimension of (6.5 x 3.0 x 12.7 mm) + 0.5 mm. Table 17 lists the result of EP (XP-1203) compared with the oxygen indices of other material.

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* This test was performed at the N.R.C. Laboratories, Ottawa, Ontario

Table 17 - Oxygen Indices

		OI (%O_2)
Polymers	XP-1203	24.6
	poly (methyl methacrylate)	17.3
	birch wood	20.5
	lauric acid	15.6
Fluids	stearic acid	16.5
	benzene	15.9

6.6.3 Differential scanning calorimetry (DSC)

This analysis was done to find the temperature at which the Emery 2204 changes phase when heated or cooled and the heat absorbed or evolved during this transformation (fig. 36).

The glass transition temperature of epoxy was found also, its thermogram is shown in figure 37.

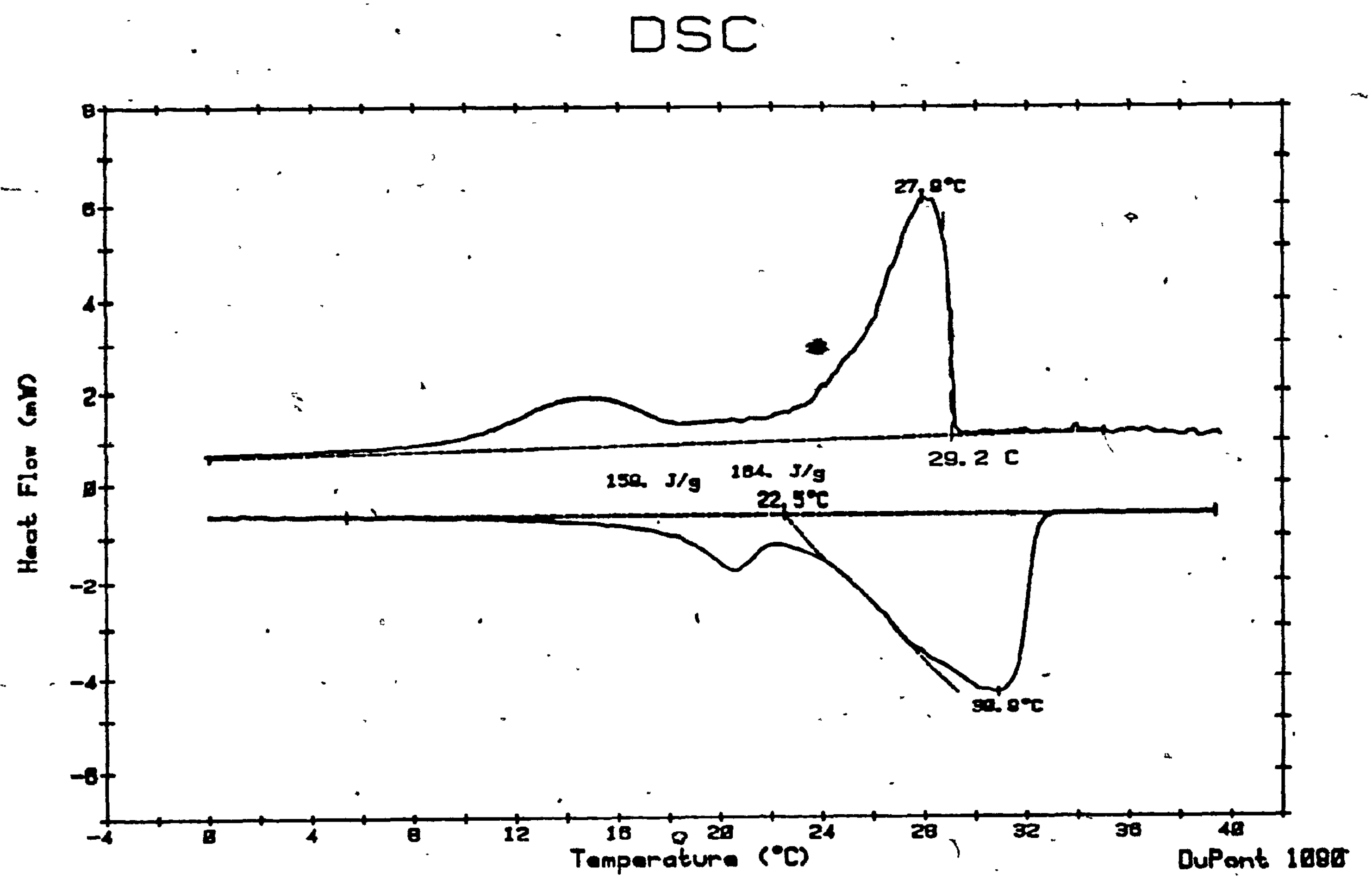

Fig.36 . The heating - cooling thermogram of Emery 2204.

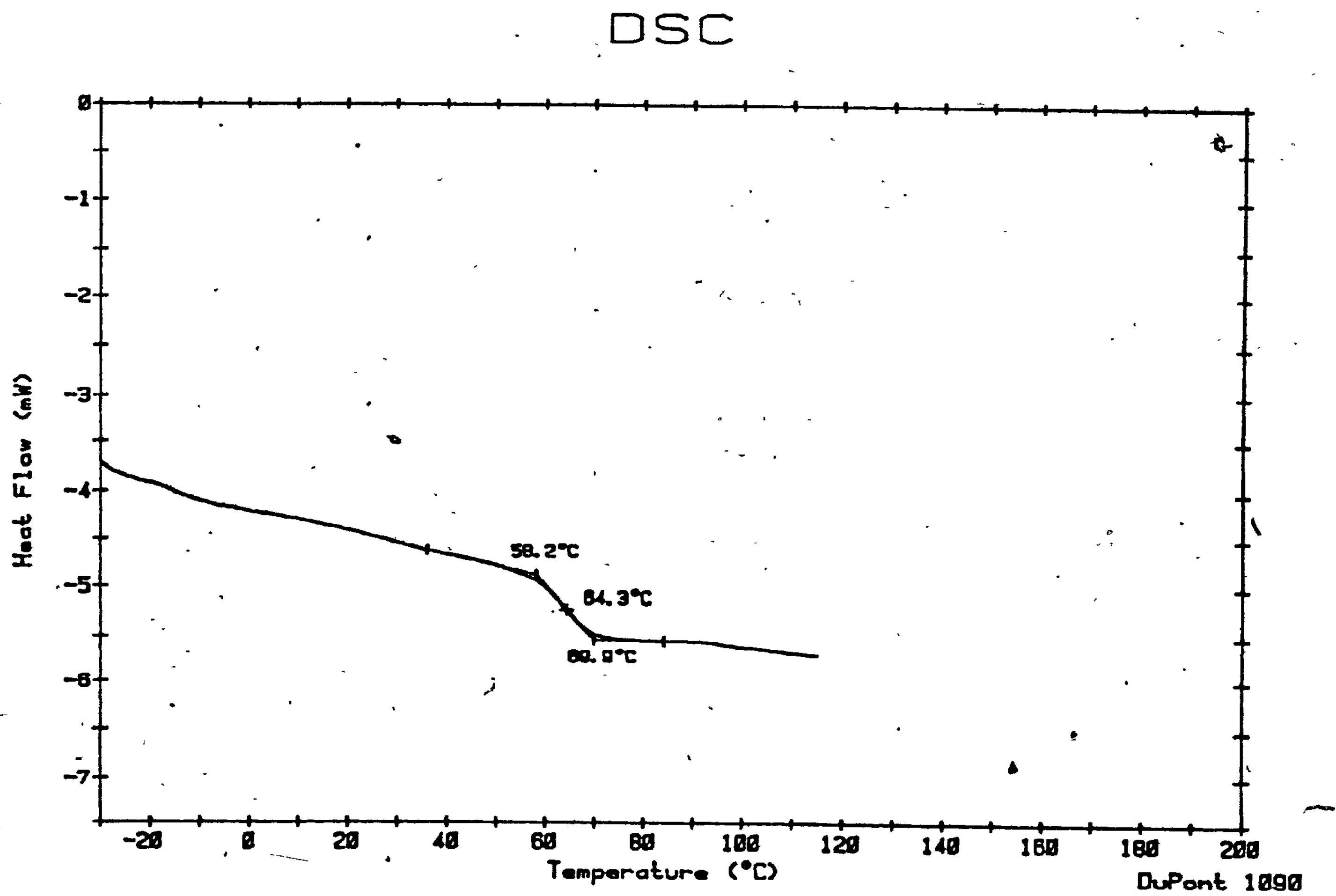

Fig.37 . The Tg. thermogram of EP XP-1203

6.7 DISCUSSION

The heat storage module showed high compressive strength, both at room temperature and at an elevated temperature of 50°C. This was 434% and 163% of the compressive strength of a (standard) clay brick of the same size. This high mechanical strength gives the module a wide application for building structures.

The heat distortion temperature (H.D.T.) of 85°C and 96°C for plastic and epoxy respectively, as well as the (Tg) of epoxy, which was about 60°C, are higher than the temperatures to which short term storage systems are normally exposed (usually 20°C to 50°C).

As shown in table 17, the flammability of the EP (XP-1203) was found to be less than that of poly (methyl methacrylate) which constitute the lateral faces of the brick. Lauric and stearic acid, the main ingredients of the PCM, have the same flammability as benzene.

Following the DSC analysis of Emery 2204 (fig.36), it was observed that the melting points of the mixture are at about 17°C and at about 22°C. During heating, the endothermic peak representing the solid-to-liquid phase change occurred between 12°C and 31°C (lower curve). The change in the phase was noticed by the deviation of the curve from the base line until the temperature reached 31°C. When the slope changed from negative to positive, the return of the curve to base line indicated that the Emery 2204 was fully melted, the range of phase-change depends on the heating rate. The two peaks rather than a sharp change result from the

Emery 2204 being a mixture rather than a pure substance. During the cooling interval (upper curve) the exothermic peak representing the liquid-to-solid state can be seen, this shows the release of the stored heat. The heat of fusion was found to be about 160 J/g.

The low thermal conductivity of (0.2 W/m.^{0}C) makes the module system a good thermal insulator for winter nights when the module wall is placed behind a large glazing. When the PCM in the module on the cold glazing side starts changing phase from liquid-to-solid, it will create a good insulator leaving the heat flow only to heat the inside space.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

Several conclusions can be drawn from the results of the study on the epoxy polymer (EP) (CA-1200) and its modification (MEP), also, on the EP application for the solar heat storage during this preliminary phase of research.

I. EPOXY POLYMER ADHESIVE AND ITS MODIFICATION

i. Applying EP (CA-1200) to bond sheet molding compounds material using a new EP riveting technique proved to have higher shear strength than the conventional metal bolts and polyurethane adhesive, especially when exposed to natural weathering and thermal shocks.

ii. Cured EP has good chemical resistance to drinkable water and benzene, it has low stability in methanol, and it is highly susceptible to deterioration in DMF, acetone and aqueous solutions of sodium and calcium chlorides.

iii. Modification of EP by blending with PVC, PVA and DBP in small concentrations (up to 4% of DBP) does not result in improvement of the tensile strength property (bonding aluminum), or the weatherability of the products. The deterioration of mechanical properties of EP and modified EP blends by outdoor exposure in the Canadian climate is believed to be caused by cryolitic and hydrolitic processes. However, slight improvement in tensile strength and in weatherability was found for EP blend containing a higher concentration of DBP (6%).

iv. Modification of EP by blending with PU, DBP and PVC in concentrations 7, 8 and 15% respectively, improved the shear strength property of the bond of aluminum substrates.

v. Incorporation of DBP and PU into EP causes a marked reduction in heat distortion (HDT) and glass transition temperatures (Tg). Addition of PVC to EP has generally a moderate influence in lowering the HDT but increase the Tg. Blending GF with EP causes an increase in both the HDT and the Tg.

vi. Blending EP with DBP and PU causes a marked increase in flammability of the blend.

vii. Modification of EP with DBP and PVC does not change the peak exothermic temperature, blending with GF causes a marked increase in this temperature.

II. EPOXY POLYMER AS ENCAPSULANT FOR THE SOLAR HEAT STORAGE MODULE

i. The produced module based on EP, plexiglass and PCM proved to have good mechanical properties which allows it to be used as a partition or structural wall, as well as, a heat storage element.

ii. The high flammability of the poly-(methyl methacrylate) (plexiglass) and the phase-change material used in the module should be considered in the application of the module.

iii. The module can be used for short term storage where the temperature usually does not exceed 50°C. This permits a wide range of domestic, commercial and industrial applications.

7.2 RECOMMENDATIONS

This preliminary research* on EP (CA-1200), its modification and use in solar energy applications, has disclosed several new opportunities for its application to building technology. However, further work is needed before its full potential may be released and the following recommendations are intended to address this issue.

i - The first requirement would consist of a detailed flammability study of the materials (EP, MEP, plexiglass and PCM). The study should be directed towards a solution of this problem through the use of additives or substitutions of some components, (e.g. using non-flammable polymers).

ii - Although the modification of EP resulted in improving some mechanical properties, additional research should be aimed at improving its compressive strength.

iii - A preliminary cost study should be undertaken to define and quantify those aspects which must be improved before the module can be cost effective. In particular, further study should be given to the following:

a) reduction of material cost by bulk purchasing and by using inexpensive fillers (e.g. mineral fillers, metallic powders, polymers, etc.).

b) improved methods of manufacture to reduce production cost.

c) improved design (e.g. multiple brick panels) aimed at reducing installation costs.

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* Resulted in two papers (43,44) and two applications for patents (45,46)

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