CHAPTER 3

RESULTS AND DISCUSSION

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The historical developments of waste treatment and disposal have been motivated by concern for public health. The industrial revolution leads to many people moving from rural areas to the cities, a massive expansion of the population living in towns and cities, and a consequent increase in the volume of waste arising. The increase in production of domestic waste was matched by increases in industrial waste from the burgeoning new large scale manufacturing processes. The waste generated contained a range of materials such as broken glass, rusty metals, food residue, human waste and plastic waste, and was dangerous to human health. In addition, it attracted flies, rats and other vermin, which in turn posed potential threats through the transfer of disease. This led to an increasing awareness of the link between public health and the environment.

Uppermost in hierarchy is the strategy that plastic waste production from industrial manufacturing processes should be reduced. Reduction of waste at source should be achieved by developing clean technologies and processes that require less material in the end products and produce less waste during manufacture. The collection and re-use of materials, for example glass bottles involves collection, cleaning and re-use of these bottles. Re-use can be attractive in some circumstances.

However, re-use may not be desirable in all cases since the environmental and economic cost of re-use in terms of energy use, cleaning, recovery; transportation etc. may outweigh the benefits. The

recovery of plastic materials from waste and processing them to produce a marketable product is well established with a net saving in energy and material costs of the resulted product compared with virgin production. Poly (ethylene terephthalate) (PET) is thermoplastic polyester showing excellent thermal and mechanical properties. Although its main application was by far the textile industry, tremendous quantities of this material are consumed in the manufacture of video and audio tapes, X-ray films, food packaging and especially of soft drink bottles. PET recycling represents one of the most successful and widespread examples of polymer recycling. PET bottle collection in Europe (European Union member states plus Norway, Iceland, Switzerland, and all EU candidate countries) is growing steadily. In 2001, 344,000 ton were collected, a 20% increase in comparison with 2000. By 2006, it is forecast that European PET collection will increase to 700,000 ton **[PETCORE Report 2002]**. The main driving force responsible for this extremely increased recycling of post-consumer PET is its widespread use, particularly in the beverage industry.

A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry is that it does not have any side effects on the human organism. It should be pointed out, that PET does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material **[Scheirs 1998]**.

Therefore, the recycling of PET does not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw

petrochemical products and energy. Among the different recycling techniques, the only one acceptable according to the principles of "Sustainable Development" is the chemical recycling, since it leads to the formation of the raw materials from which the polymer is made of, as well as of other secondary value-added products **[Achilias et al. 2002]**. A successful recycling program does not only depend on post-consumer waste collection, it also depends on whether the products made out of collected, reclaimed and recycled material respond to consumers needs, in other words if recycled products are actually bought. This is the reason why the PET industry constantly researches for reclaimed material new applications. The collection of bottles made of PET from waste where there is no end market for them merely results in large surpluses of unwanted material unless they are converted to another marketable product.

Recycled PET manufactured into numerous products, the five major generic end-use categories for recycled PET plastics are:

- Packing applications (such as; new bottles).
- Sheet and film applications (such as; laundry scoops).
- Strapping.
- Engineered resins applications (such as; reinforced components for automobile.
- Fiber applications (such as; carpets, fabrics and fiberfill).

Today, PET bottles have become one of the most valuable and successfully recyclable materials. Recently, a growing interest has been observed in the use of PET wastes for the production of specialized products such as unsaturated polyester, epoxy resins and polymer

concrete. As a step further, in this work, glycolysis of PET is examined as a process for the production of raw materials used in coating resins.

The aim of this study was to use the oligoester diols produced from PET recycling as potential raw materials for the production of epoxy, vinyl ester and unsaturated resins used as coatings. In order to fulfill these goals three steps were distinguished:

1- The first step includes the depolymerization of PET using diethylene glycol and tetraethylene glycol and the identification of the oligomers produced.

2- In the second step, the curing behavior of epoxy resins, vinyl ester and unsaturated polyester resins used for the production for ambient temperature coatings was investigated by manipulating the amounts of the initiators used.

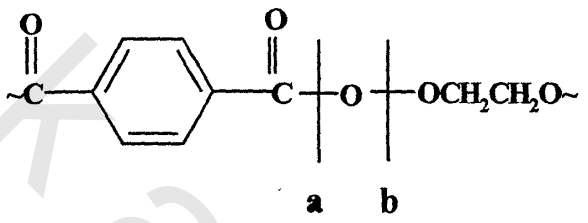
3- In the final step, the glycolyzed products (glycolyzates) taken from PET recycling replace the diols used for the conventional production of the epoxy, vinyl ester and unsaturated polyester resins and the final mechanical properties of the resins were compared.

3.1 DEPOLYMERISATION OF PET

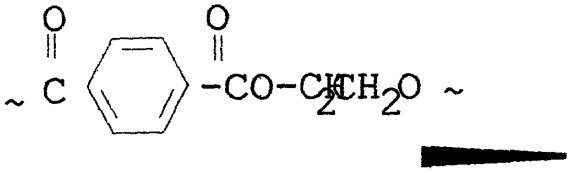
Transformation of PET into oligoester polyols by glycolysis is an efficient route to reuse PET. The various possibilities for utilization of PET waste include glycolysis by glycols such as ethylene-, diethylene-, triethylene- and tetraethylene glycol **[Douglas 1980], [Makhlouf 1983],** and **[Selley 1985]**. In the present study, the appropriate conditions for the preparation of oligoester polyols by glycolysis of PET with different glycols DEG and TEG were investigated. The depolymerzation of PET was carried out in nitrogen atmosphere in the presence of 0.5% Mn-

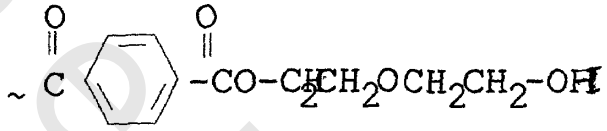
acetate as trans-esterification catalyst at over all reaction times 8h. Two glycolyzed products with DEG and TEG were coded as GD and GT, respectively.

The glycolysis consists of trans-esterification of PET and destruction of its polymer chain, resulting in the decrease of PET molecular weight. Destruction of PET can take place at elevated temperatures by affecting the bonds (a) and (b) in the polymer chain:



When glycols used as destructing agents, the oligoesters obtained have two hydroxyl end groups, i.e. oligoester diols are formed. The glycolysis of PET with both DEG and TEG was carried out at a reaction temperature not more than 220°C. This can be attributed to the formation of alicyclic derivatives between hydroxyl groups of produced poly-hydroxy glycolyzed PET **[Boyd et al. 1972]**.





$$HOCH_2CH_2O \qquad (3.1)$$

The glycolyzed products were analyzed for hydroxyl values (in mg KOH/g) after removal of free glycol DEG and TEG (expressed as wt %). The data are listed in ***Table (3.1)***.

Based on the obtained value of the hydroxyl number after removing the free glycol and the ^{1}HNMR study carried out by Tong et al. **[Tong et al. 1983]**, the following monomer, dimer and trimer compounds are existed as following:

(Monomer)

HO-R-O-CO-C_6H_4-CO-O-$(CH_2)_2$O-CO-C $_6H_4$-CO-O-R-OH

(Dimer)

HO-R-O-(CO-C_6H_4-CO-O-CH_2CH_2-O)$_2$-CO-C_6H_4-CO-O-R-OH

(Trimer)

$$R = (CH_2OH)_2O \text{ or } CH_2CH_2OCH_2CH_2OH)_2$$

The alcoholysis of PET with DEG and TEG proceeds according to the above reaction. The alcoholysis consists of the transesterification of PET and the destruction of its polymer chain, resulting in the decrease of its molecular weight. Using glycols in the depolymerization of PET, the oligoesters obtained have two hydroxyl end groups, i.e. oligoester diols are formed. The choice of DEG and TEG to carry out the glycolysis is usually determined by the necessity of having well flexural properties in the UP, since the long chains of the glycol improves flexibility.

In a previous study **[Abdel-Azim et al. 1986]** it was indicated that, the best ratio between DEG or TEG and PET is (1:1, wt: wt) which affords better chance for dissolving the initially destructed materials and hence enhances the reactivity between the solvent (DEG or TEG) and the dissolved glycolyzed product. This certainly leads to more and more destruction due to the increased probability of collisions between the reactants. It is well known that the use of a large excess of glycol in destructing PET leads to formation of secondary OH groups in the formed oligoesters **[Halacheva et al. 1995]**. These secondary OH groups cause troubles (formation of gel) during converting the polyol into unsaturated polyester. Accordingly, the ratio of PET: DEG and PET: TEG equal 1:1 (wt/wt) was not exceeded throughout the present study.

The data listed in ***Table (3.1)*** reveal, also, that the amount of glycol consumed in producing GD is only 16%. This percentage increases to

20 % of TEG. The hydroxyl number after removing the free glycol indicates that the extent of depolymerization was considerable and that the resulting oligomers were mostly terminated with hydroxyl groups. The number of reacted molecules of TEG (n) was calculated from the number of moles of the reacted TEG divided by the number of moles of PET.

Thus, for the oligomer samples reacted for 8h, 100g of PET (=1.58 mmol) would have reacted with 20 g of TEG (=103 mmol) and the molecular weight should have been lowered to (63200/ (1+103/1.58) = 956 g mol^{-1}. The molecular weight of the GT was determined by GPC, as described in the experimental section, and equal 965 g mol^{-1}. Results based on the average molecular weights of the two glycolyzed products are listed in ***Table (3.1)***. In this table results are included on the number average molecular weight <Mn> of the polyester oligomers produced using the hydroxyl number or the GPC. Also, the weight average molecular weight <Mw> and the polydispersity of the molecular weight distribution of these samples obtained from GPC are included. It was noted that, the results obtained from GPC where always higher than the corresponding from the hydroxyl number. The polydispersity of the molecular weight distribution, which was always greater than 1, revealed that the distribution was not unimodal. Actually, in every sample three distinct peaks (trimodal shape) were identified.

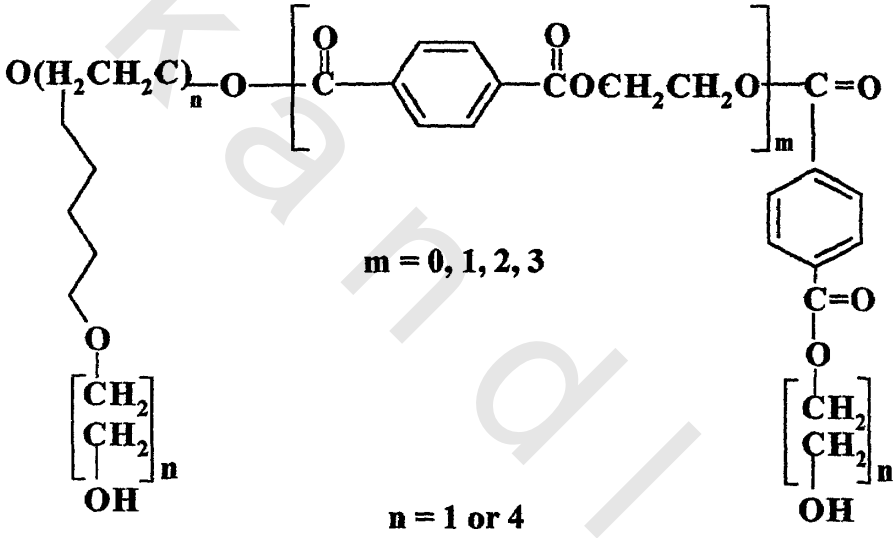
Table (3.1) Specifications of Glycolyzed Products (GT & GD)

Designation	Wt ratio of DEG or TEG: PET	% of DEG or TEG	Hydroxyl no. (mg KOH/g)	GPC Data			Mn	
				Mn	Mw	Mw/Mn	Theo.	Calc*
GD	1:1	16	170	684	779	1.14	654	660
GT	1:1	20	117	965	1080	1.12	956	958

*** Calculated from OH values**

The three peaks identified correspond to molecular weights of 350, 540 and 725. That means that PET glycolysis using DEG results mainly in three kinds of oligoesters. It was noted that, the area under the peak corresponding to the lowest molecular weight was increased and the area under the peak of the higher molecular weight was lowered. Hence, amount of DEG or TEG are better for depolymerization of PET.

On trying to identify the oligoester diols produced, the following structure was proposed **[Halacheva et al. 1995]**.



Where m = 0-3. According to the above structure if one replaces m with 0, 1 and 2 the following molecular weights are obtained: 342, 534 and 726, respectively. By comparing these values with the values obtained by GPC, it can be concluded that the above structure is confirmed with m = 1 and 2. Similar structures have been observed also in literature **[Farahat et al. 2001]**. However, a definite identification of the components of the glycolyzed PET products could be done for example by using ^{1}HNMR.

The structure of the GD and GT oligomers was verified from their IR spectra. In this respect IR spectrum of GD was selected and represented in ***Figure (3.1).*** The presence of strong peak at 3450cm^{-1}, in all spectra, indicates the termination of the glycolyzed products with hydroxyl groups and the band observed at 810 cm^{-1} for all depolymerized PET is assigned to –CH out-of-plane bending of p-substituted phenyl. This confirms the presence of phenyl rings in depolymerized products without destruction. The presence of strong peaks at 1745 cm^{-1} and 1150 cm^{-1} , which were assigned for C=O stretching and C-O stretching of ester groups, indicates the incorporation of ester groups in all depolymerized PET products.

A further confirmation for glycolysis of PET with DEG and TEG is given by ^{1}HNMR. In this respect, the spectrum of GD was selected as representative samples and represented in ***Figure (3.2).*** It shows the signals at chemical shifts (δ) 8.0 ppm, 3.87 and 4.8 ppm represent p-substituted phenyl group, -(-CH_2CH_2O-)- and $OOCCH_2CH_2COO$ of glycolyzed PET respectively. The signal observed at 2.6 ppm in the spectra, which represent OH group of glycolyzed DEG and TEG, indicate the presence of terminal OH in all glycolyzed PET samples.

3.2 Synthesis of Glycidyl Ether of Glycolyzed Products

Epoxy binders were prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin (EC) followed by dehydrohalogenation in presence of NaOH. The most commonly used epoxy resins are those derived from bisphenol-A by reaction with EC.

The simplest diepoxide formed in this proceed is the glycidyl ether derivatives. Although these materials are used as adhesives, they suffer from a lack of flexibility, which arises from short rigid aromatic groups in the chains. Improvements in flexibility can be obtained by incorporation of long chain compounds into the resin before cure **[Cunliffe et al. 1975]**. In the present work, the formation of long chain resin including DEG or TEG would improve the flexibility and adhesion properties of epoxy resins. In this respect, the glycolyzed derivatives of PET oligomers with DEG or TEG (i.e. GD or GT) were reacted with EC in presence of 50% aqueous NaOH to produce glycidyl ether coded as GDE and GTE.

The results of characterization of glycidyl ether derivatives of PET oligomers include epoxy content and hydroxyl content is given in ***Table (3.2)***.The chemical structure of both GDE and GTE was confirmed by ^{1}HNMR analysis.

In this respect, the spectra of both GTE and GDE were represented in ***Figure (3.3)***. The disappearance of -OH peak and appearance of two peaks at 2.82 ppm (CH_2 epoxy), 2.94 ppm (OCH_2 epoxy), and 3.43 ppm (CH epoxy) indicates the formation of glycidyl ether group **[Tong et al. 1983]** and **[Narasimhaswany et al. 1991]**.

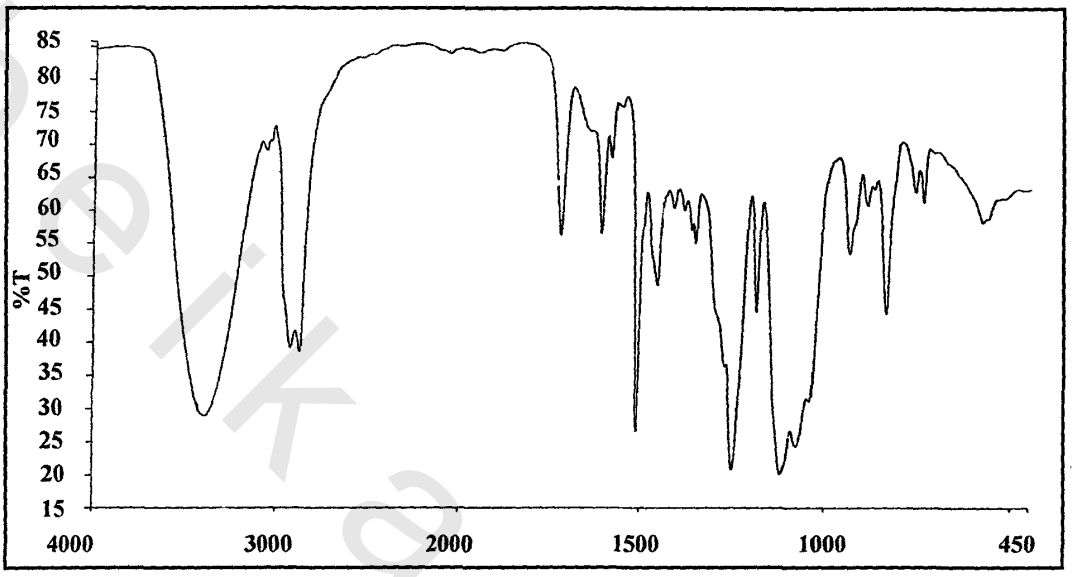


Figure (3.1): IR Spectrum of GD oligomer

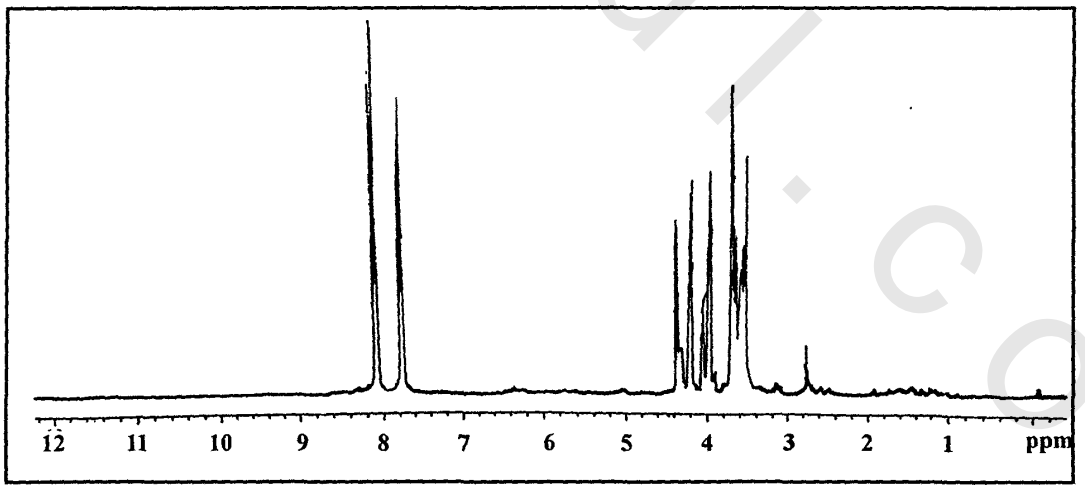


Figure (3.2): ^{1}HNMR Spectrum of GD oligomer

Table 3.2: Physico-chemical Characterization of Glycidyl Ether of GDE and GTE Oligomers

Oligomers	EEW	Epoxy functionality	M. wt. (mol/g)
GDE	350	2.2	770
GTE	595	1.8	1072

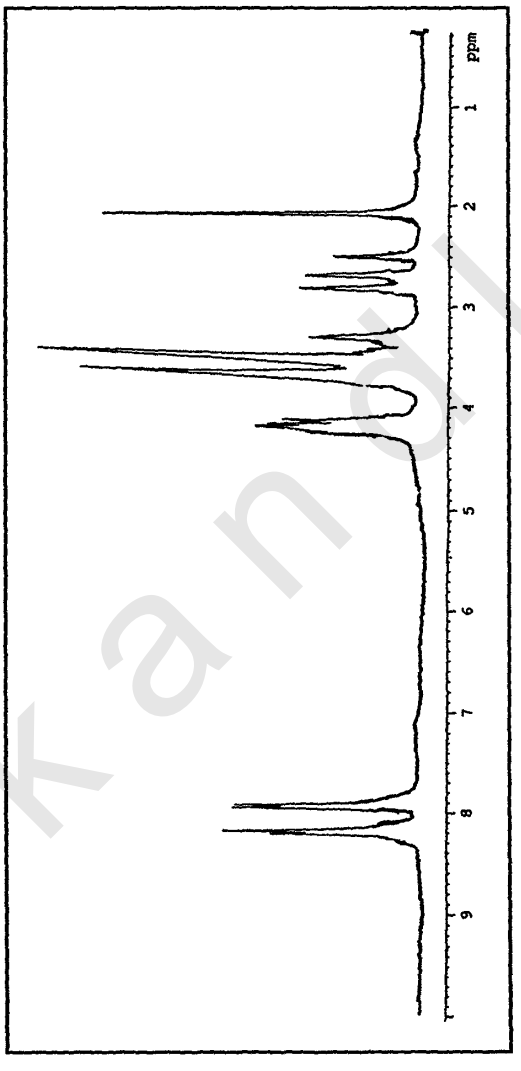


Figure (3.3): ^{1}HNMR Spectra of GDE Epoxy Resins

3.3 Synthesis of Divinyl ester Cross-linkers from R-PET

Today, they are one of the most important thermosetting materials. Vinyl ester resins have been widely recognized as materials with excellent resistance to a wide variety of commonly encountered chemical environments. Vinyl ester resins used to fabricate a variety of reinforced structures, including pipes, tanks, scrubbers and ducts. They are prime candidates for use in composites for transportation and /or infrastructures. Such applications include fabrication of parts for automobiles and other surface transportation vehicles, fascia for building, reinforcements for bridges, etc. In addition to these applications, vinyl ester resins are also, being used in coatings, adhesives, molding compounds, structural laminates, electrical applications and military /aerospace applications **[Kelly 1976], [Yeh et al. 1977], [Sorathia 1977], [Singh 1994], [Sonti 1996], [Hag et al. 1996], [Brown 1997]** and **[Liao 1997].**

Although vinyl ester resins have been used in industry for more than 30 years, they are generally categorized together with unsaturated polyester family. There is much less research cited in the literature on vinyl ester resins compared to the studies on unsaturated polyesters and epoxy resins, especially the studies on the formation-structure-properties of vinyl ester resins.

Commercial vinyl ester resins are a mixture of styrene with a methacrylated epoxy compound based on bisphenol-A. Using the recycled PET offers the possibility of a lower cost source for the latter component. Vinyl ester resins are usually produced from reaction of epoxide resins with unsaturated monocarboxilic acid. This reaction is

usually catalyzed by tertiary amines, phosphines, and alkalis or ammonium salts. Triphenyl phosphine is more effective catalyst as compared to other catalysts **[Sandner 1992]**. The vinyl ester resins can also be prepared by the reaction of glycidyl methacrylate with multifunctional phenol **[Bowen, 1965]**.

The present study intended to prepare vinyl ester resin from recycled PET waste. The first step includes the depolymerisation of PET using tetraethyleneglycol (TEG) and the reaction of its products with EC to produce epoxy resin. We decided to model the process and characterize the reaction products for each step of the process. The second part of the synthesis was based on the reaction between the epoxy resin and acrylic or methacrylic acid in presence of triphenyl phosphite to produce vinyl ester resins having acrylate or methacrylate end groups. Tong et al. **[Tong et al. 1983]** found that unsaturated polyesters based on bis (2-hydroxyethyl) terephthalate, maleic anhydride and ethylene glycol were not compatible with styrene monomer. These authors found that it is necessary to replace part of the ethylene glycol by another type of glycol to enhance the compatibility of the products with styrene monomer. Accordingly, in the present study, TEG was incorporated in the vinyl ester to increase the miscibility of the synthesized resins with styrene monomers. Schulze et al. **[Schulze et al 1997]** have reported the modification of unsaturated polyesters by poly (ethylene glycol) end groups in order to influence the solution behavior in styrene and to modify the mechanical properties of the cured resin.

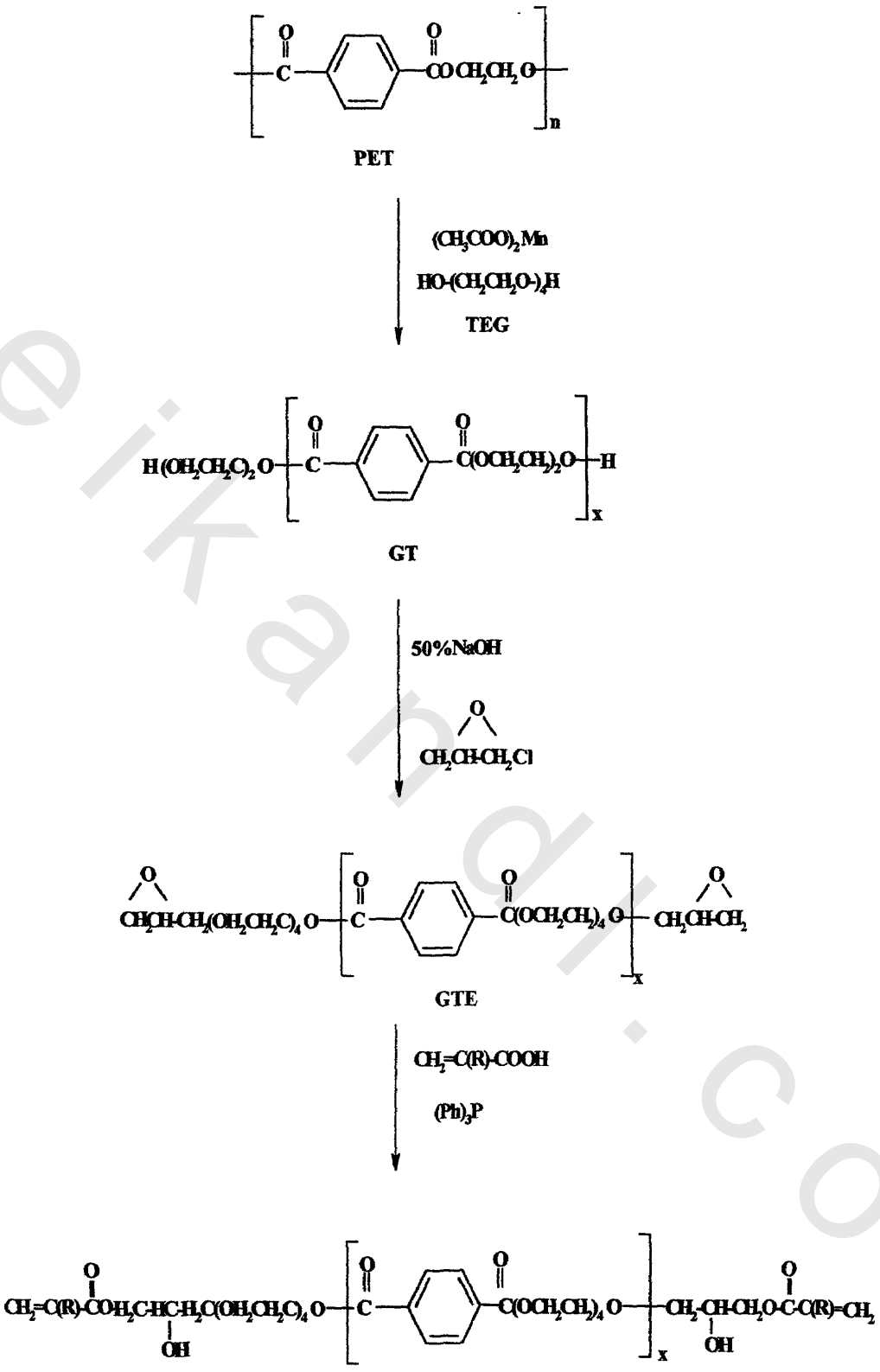
The synthesis of the block copolymer was carried out by reacting carboxyl-terminated unsaturated polyester with various poly (ethylene

glycol) monomethyl ethers of molecular weights from 350 to 2000 g/mol. The block copolymers could be easily diluted in styrene to create curable resins. The conversion of the typical polar end groups to poly (ethylene glycol) end groups should improve the flexibility of the cured material. The intermolecular chain interactions will also change considerably.

Instead of hydrogen bonds, which are responsible for aggregation and the high viscosity of the resin in styrene, van der Waals interactions are dominant. Accordingly, we presumed that the incorporation of TEG into the structure of the vinyl esters enhances their solubility in styrene monomer. In the present work, vinyl ester resins are produced from reaction between glycidyl ether coded as GTE and acrylic or methacrylic acids AA or MA, respectively. The produced vinyl esters are coded as GTA or GTM. The reaction schemes were illustrated in ***Figure (3.4)***. PET was depolymerised with an excess of TEG, and manganese acetate $(CH_3COO)_2$ Mn as a catalyst.

The chemical structure of the recycled vinyl ester resins based on the reaction of epoxy resin based on PET with acrylic or methacrylic acids was confirmed by ^{1}HNMR analysis. In this respect, ^{1}HNMR spectrum of vinyl ester resins based on acrylic (GTA) or methacrylic groups (GTM) were represented in ***Figure (3.5a&b)***, respectively. It was observed that the appearance of strong peak at 1.916 ppm (δ), 5.5 ppm and 6.1 ppm, represent CH_3, H_a and H_b of methacrylate group, indicates the formation of dimethacrylate vinyl ester resin from recycled PET. While the appearance of peaks at 5.7, 5.99 and 6.1 ppm, represent H_a,

H_b and H_c of acrylate group, indicates the formation of acrylate vinyl ester resin from recycled PET.



GTA (R = H), GTM (R = CH_3)

Figure (3.4): Reaction Scheme for Synthesis of GTA and GTM Resins.

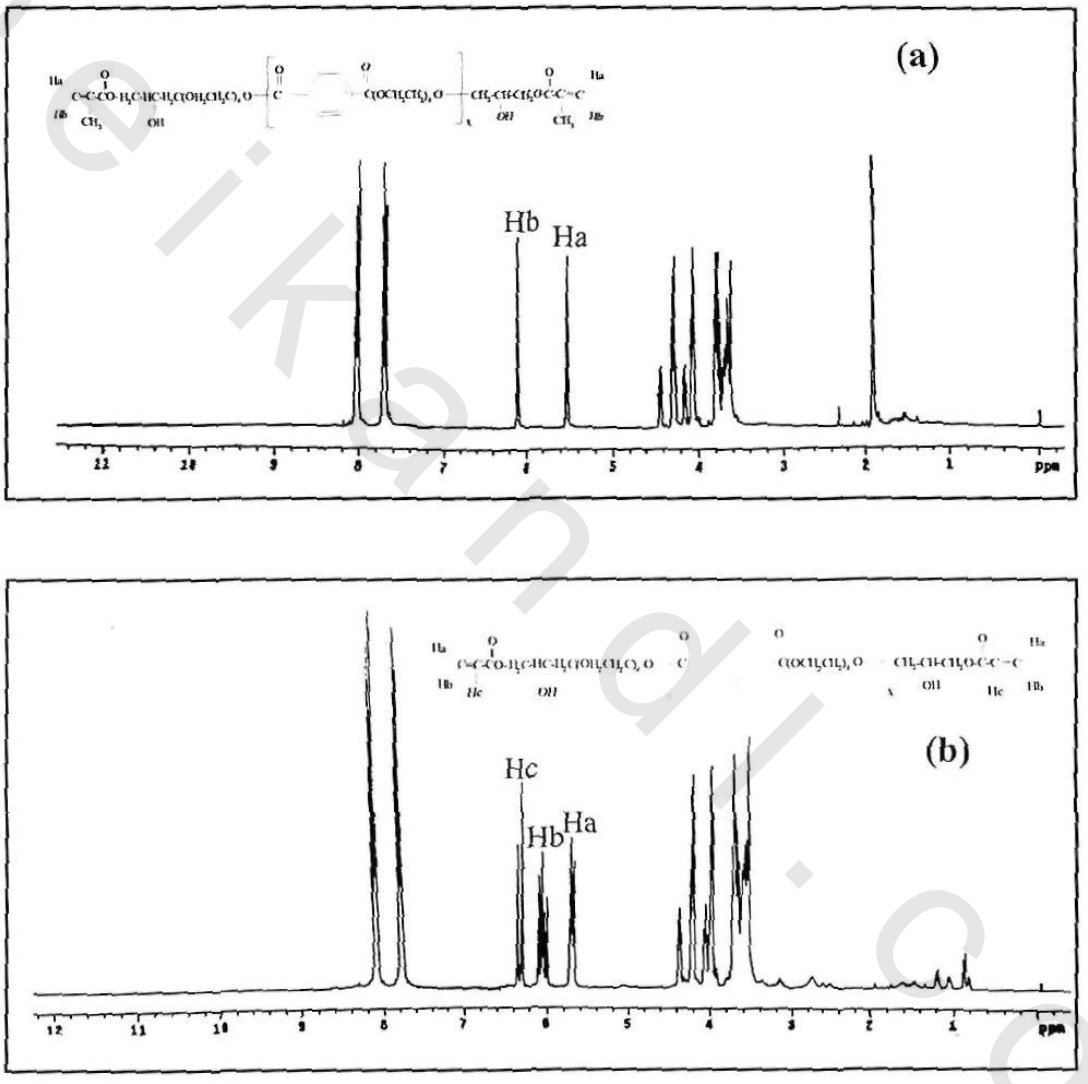


Figure (3.5): ^{1}HNMR Spectra of a)-GTM and b)-GTA Resins

3.4 SYNTHESIS OF UNSATURATED POLYESTER FROM R-PET

A very considerable number of raw materials, which can be used for making polyester resins, are potentially available. The glycols, dibasic acids and monomers, which are commercially available in prices, limit the usage of the produced resin in many applications. However, a vast number of permutations are possible. Recycling of poly (ethylene terephthalate) has attracted attention of several investigators **[Vaidya et al. 1987]** and **[Rebeiz et al. 1991 and 1992]**.

Depolymerization of this polyester has been studied in the presence of a variety of catalysts and glycols to obtain dimethyl terephthalate or oligomeric polyester, **[Matsuura et al. 1975]**, **[Toshima 1975]**, **[Miyake et al. 1975]**, **[Omoto et al. 1977]** and **[Makimura et al. 1978]**. Vaidya and Nadkarni **[Vaidya and Nadkarni 1987 and 1989]** were among the first who systematically studied the formation of unsaturated polyester resins (UP) from PET glycolysis. Baliga and Wong **[Baliga and Wong 1989]** carried out the glycolysis of PET with ethylene glycol (EG) using various catalysts. They found that glycolyzed products had 1–3 repeating units depending on the catalyst used. Halacheva and Novakov **[Halacheva 1995]** have investigated the chemical structure of the oligoesters produced from PET glycolysis with diethylene glycol (DEG). Furthermore, Suh et al. **[Suh et al. 2000]** examined the properties of unsaturated polyesters produced from glycolyzed PET with various combinations of the glycols DEG/propylene glycol (PG).

Farahat and Nikles **[Farahat et al. 2001 and 2002]** provided results on the glycolysis of PET and the production of novel binder systems for solvent less magnetic tape manufacturing. Farahat also synthesized modified UP from PET glycolysis using different DEG/PET molar

ratios **[Farahat et al. 2000 and 2002]**. The production of unsaturated polyester from recycled PET was reported in previous works **[Abdel-Azim 1995]**. The preparation of unsaturated polyester is based on condensation reaction between glycolyzed oligomers from R-PET and maleic anhydride. In this respect, DEG and TEG were used in the glycolysis processes of PET to produce GD or GT. The oligomer, GD was reacted with ethylene glycol (EG) and maleic anhydride (MA) by fusion method as reported in the experimental section. On the other hand, unsaturated polyester resin (UP1) obtained from Sir Company was used to make a comparative study. The resin is a mixture of styrene with unsaturated polyester based on (isophthalic acid with propylene glycol and maleic anhydride) as a commercial source in this study.

The hydroxyl number of the glycolyzed products after separation of the free glycol was used for estimating the amount of dibasic acids required for the completion of the esterification reactions. After the complete esterification, the polyester was viscous liquid having dark yellow to pale brownish color diluted by a sufficient quantity of styrene monomer to give 60% solution of unsaturated polyester (UP2). The molecular weights of the prepared UP2 resin were determined using end group analysis as described in the experimental section. The acid and hydroxyl values in (mg KOH/g) and the number average molecular weights (M_n) derived from these values are listed in ***Table (3.3)***. Preliminary tests have shown that 40% of styrene was found to be the least amount of styrene, which can dissolve the polyester under investigation.

The chemical structure of UP1 and the prepared UP2 was confirmed by ^{1}HNMR analysis. In this respect, the spectra of UPI and UP2 were

represented in ***Figure (3.6 a&b),*** respectively. The bands at δ = 7.8, 5.3 and 4.2 ppm are assigned to phenyl ring unsaturation system (C=C), and –OH of terminal alcoholic glycol, respectively. The signals at 2.18-2.98 ppm are assigned to (CH_2 ester). These bands were observed in all spectra of UP1 and UP2, The band at 0.9 ppm for UP1 spectrum,-CH_3 of propylene glycol, indicates that the glycol used in UP1 is propylene glycol. In addition, the average molecular weight of UP and styrene content of the prepared polyester UP2 and commercial UP1 were determined using ^{1}HNMR spectroscopy. The molecular weight of UP was determined from an average value of (n) that can be calculated from the ratio between integration peak of vinyl group of maleic peak area to the integration peak area corresponding to the -OH end groups.

On the other hand, the styrene content of UP was calculated from the integration ratios of styrene to vinyl groups of -HC=CH- of UP. Using this approach, the average M. wt of UP1 and UP2 and styrene content of UP1 were calculated and listed in ***Table (3.3)***. Careful inspection to the data listed in this table indicates that the calculated number average molecular weights of UP1 and UP2 from ^{1}HNMR analysis agree with the data determined from hydroxyl and carboxylic values as illustrated in experimental section. This indicates that ^{1}HNMR can be used as useful method to determine the molecular weigh of UP resins **[Ziaee et al. 1997]**.

Table (3.3): Molecular Mass Determination of UP1 and UP2

Code	Acid no. (mg/KOH)	Hydroxyl no. (mg/KOH)	<Mn> g/mol	$<M_n>$* g/mol	Styrene Content
UP1	—	—	—	6720	45%
UP2	7.29	26.6	3310	3475	40%

*** Determined from ^{1}HNMR.**

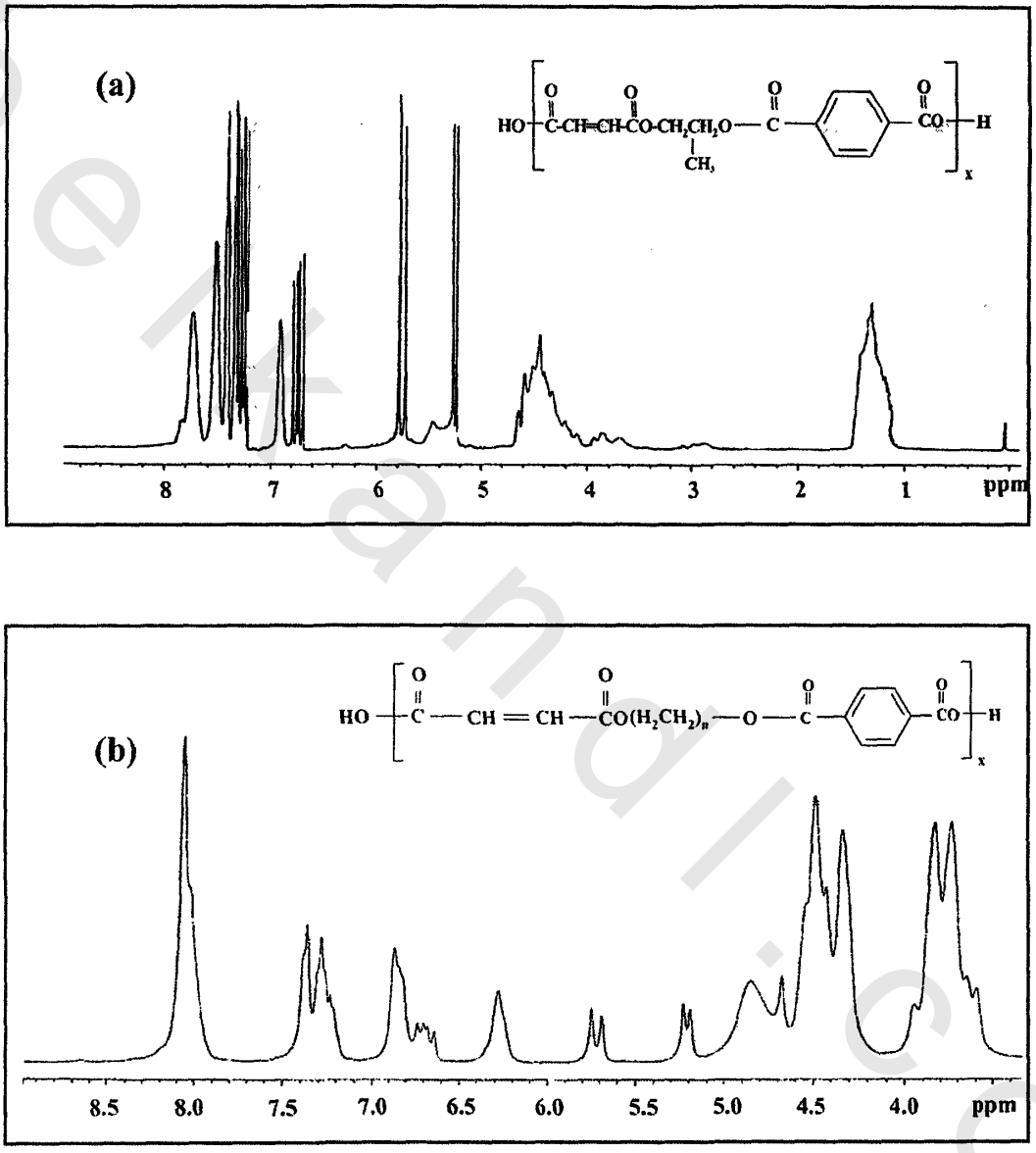


Figure (3.6)^{1}HNMR Spectra of a)-UP1 and b)-UP2 Resins

3.5 CURING EXOTHERMS

The curing stage is the second step in the preparation of thermoset polymers. The choice of resin and of curing agent depends on the application and on handling characteristics (viscosity, pot life and gel time); curing temperature and time; properties (mechanical, chemical and thermal) and costs. Vinyl esters networks are based on polyfunctional methacrylate monomers dissolved in styrene and are cured by free radical initiated polymerization. Organic peroxides and aliphatic azo-compounds are two of the more common families of free radical initiators used. In contrast, epoxy resins are commonly cured by step growth polymerization with aliphatic and aromatic amines **[Shechter et al. 1956]**.

Several methods based on data of dynamic me`chanical analysis (DMA) **[Mijovic et al. 1981]** rheological measurement, near infrared analysis **[Deank et al. 2000]** and thermal differential scanning calorimetry (DSC) were used to study the curing kinetic mechanisms. In this respect, the preset section concerns with studying the curing mechanisms of epoxy, vinyl ester and unsaturated polyester resins at different conditions.

3.5.1 CURING EXOTHERMS of EPOXY with AMINE

Curing, a process, which finds wide technical application, is understood here as the transfer of epoxide oligomers into cross-linked polymers by means of curing agents or catalysts. Some curing agents promote curing by catalytic action while others participate directly in the reaction, being chemically bound into the resin chain **[Lee 1967]**. The oxiran ring has a strongly polar character and a considerable internal stress (92 - 109 kJ

mol^{-1}) so that it reacts with numerous compounds having nucleophilic and electrophilic characters. The reactivity of the epoxide ring depends upon its location either at the end or in the middle part of the chain or on the cycloaliphatic ring. So far, the most widely used epoxide oligomers are those with two glycidyl groups in the resin molecule. Any substance of either acid or basic character may be used as a curing agent **[Lee 1967]**. Various polyamines and fatty-polyamides are also suitable, not to mention the so-called ion-hardeners (catalysts). Quite a number of papers have been published aiming to elucidate the mechanism and kinetics of curing processes of epoxide oligomers. Knowledge of a detailed mechanism and reaction rate allows the curing process to be quantitatively described and curing parameters to be selected, on the basis of scientifically selected principles, thus improving the production of materials possessing the required properties **[Rozenberg et al. 1980].**

There are several types of cross-linkers used to prepare cross-linked epoxy polymers, which include polyamines, polyamides and anhydrides. The curing stage of epoxy polymers is considered structoterminal or structopendant depending on weather cross-linking occurs through the epoxy end groups or the hydroxyl groups. The pre-polymer is structoterminal when polyamines or polyamides are used for cross-linking; in this case, curing involves the opening of the epoxide groups. Hardening occurs primarily through the hydroxyl groups when anhydride is used as cross-linking agent; in this situation, epoxy pre-polymer is considered as structopendant. The curing mechanisms of epoxy binders and the structures of cured epoxy with amines, amides and anhydride have been thoroughly studied and the systems of epoxy resins with different types of hardeners are used extensively in many

industrial applications **[Hakala et al. 2000]** and **[Ishii et al. 2000]** Curing agents are either catalytic or corrective. Catalytic curing agent functions as an initiator for epoxy resin homopolymerization, where the corrective curing agent acts as a comonomer in the polymerization reactions.

The curing agent can react with the epoxy and pendent hydroxyl groups on the resin backbone by way of either an anionic or cationic mechanism. Catalytic curing agents can be used for homopolymerization, as a supplemental curing agent with polyamines or polyamides, or as accelerators for an anhydride cured system catalytic cures are initiated by Lewis acids, e.g. boron trihalides, and Lewis bases, e.g. tertiary amines.

The reactivity of epoxy binders to be cured, and the properties of the end products, affect the choice of curing system. The type and concentration of curing agents may be able to control the length of cross-links (cross-link density), and consequently the mechanical properties of the cured epoxy resins. Mijovic et.al. **[Mijovic et.al 1981]** highlight the importance of cross-linking agent (hardener) concentration and consider that higher hardener concentrations led to more excessive intermolecular reactions at the expense of the intermolecular matrix. So it is important to select the best curing systems which include types of hardener and epoxy, concentration of hardener, type of catalyst and temperature of curing. In the present work triethyl amine Et_3N was used as catalyst with 1% based on the weight of epoxy resins for all cured systems for prepared epoxy resins and hardener based on resin acid derivatives. On the other hand 2-amino ethyl piprazine, AEP, is used as polyamine hardner for the present epoxy resins. For this reason, the

succeeding sections endeavor to add more detailed information concerning these subjects.

The curing exotherms of the prepared formulae were obtained by plotting the curing temperature as a function of time at different temperature ranged from 40°C to 60°C. Since the amount of heat evolved upon curing depends on the sample size, it was desirable to consider this parameter. For this reason, it was very important to use glass bottles of the same volume in all measurements to achieve the repeatability of the measurements and affording legitimate comparative study. The curing exotherms curves of the GDE and GTE cured with different weight ratios of AEP curing agents were represented in ***Figures (3.7-3.8).*** The maximum heat evolved, T_{max}, upon curing and time required for complete curing, t_{max}, obtained from these plots are included in ***Table (3.4-3.5).*** The S-shaped gelation curve, ***Figures (3.7&3.8)***, and the vitrification curve divide the time-temperature plot into four thermosetting-cur process: liquid, gelled rubber, un gelled glass and gelled. As curing proceeds, the viscosity of the system increases as result of increasing molecular weight, and the reaction becomes diffusion-controlled and eventually is quenched as the material vitrifies **[Enns et al. 1983]** after quenching, the yield can be increased by raising the temperature. In the present systems, $(Et)_3N$ acts as supplemental curing agents with polyamides and reacts with epoxide to produce zwitterions which initialed the reaction of epoxy with polyamines **[Ricciardi et al. 1983]**.

These ions initiate the exothermic precautions with polyamine and the temperature rises when the number of catalyst-epoxy zwitterions

intermediate is sufficient to make the rate of heat generation, due to reactions with active hydrogen of polyamines, larger than the heat dissipation. Consequently, the heat accumulation increases the reaction rate and the polymer molecular weight rises steadily throughout the reaction (liquid phase). The viscosity increases due to the increasing of polymer molecular weight and the length of the crosslinks (gelled rubber phase). This increase in viscosity causes a decrease in the rate of curing, as described in above kinetic investigation, because of the retardation of diffusion.

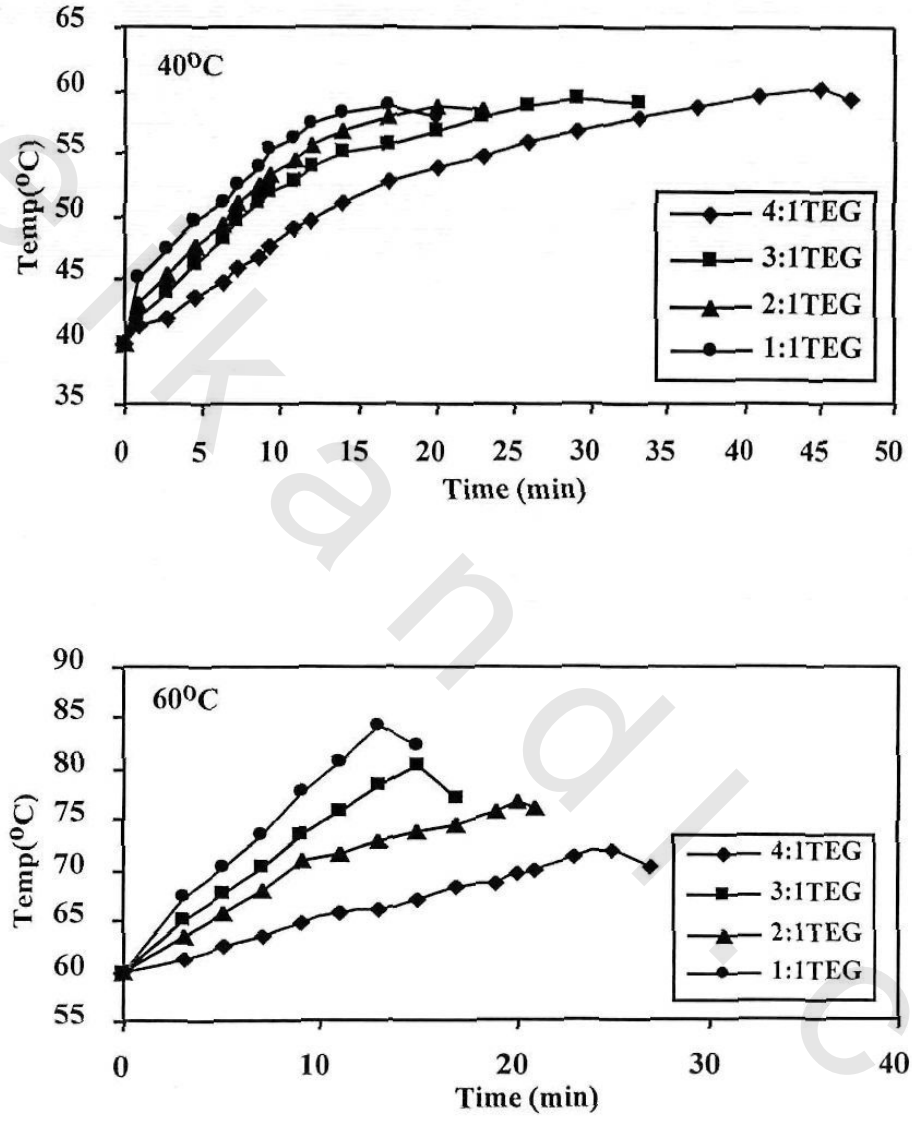


Figure (3.7): Curing Exotherm of GTE

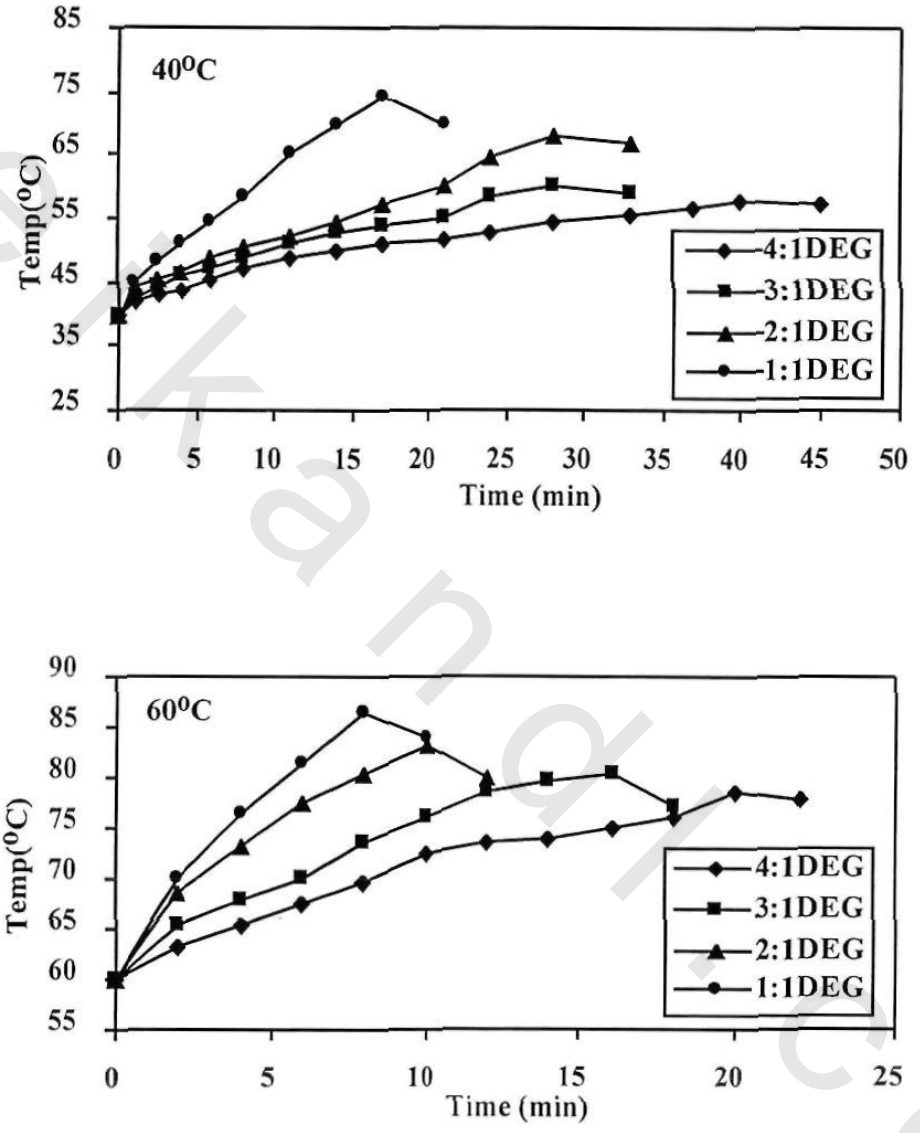


Figure (3.8): Curing Exotherm of GDE

Table (3.4): Curing parameters of GDE at Different Temperatures

Sample no.	GDE: HEP (wt: wt %)	Curing parameters at different temperatures			
		t^1_{max}	T^1_{max}	t^2_{max}	T^2_{max}
GDE1	4:1	40	57.7	20	78.7
GDE2	3:1	34	60.3	16	80.2
GDE3	2:1	23	67.8	10	83.2
GDE4	1:1	15	74.5	8	86.6

1: at temperature 40°C

2: at temperature 60°C

Table (3.5): Curing parameters of GTE at Different Temperatures

Sample no.	GTE: HEP (wt: wt %)	Curing parameters at different temperatures			
		t^1_{max}	T^1_{max}	t^2_{max}	T^2_{max}
GTE1	4:1	48	54.6	25	71.7
GTE2	3:1	39	57.6	20	76.8
GTE3	2:1	25	62.2	14	80.3
GTE4	1:1	16	70.0	12	84.2

1: at temperature 40°C

2: at temperature 60°C

The mobility of linear units that have not yet reacted is reduced not only by the increasing the viscosity of resin but also and primarily, by the incorporation of those units into the three-dimensional network; thus the diffusion of units towards the growing is inhibited to a greater extent than the diffusion towards crosslinking (ungelled glass).

Hence the reaction temperature continues to increase at slower rate. At $T_{max,}$ the rate of heat dissipation starts to become larger than the rate of heat generation and the temperature decreases. As the cross-linking is almost completed, the temperature decreases rapidly due to the normal cooling of the hot body in the absence of head generation (gelled glass state). The effect molecular weights of the prepared epoxy binders (determined by GPC techniques), structure of these binders and their epoxy functionality have been investigated. It was observed that the values of both T_{max} and t_{max}, which listed in ***Tables (3.4& 3.5)***, are related to the structure of epoxy binders. In this respect it was observed that the curing exotherms of GTE have greater t_{max} and lower T_{max} values than GDE when cured with AEP hardener at different temperatures. This can be related to the effect of molecular weight of the epoxide resin on the ease of curing process.

It is well known that the shorter epoxy having low molecular weight is cured more easily than longer epoxy having high molecular weight. In this respect, the molecular weight of GDE is 770 g/mol, while molecular weight of GTE is 1072 g/mol This can be related to the network formed in GTE would be very light, under some of remains hydroxyl groups of GTE may be buried in the microgel particles of epoxy and the further reaction of these groups with polyamine hardener requires their

diffusion into the core of microgels. This may lead to increases values of t_{max} and decreases T_{max} values for cured GTE with AEP. It was also observed that the increase of temperatures for curing of all prepared epoxy with polyamide hardeners,from 40 to 60℃ decreases t_{max} of curing. This can be attributed to the increment of temperature strongly influences the ultimate cross-link density and increases molecular mobility resulting in higher cross-link density.

3.5.2 Curing Exotherms of UP with VE

The unsaturated polyesters are long chain polymers containing a number of reactive double bonds. In order to form cross-linked networks, they are dissolved in a free-radical polymerizable monomer such as styrene. This polymerizable monomer, which also contains reactive double bonds (C=C), acts as a curing agent by bridging adjacent polyester molecules at their unsaturation positions. The content of styrene in the final resin is important to ensure good process ability. Moreover, if its content is very high or very low, we can have high shrinkage on curing or a tendency not to cure fully, respectively.

Vaidya and Nadkarni **[Vaidya and Nadkarni 1987]** proposed an effective range for the styrene percentage in a polyester resin from 30 to 40 wt. %. In this investigation, a 40 wt. % for the blank resin was used, in accordance also to other literature sources **[Suh et al. 2000]**. In this respect, styrene has been the chief monomer used as solvent. The functions of the monomer in unsaturated polyesters are two-fold:

- To act as a solvent for the unsaturated polyesters, which are extremely high in viscosity and frequently solid;
- To copolymerize with the unsaturation in the linear polyester chain to yield a cured thermoset plastic.

Styrene monomer fulfills these requirements admirably. It is a good solvent with high boiling point (146°C) for most polyester. It co-reacts very rapidly with fumaric acid to give high performance resins **[Smith et al. 1958]**. Furthermore, the price of styrene is among the lowest of the usable monomers. It is only natural; therefore, that styrene has dominated other monomers for use in this rapidly growing field. The curing behavior of unsaturated polyester resins has been extensively studied in literature **[Lucas et al. 1993], [Lee et al. 1997], [Eisenberg et al. 1997], [Delahaye et al. 1998], [Vilas et al. 2001], [Lu et al. 2001]** and **[Simitzis et al. 2002]**. Our model is based on the following assumptions:

- Homopolymerization of unsaturated polyester is negligible.
- Homopolymerization of styrene and co-polymerization of styrene monomer and polyester can be expressed by a single average rate constant.
- No monomer reacts until the number of all initiator radicals created is equal to the effective number of inhibitor molecules initially present
- Free radical termination is significantly slower than that in the polymerization of low molecular weight species.

Generally, the free radical polymerization consists of initiation, inhibition, propagation, and termination steps. The termination step may be neglected at the later stage of polymerization due to the formation of highly cross-linked microgels **[Suspene et al. 1991]**. To prevent premature gelation and to inhibit the spontaneous polymerization of the resin, hydroquinone was added as an inhibitor **[Aslan et al. 1997].**

Vinyl ester networks are an important commercial class of thermosets for polymer matrix composites due to their excellent mechanical and

adhesive properties. The matrix resins are comprised of methacrylate-terminated oligomers with styrene added as a reactive diluent. The methacrylate and styrene double bonds are copolymerized by free radical reactions to yield cross-linked networks. The processability (i.e., low viscosities) of the vinyl ester-styrene mixtures at room temperature, coupled with tailor able free radical cure schedules, make them prime candidates for large composite structures for transportation, infrastructure and marine applications. Vinyl ester resins (VERs) were developed from unsaturated polyester resins and typically consist of a bisphenol-A based dimethacrylate oligomer and styrene **[O'Hearn 1988]**. The concentration of reactive monomer diluent is an important consideration in the formulation of VERs for glass reinforced composites. Typical bisphenol-A based dimethacrylate oligomers are very viscous, thus low concentrations of diluent hinders the wetting of the reinforcing fibers however very high concentrations of diluent may result in inferior mechanical, thermal or chemical properties of the cured matrix.

The formulation of a VER is thus a trade-off between its viscosity and the properties of the material when cured. A third, often overlooked, consideration is the effect of diluent concentration on the kinetics of polymerization of the resin. For thermally cured VER systems, generally recognized **[Li L et al. 1999]** and **[Scott et al. 2002]** that lower concentration of styrene increases the rate of cure. As suggested by **[Scott et al. 2002]**, this is perhaps due to a decrease in the termination rate constant with increased the concentration of cross-linking species. (i.e. the dimethacrylate) that raises the polymerization rate **[Batch et al. 1992]** or it may be caused by an increase in the propagation rate due to

the replacement of the less reactive styryl radicals by the more reactive methacryloyl radicals, as claimed by Rey et al. **[Rey et al. 2000]**

Addition of bisphenol-A to the structure improves the rigidity of the polymer backbone and leads to improved mechanical properties **[Joseph et al. 1984]** and **[Clausen et al. 1987]**. In addition, bisphenol-A can be used as a co-reactant to decrease viscosity and increase ductility of the cured resins. The pendant hydroxyl groups on the backbone can provide adhesion and a reactive site for further modification. For example, they can be reacted with anhydrides to improve the chemical resistance of the product.

In the present work, we shall describe the modification of an unsaturated polyester resin by the prepared vinyl ester resins, GTA and GTM, in order to influence their curing behavior and mechanical properties. The incorporation of a vinyl ester resin into the unsaturated polyester should improve the flexibility of the cured material. In this respect, TEG was selected to modify the chemical structure of the vinyl ester resin, so as to prepare a more flexible resin. Blending a vinyl ester with an unsaturated polyester resin could lower the cure time, which would be an advantage in polymer concrete and coating applications.

The curing exotherms of the prepared formulae based on CUP, RUP and vinyl ester resins diluted with styrene were obtained by plotting the curing temperature as a function of time. Temperature / time plots of curing process for the synthesized VE (GTA and GTM) resins, UP dissolved in styrene monomer (60% both resins /40% styrene) cured by 2 wt% initiator in presence of 0.2 wt% activator are illustrated in ***Figures (3.9 to 3.12).*** In this respect, MEKP and CO were used as

initiator and activator, respectively. They are generally employed for cross-linking of UP. The formulae are based on UP and styrene in presence of 0%, 5%, 10%, 15% and 20% from VE (based on the total weight of UP and styrene). Styrene is a reactive diluent, and VE serves as cross-linking agent. The cure of this resin proceeds via free radical bulk copolymerization. The curing behaviors of VE (60%) and styrene (40%) are studied at different temperatures in presence of the same initiator and activator.

As it was expected, an increase in the initial initiator concentration led to higher reaction rates accompanied by shorter induction times, higher maximum polymerization rate and completion of the reaction at shorter times. According to the previous results **[Abdel-Azim 1996]**, a weight fraction of MEKP 4% may be adequate in industrial use, and then the curing must be completed faster.

However, in laboratory scale experiments the low weight fraction of 2% is preferable in order to, have enough time to process the material and produce films that are necessary for preparing the specimens that will be used in the mechanical properties testing. Previous studies of curing behavior of vinyl-divinyl systems showed that the initial curing for such a system begins with an induction period, due to the presence of inhibitors and cage effects, followed by the formation of micro-gels **[Dusek et al. 1979 and 1980]**.

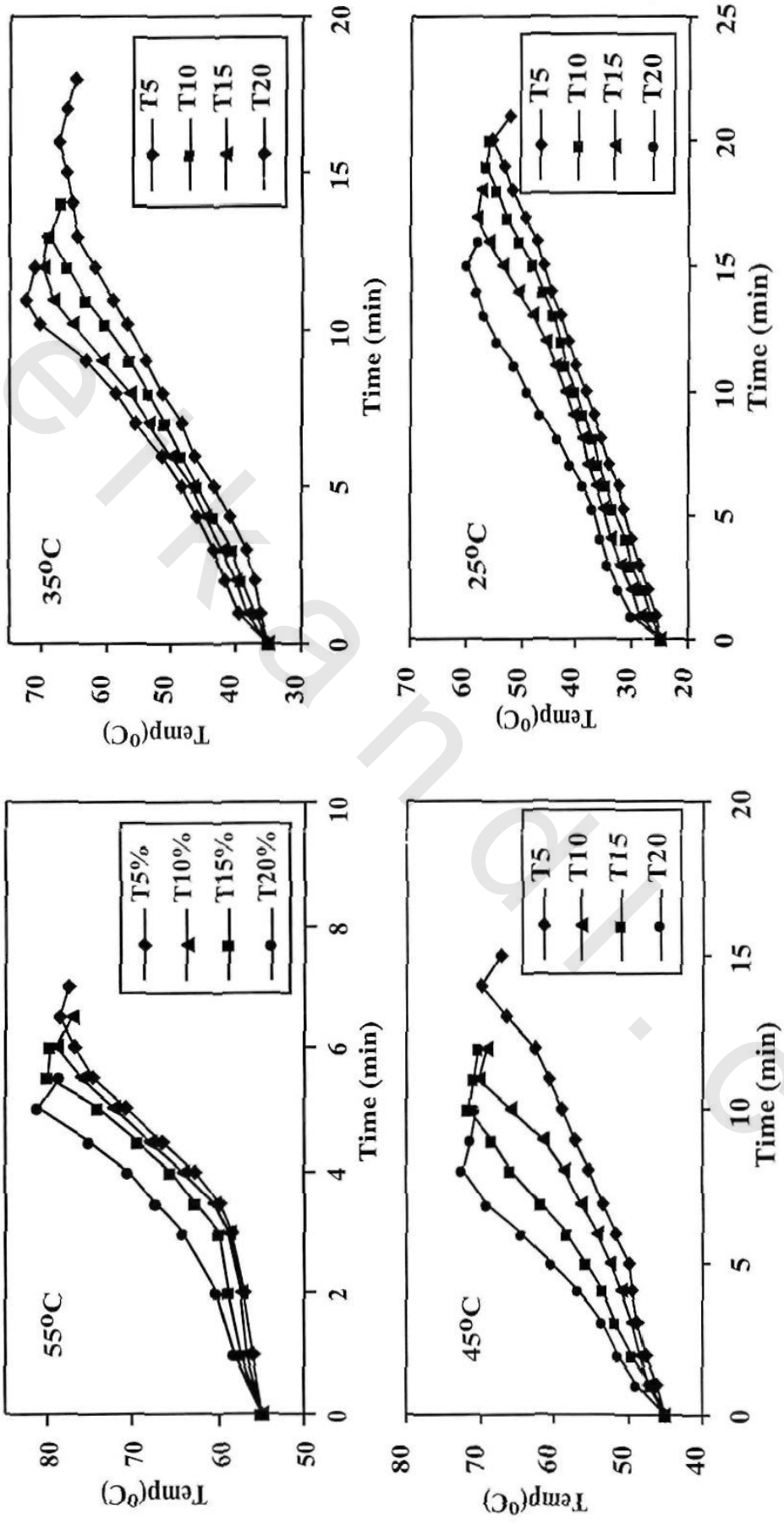


Figure (3.9): Curing Exotherm of UP1 with GTA

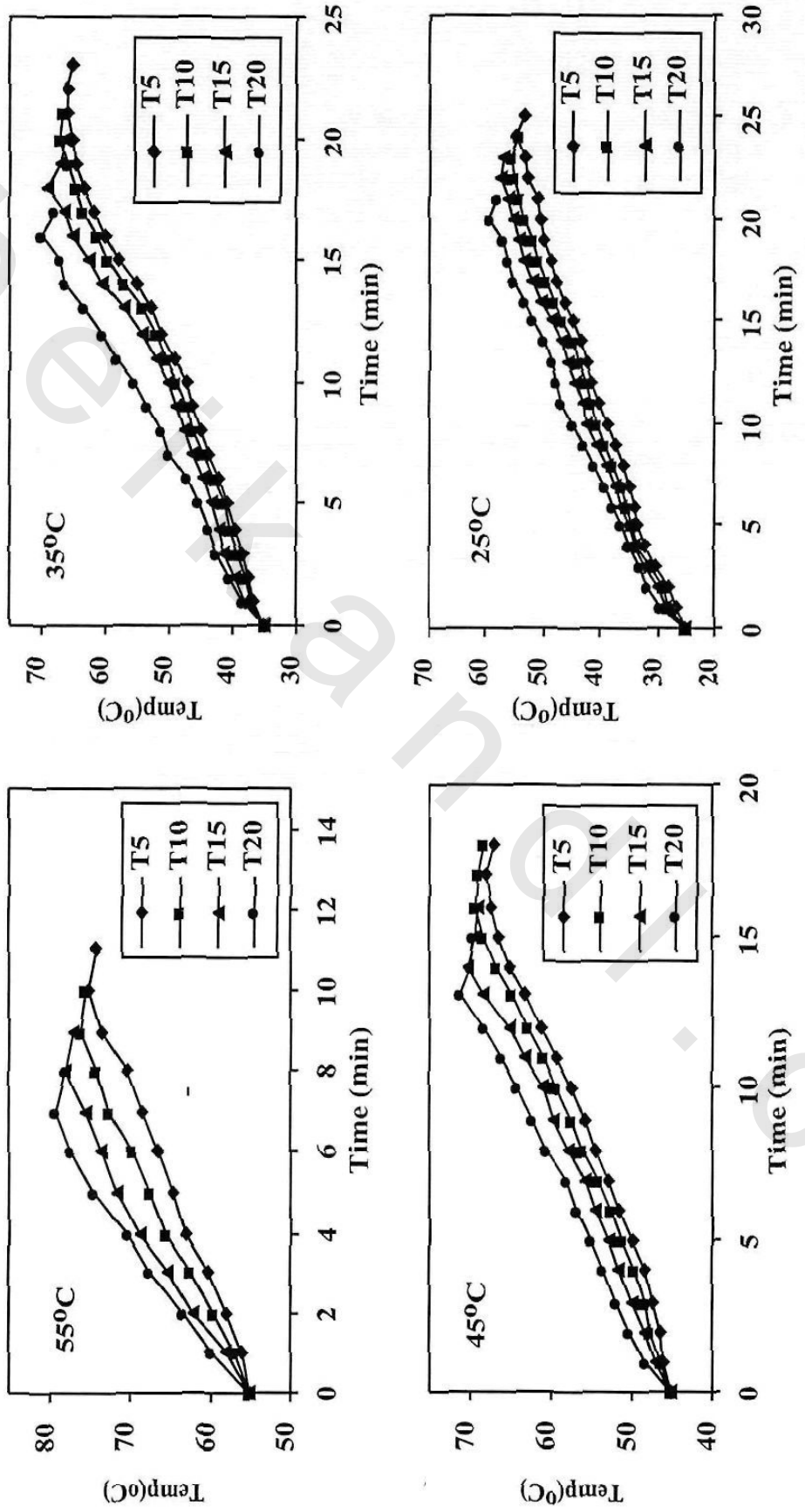


Figure (3.10): Curing Exotherm of UP1 with GTM

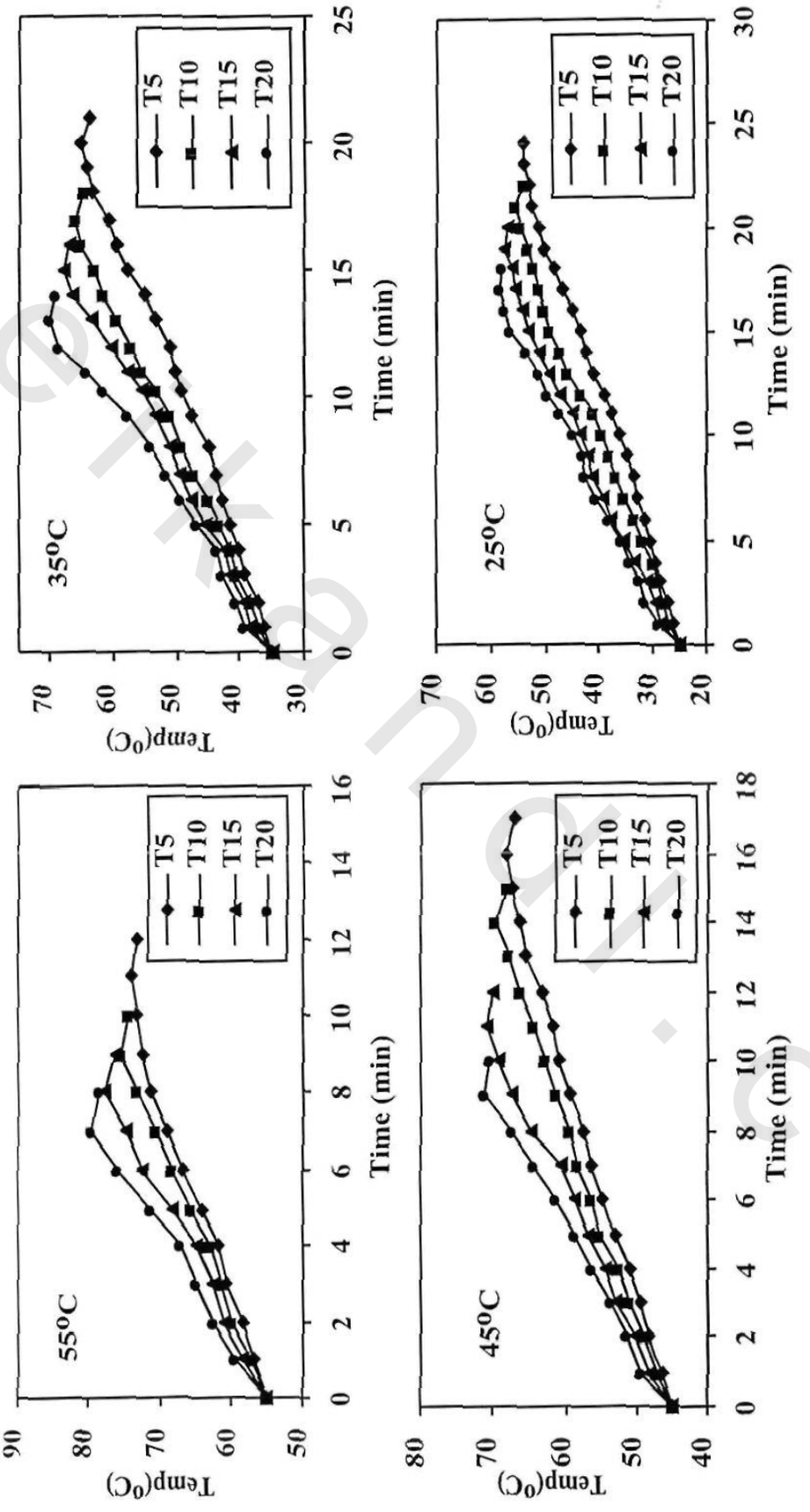


Figure (3.11): Curing Exotherm of UP2 with GTA

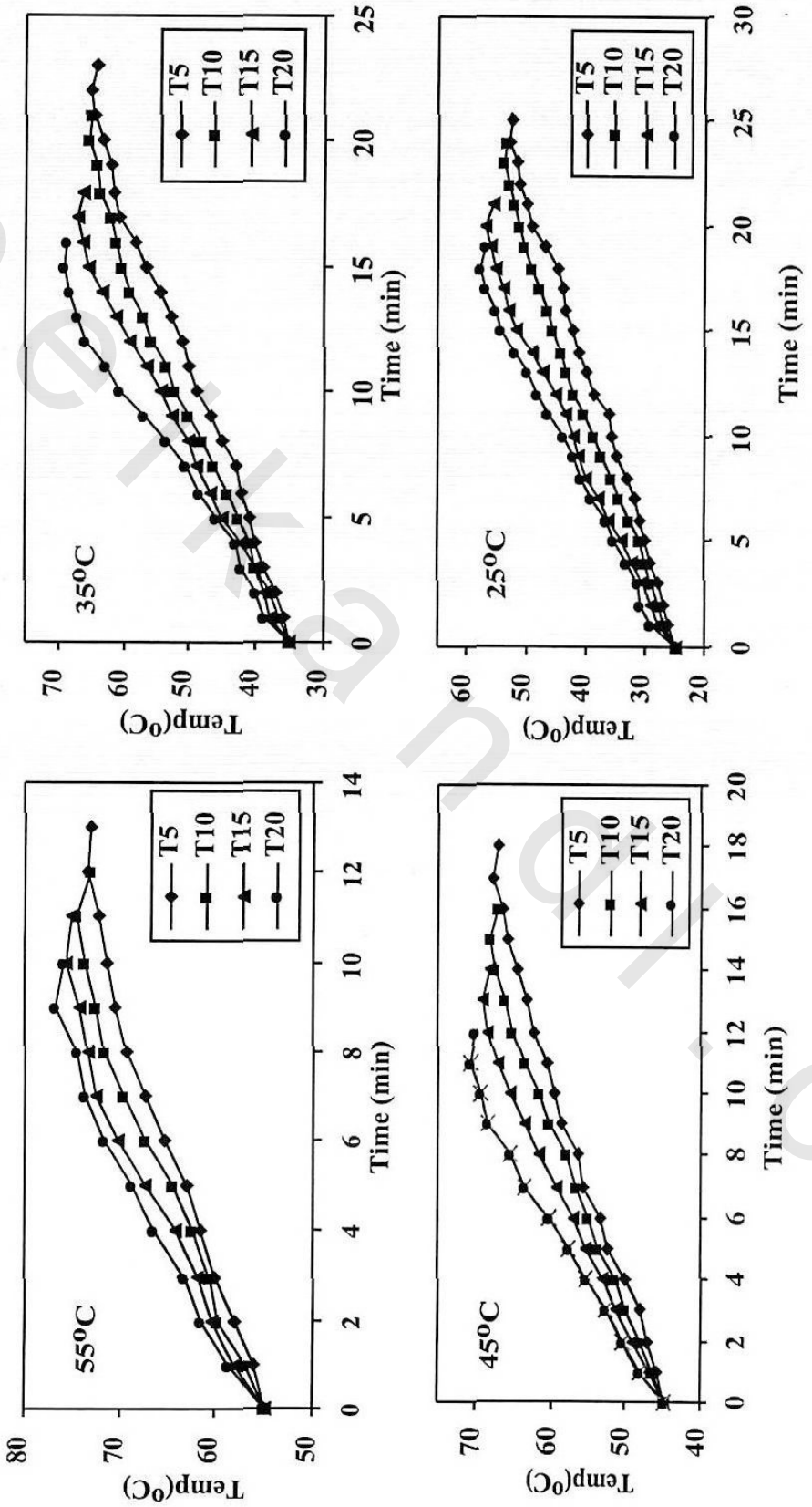


Figure (3.12): Curing Exotherm of UP2 with GTM

Micro-gels have been defined as domains of high cross-link density dispersed in a pool of un-reacted monomers. The cross-link of such micro-gels does not contribute to the global network structure until they are incorporated into the gel phase. Little information is available on which pertains to the effect of VE on the curing rate, exotherm peak temperature and mechanical properties of the cured resins. For this reason, the succeeding sections endeavor to add more detailed information concerning with these subjects. It is also important to know exact chemical structure and molecular weight of UP. The average molecular weight of UP1 and UP2 and styrene content of them were determined using ^{1}HNMR spectroscopy as mentioned before. The maximum heat evolved, T_{max}, upon curing and time required for complete curing, t_{max}, obtained from these plots are included in ***Table (3.6)*** to ***Table (3.9)***. The following section concerns with, the possibility of modifying the curing behavior of UP resin by changing the amounts and types of the prepared VE (GTA and GTM), at constant concentrations of both MEKP and CO that will be 2 wt% and 0.2 wt%, respectively. The effect of curing temperature on the curing exotherms was also discussed. In this respect, the curing exotherms were determined at 25°C, 35°C, 45°C and 55°C. The S-shaped gelation curve, ***Figure (3.9-3.12)***, was also observed as discussed with GTE and GDE epoxy resins. While, in the present system CO and MEKP are produced radicals. These radicals initiate the exothermic precautions with UP and the temperature rises when the number of radical is sufficient to make the rate of heat generation larger than the heat dissipation. Consequently, the heat accumulation increases the reaction rate and the polymer molecular weight rises steadily throughout the reaction *(liquid phase)*. The viscosity of reaction increases due to the increasing polymer

molecular weight and the length of the cross-links *(gelled rubber phase)*. This increase in viscosity causes a decrease in the rate of curing, as described in above kinetic investigation, because of the retardation of diffusion. The mobility of linear units, that have not yet reacted, is reduced not only by the increasing the viscosity of resin but also and primarily, by the incorporation of those units into three-dimensional network.

Thus, the diffusion of units towards the growing is inhibited to a greater extent than the diffusion towards cross-linking *(ungelled glass)*. Hence, the reaction temperature continues to increase at slow rate. At T_{max} the rate of heat dissipation starts to become larger than the rate of heat generation and the temperature decreases. As the cross-linking is completed, the temperature decreases rapidly due to the normal cooling of the hot body in the absence of heat generation *(gelled glass state)*.

Table (3.6): Curing Parameters of UP1 with GTA at Different Temperatures

GTA (wt %)	Curing parameters at different temperatures							
	t^1_{max}	T^1_{max}	t^2_{max}	T^2_{max}	t^3_{max}	T^3_{max}	t^4_{max}	T^4_{max}
0	25	52.2	23	64.5	18	67.2	12	72.5
5	20	55.4	16	67.5	14	69.7	6.5	78.5
10	19	56.3	13	68.5	11	70.1	6	79
15	17	58.0	12	70	10	71.5	5.5	80
20	15	59.8	11	72.3	8	72.4	5	81
GTA55*	27	52	22	58	18	67.1	12	74

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

*:55%GTA, 45% styrene

Table (3.7): Curing Parameters of UP1 with GTM at Different Temperatures

GTM (wt %)	Curing parameters at different temperatures							
	t^1_{max}	T^1_{max}	t^2_{max}	T^2_{max}	t^3_{max}	T^3_{max}	t^4_{max}	T^4_{max}
0	25	52.2	23	64.5	18	67.2	12	72.5
5	24	53.4	22	66	17	68	10	75
10	23	55.4	20	67.1	16	69.2	9	76.2
15	22	57.2	18	69.2	14	70.1	8	78.1
20	20	59.3	16	70	13	71.0	7	79.2
GTM55*	29	60	25	66	21	72	14	78

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

*:55%GTM, 45% styrene

Table (3.8): Curing Parameters of UP2 with GTA at Different Temperatures

GTA (wt %)	Curing parameters at different temperatures							
	t^1_{max}	T^1_{max}	T^2_{max}	T^2_{max}	t^3_{max}	T^3_{max}	t^4_{max}	T^4_{max}
0	27	50.4	25	60.5	21	63.6	16	68.7
5	23	59.3	20	65.1	16	68.3	11	74.1
10	21	55.5	17	66.3	14	69.6	9	75.6
15	19	57.7	15	68.1	11	70.8	8	77.8
20	17	58.5	13	70.0	9	71.3	7	79.6
GTA55*	27	52	22	58	18	67.1	12	74

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

*:55%GTA, 45% styrene

Table (3.9): Curing Parameters of UP2 with GTM at Different Temperatures

GTM (wt %)	Curing parameters at different temperatures							
	t^1_{max}	T^1_{max}	t^2_{max}	T^2_{max}	t^3_{max}	T^3_{max}	t^4_{max}	T^4_{max}
0	27	50.4	25	60.5	21	63.6	16	68.7
5	24	53.3	22	64.7	17	67.7	12	73.5
10	23	54.2	20	65.3	15	68.1	11	74.6
15	20	57.0	17	67.0	13	69.0	10	75.8
20	18	58.0	15	69.1	11	70.6	9	76.8
GTM55*	29	60	25	66	21	72	14	78

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

*:55%GTM, 45% styrene

The proposed mechanism for curing of UP with styrene is based on the chain reaction mechanism. It may be explained by the capability of the accelerator to decompose the initiator molecules into free radicals. These free radicals initiate the exothermic copolymerization reaction. The temperature of the reaction mixture rises only when the number of initiator free radicals is sufficient to make the rate of the heat generation, due to copolymerization, larger than the heat dissipation, consequently, the heat accumulation increases the reaction rate and the polymer molecular weight rises steadily throughout the reaction *(3.2)*.

$$\text{R-OOH} + CO^{2+} \longrightarrow RO^{\cdot} + OH + CO^{3+}$$
$$\text{R-OOH} + C \longrightarrow \text{R-OO}^{\cdot} + H^{+} + CO^{2+} \qquad (3.2)$$

In the final stage of curing, the viscosity of the reaction mixture increases due to the increasing in polymer molecular weight and increasing the length of the cross-links. This increase in viscosity causes a decrease in the rate of polymerization, as shown in the above kinetic investigation, because of the retardation of diffusion. The mobility of UP units that have not yet reacted is reduced not only by the increasing viscosity of the resin but also, and primarily, by the incorporation of these units into three-dimensional network. Thus, the diffusion of unsaturated acid units towards the growing radical chains is inhibited largely than the diffusion of the remaining free styrene molecules towards there radials. The reaction of the unsaturated acid units is therefore, expected to drop rapidly, and the curing proceeds primarily through the reaction styrene units; hence, the temperature continues to increase at a slower rate. At T_{max}, the rate of heat dissipation starts to

become larger than the rate of heat generation and the temperature decreases slowly. As the copolymerization is almost completed, the temperature decreases rapidly due to the normal cooling of the hot body in the absence of heat generation.

It is expected that the curing time should be inversely related to the reaction rate because the gel point corresponds to the first formation of an infinite network, and this is usually occurs at a fixed conversion for the particular system. In order to study the effect of the resin structure on the curing behavior, as mentioned before, variation in type and amount of individual components allows a great variety in the design of the resin formula. We can conclude that the structure of UP1 based on phthalic acid shows the high temperature T_{max} and low curing time t_{max} than UP2 based on glycolyzed PET may be that can be attributed low double bond content, polymerizable double bond, for UP2 due to higher molecular weight of the glycolyzed PET oligomers.

To study the influence of VE content on the curing time and reaction rate of Styrene, UP and VE system, four different resin solutions for each VE were prepared. The weight percentage of VE resin in these solutions was ranging from 5% to 20% respect to UP. The data listed in ***Tables (3.6-3.9)*** indicate that, in all cases, the curing time slightly reduces with increasing VE content. This may be attributed to increasing numbers of double bonds and hence this facilitates the diffusion of styrene molecules towards the un-reacted double bonds embedded in the three dimensional network. On the other hand, the type of VE affects the reaction and curing rate. This was indicated from the data listed in ***Tables (3.6-3.9)***, which indicate that GTA have lower t_{max} and T_{max}

values than GTM. This can be attributed to ability of styrene to react with divinyl monomers based on methacrylates than that based on acrylates. It was noted that the curing time values, t_{max}, are higher for GTA than GTM that reacted with styrene monomer. This behavior can be referred to increasing of the reaction viscosity at beginning of reaction which lead to decrease the diffusion of styrene towards VE based on GTM and will increase the curing reaction time.

3.5.2.1 Effect of cross-linking temperature

The nature of the formed networks based on vinyl ester, styrene and UP is difficult to understand and could be influenced by the reaction conditions such as temperature of reaction. The effect of the cross-linking temperature on the curing was investigated. In radical polymerization induced by thermal decomposition of an initiator, generally, as the polymerization temperature increases, the dissociation rate of the initiator and the rates of initiation, propagation, and termination are enhanced **[Liska 1973]**. All these factors except the rate of termination increase the rate of polymerization; however, a further increment in the polymerization temperature reduces the molecular weight of the polymer, due to an increase of the rate of termination and chain transfer, and increases the relative amount of the polymer chain end. Generally, it is well known that low temperature peroxide is chosen to rapidly initiate the polymerization, while higher temperature peroxide decomposes slowly initially, but becomes highly activated due to the reaction exotherm to propel the reaction towards completion. In this respect, temperature of reaction of the proposed system was varied from 25 to 55°C. The data of curing at these temperatures were listed in ***Tables (3.6-3.9)***. It was observed that as curing temperature increases

the values of t_{max} decreases. This can be attributed to the increasing of reaction temperature lead to decrease the viscosity of reactants and consequently affect the diffusion and reactivity ratios between reactants. In this respect, curing kinetics of styrene VE resins was studied at different temperatures. Ziaee et al. **[Ziaee et al. 1999]** reported that the reactivity ratios of VE to styrene affected by curing temperature. ***Figures (3.9-3.12)*** show different behaviors as the reaction temperature increase. For low curing temperatures at 25 and 35°C, the rate is initially low but it passes through a broad maximum as the reaction proceeds. The reaction then slows and finally ceases before all of the monomer has been consumed.

The cessation polymerization prior to total monomer consumption has been widely observed in the cure of glass forming networks **[Horie et al. 1970], [Cook 1992] and [Verchere et al. 1990]** and is due to diffusion control of the curing process when the glass transition temperature (T_g) approaches the curing temperature (T_{cure}). As indicated in ***Figures (3.9-3.12)*** when the curing temperature is between 45 and 55°C, the final degree of cure is increased because the material can polymerise further before the T_g rises above T_{cure}. As indicated in ***Figures (3.9-3.12)***, the curves were too flat when the curing temperatures were 45 and 55°C. This indicates that the final degree of curing was high **[Cook 1992]**.

3.5.2.2 Effect of UP and VE chemical structures

There is now great scientific and technological interest in the structure–property relationships in the field of thermosets. However, several problems were related with the cure reaction and were not completely elucidated, which justifies the relative abundance of literature on all aspects of the cure and production of these resins. Unsaturated polyesters become insoluble and infusible by cross-linking with a monomer, usually styrene (ST). The commercial resins contain about 45% by mass of styrene. The miscibility of the resins and the styrene depends on the resin composition. The morphological state of a polymeric material may be highly affected by the interaction between the polymerization kinetics and the thermodynamics and kinetics of phase separation. This is especially relevant to the preparation of high-impact polystyrene from a styrene solution of an unsaturated rubber.

An unsaturated polyester resin is analogous except that it consists of a relatively low-molecular-weight polymer dissolved in styrene. In this case, a distinct phase has not been observed but the development of a microstructure consisting of regions with a wide variation in the cross-linking density is generally becoming accepted **[Jacobs et al. 1993]**. However, some researchers accept that the copolymerisation of unsaturated polyester with styrene, UP/ST, results in the formation of a heterogeneous structure through strong intramolecular reactions and phase separation **[Hsu et al. 1993]**. Abdel-Azim et al. evaluated the effect of the resin microstructure on its cure behaviour concluding that the maximum cure temperature is related to the molecular weight of the glycol segment incorporated in the resin **[Abdel-Azim et al. 1994]**. The

influence of the molecular weight and the chain termination groups has been investigated. In general, an increase in molecular weight decreases the miscibility. Chain termination of UP resins consists in hydroxyl and carboxyl groups whose polarity has an unfavorable effect on the UP/ST miscibility. Hydroxyl and carboxyl groups are always present. Consequently, the resin miscibility can only be changed by controlling the copolymer composition **[Buffa et al. 1994]**. Kinetic models have been reported for the cure of UP/ST and mechanisms have been proposed for the microstructure formation **[Hsu et al. 1991]**. The present formulations are based on using two different types of UP and VE in presence of styrene as cross-linker and in the same time it used as solvent for UP. The present study used two types of UP having two different chemical structures.

The prepared UP is based on R-PET which includes long chain length having both aromatic moieties and aliphatic moieties in the glycolyzed oligomers. Commercial UP contains of short chain length glycol having aliphatic moieties, which includes propylene glycol. On the other hand, the length of glycol moieties affects the molecular weight of UP and number of polymerizable double bond of maleic anhydride group in UP structure. In the present systems, the length of PG in commercial UP is shorter than that used in the prepared UP2. Accordingly, the number of polymerizable double bond in UP1 is higher than UP2. So the curing time of UP1 should be lower than of UP2.

3.5.2.3 Gel-time of UP/VE based on R-PET

Three-dimensional, covalently bonded arrays of atoms, organic or inorganic, rank among the largest molecules known. Their molecular

weight is given by the macroscopic size of the object; for instance, a car tire made of vulcanized rubber or a layer of chemically dried (cross-linked) protective coating can be considered a single giant molecule. Such networks are usually called macro-networks. On the other hand, micro-networks can be several nanometers to several micrometers small (e.g. cross-linked micro-emulsions or microgels). Functional micro-networks (micro-networks carrying functional groups) can serve as precursors for macro-networks. Polymer networks are formed from functional precursors by reactions between their functional groups resulting in bond formation. Branched and cross-linked structures are formed by this process. First, molecular weights and polydispersity of branched molecules increase; the largest molecule progressively becomes larger and larger than any other one in the system until the critical state, the *gel point*, is reached when the largest molecule becomes "infinite", i.e. commensurable with the macroscopic dimensions of the system. At this point, an infinite structure (molecule) - ***gel***- is formed for the first time. Beyond this point, if the degree of conversion and connectivity of the system further increase, the gel fraction increases at the expense of still finite (soluble) molecules called ***"sol"***.

The sol molecules become gradually bound to the gel and, eventually, under certain conditions, all precursor molecules can be parts of the -gel- the network. This happens in the case when formation of finite molecules carrying no functional groups can be excluded (e.g. systems with monofunctional components, or off-stoichiometric alternate systems). Along with a decrease in the sol fraction, the network structure becomes "denser", containing increasing amounts of cross-

links and strands between them called ***elastically active network chains (EANC)***. The concentration of elastically active network chains determines equilibrium mechanical properties of networks in the rubbery state. Curing of UP and VE resins is difficult due to the change in physical properties during the cure process **[Hong et al. 1991]** and it has been characterized, as for every thermosetting system, by the gelation and vitrification processes. The gel time is an important characteristic of the cure process of these materials as it conditions their processing. In this work, the gelation process of UP and VER will be investigated from rheological behavior of these resins. The investigation of rheological behavior of these resins, especially the dependence on the reactive diluent, concentration and temperatures becomes a pre-requisite for gaining an insight of the structure-property relationship. The exothermic curing reaction of such resins may occur between the vinylic double bonds of the resin or with that of a reactive diluent in the presence of free radical initiators, or by irradiation with UV, electron beams etc. It becomes essential to understand the cure kinetics for controlling the rate of heat generation and temperature variation during processing of these materials. The cure kinetics of VE based on bis-phenol-A epoxy in the presence of styrene **[Han et al. 1984]**, methylstyrene **[Bhatnagar et al. 1989]** and acrylates **[Kant et al. 1992]** have been investigated. In this work, the rheological behavior as well as the cure and decomposition kinetics of VER and UP based on R-PET, in the presence of styrene as reactive diluent will be investigated.

In this respect, the cross-linking reaction was characterized by change of viscosity as function of time at constant temperature and shear rate. Using the initial viscosity of the sample and variation of the viscosity

with the time, the critical value for the viscosity (ηc) and time (tc) corresponding to the gel point *(pot-life)* was calculated **[Lyman 1966]**. The apparent activation energy for the curing process can be calculated from the slope of the lines using the logarithmic graph ln tc versus 1/T (K).

The relation between viscosity of UP/VE mixtures and time is characterized in the first stage by a constant mixture viscosity with increasing reaction times. In the second stage, a sharp increase in mixture viscosity was observed. The critical values evaluated for the viscosity and the time at gel point for the cured UP and VE resins were obtained according to the Liska method **[Lyman 1966]** and are listed in ***Tables (3.10)*** to ***(3.13)***. The gel time values agreed with the results reported on curing exotherms. The energy of activation for viscous flow at constant shear stress (Er) was calculated using the Arrhenius equation:

$$\eta_c = A\, e^{Er/R} \qquad (3.3)$$

where A is a constant characteristic of the polymer at a shear stress or shear rate, Er is the activation energy for the flow, R is the gas constant, ηc is the viscosity at constant shear stress or shear rate and T is the temperature in degrees Kelvin. Er was calculated from the slop of the relations between log ηc (critical viscosity) and reciprocal of temperature using the Arrhenius equation.

The values of activation energies were listed in ***Tables (3.10-3.13)***. These values are comparable with the data in literature

[De la Caba et al. 1996]. Careful inspection of data listed in ***Tables (3.10-3.13)*** indicates that the viscosity of UP/ VE blends decreased with increasing VE content. This indicates that the prepared VE resins are compatible with two types of UP. This will reflects on the ease of reaction between VE and UP. It was noted that the results of gel times agree with the results reported on curing exotherms. This shows that, two methods used to investigate the curing and gel times are useful to study the kinitic of crosslinking of resins. On comparing the reaction rate characteristics between the different resins UP1 and UP2, it can be noticed that UP2 have lower Ea values than that resins based on UP1. Accordingly, a high reaction rate has been observed with UP2 compared to blank and UP1. The greater reactivity of the UP2 can be attributed to a reduced steric hindrance of the reactive double bonds due to the longer chain of the repeated structural unit. UP1 with a slightly higher average chain length compared to UP2 exhibits a slightly slower reaction rate.

Table (3.10): Variation of Critical Time and Critical Viscosity in Temperature (25-55°c) For Cured UP1 with GTA

Mixing ratio GTA (%)	Temperature (°C)								Activation Energy (K.J/mol)	
	t^1_C (min)	η^1_C (CP)	t^2_C (min)	η^2_C (CP)	t^3_C (min)	η^3_C (CP)	t^4_C (min)	η^4_C (CP)	Er	Ea
0	23	16554	21	9122	17	4238	11	1258	82	23.3
5	18	13172	15	7549	12	3067	5	1848	65.5	39.1
10	17	8674	12	6566	10	2634	4	1691	56	43.4
15	15	6840	10	5034	8	2320	3.5	1422	52.9	44.2
20	13	5281	9	3735	7	2005	2	1258	47.5	56.4

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

Table (3.11): Variation of Critical Time and Critical Viscosity in Temperature (25-55°c) For Cured UP1 with GTM

Mixing ratio GTM (%)	Temperature (°C)								Activation Energy (K.J/mol)	
	t^1_C (min)	η^1_C (CP)	t^2_C (min)	η^2_C (CP)	t^3_C (min)	η^3_C (CP)	t^4_C (min)	η^4_C (CP)	Er	Ea
0	23	16554	21	9122	17	4238	11	1258	82	23.3
5	22	9319	20	6095	16	2359	9	1376	64.4	28
10	21	6960	18	4522	14	1730	8	1219	59.5	30.2
15	20	5068	15	3830	13	1308	7	998.4	55.3	31.7
20	18	4460	14	3539	11	1416	6	825.7	57.5	34

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

Table (3.12): Variation of Critical Time and Critical Viscosity in Temperature (25-55°c) For Cured UP2 with GTA

Mixing ratio GTA (%)	Temperature (°C)								Activation Energy (K.J/mol)	
	t^1_C (min)	η^1_C (CP)	t^2_C (min)	η^2_C (CP)	t^3_C (min)	η^3_C (CP)	t^4_C (min)	η^4_C (CP)	Er	Ea
0	25	5348	23	1966	19	943.7	15	668.4	67.1	16.4
5	21	2713	18	1730	14	825.7	10	707.8	46	23.7
10	20	2399	16	1376	11	708	8	589.8	46.9	30
15	18	2290	14	1220	9	680	7	503.6	49.3	31.5
20	14	2127	11	1181	6	551	5	432.5	53.3	35.6

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

Table (3.13): Variation of Critical Time and Critical Viscosity in Temperature (25-55°c) For Cured UP2 with GTM

Mixing ratio GTM (%)	Temperature (°C)								Activation Energy (K.J/mol)	
	t^1_C (min)	η^1_C (CP)	t^2_C (min)	η^2_C (CP)	t^3_C (min)	η^3_C (CP)	t^4_C (min)	η^4_C (CP)	Er	Ea
0	25	5348	23	1966	19	943.7	15	668.4	67.1	16.4
5	23	2613	21	1691	15	800	11	629.1	48.4	24.4
10	21	2281	19	1258	13	629	10	511.2	50	25.1
15	18	2120	16	1180	12	590	9	471.8	50	22.6
20	10	1923	13	1100	9	500	7	390.7	53.8	13.8

1: at temperature 25° C 2: at temperature 35°C

3: at temperature 45°C 4: at temperature 55°C

3.6. EVALUATION OF CURED RESINS for COATING and CONSTRUCTION APPLICATIONS

A large majority of organic coating films in the end-use state exist in the form of a three-dimensional (3D) polymer network. Classifying polymer networks according to their end-use properties, the main representatives of cross-linked polymers include vulcanized rubbers, cross-linked thermosetting materials, adhesives, polymeric sorbents, electric and electronics materials, soft gels, etc. Special features of polymer networks in comparison with uncross-linked polymers include their dimensional stability, increased thermal, physical and chemical stability and ability to store information about their shape and formation history when the gel point is surpassed.

Epoxy resins and polyester resins have firmly established themselves as important matrix materials in the field of reinforced plastics and coatings, although phenol formaldehyde resins are preferred when specific fire and smoke resistance qualities are required. Epoxy vinyl ester resins are one of the most widely used thermoset resins in polymeric composite due to their excellent resistance to a wide range of chemicals and to their outstanding combination of thermal and mechanical properties. These very positive properties are the result of their molecular structure. The secondary hydroxyl groups present on the backbone of the resin are responsible for producing composites with very good mechanical performance, **[Liu et al. 1994], [Ramis et al. 1997], [Saalbrink et al. 1998], [Kok et al. 1999]** and **[Mouritz et al. 1999]**. In this work, the mechanical properties of cured resins based on epoxy vinyl ester resin and UP were evaluated. It is well known that VE resins are the addition products of an epoxy resin and an unsaturated

carboxylic acid **[Clayton et al. 1965]** and **[Takeyama et al. 1971]**. The esterification produces a multifunctional VER depending upon the number of available epoxy groups in the main chain. Therefore, VER yield highly cross-linked rigid structures having high strength and good chemical resistance. These resins may be used in the neat form or may contain reactive diluents **[Kay 1981]** and **[Launkitis 1982]**.

3.6.1 Evaluation of Cured Epoxy/ Amine Systems Based on RPET as Organic Coatings

Organic coatings are prepared from one or more types of precursors of the final cross-linked polymer network. The precursors are either simple compounds carrying functional groups or, more frequently, prepolymers of more complex architecture. At present, not only the chemical composition of precursors and cross-linking chemistry but also their architecture can be tailored. Through the architecture, the processing properties, particularly the viscosity build-up and gelation, and materials properties are controlled. By integrating certain structure elements, certain functions of the final coating film, such as surface activity or hardness can be satisfied.

However, in some cases it is possible to generate in situ substructures similar to certain precursors during the cross-linking reactions. The substructures are called chemical clusters (for instance, hard clusters) and their size and shape can be controlled to a certain degree. Also, multistage processes are important in preparation and modification precursors for binders of specific architectures.

Introduction of new precursor architectures brings about new problems in description and modeling of the network build-up. For instance, one

can observe the so-called neighbor effect on reactivity of a functional group in a functional copolymer: the apparent reactivities of functional groups are controlled by the nature and state of neighboring units. Also, some groups are accessible with difficulties due to steric effects. This makes the apparent reactivity of a functional group dependent on the size and shape of the precursor.

Epoxy resins provide durable coatings of high mechanical strength with good adhesion to many substrates. Solvent- and chemical-resistance films are obtained by curing at ambient and at elevated temperatures. Epoxy resin in solid or liquid state was dissolved in solvents at room temperature to cure with amines. The curing process usually takes 7 days; resin and hardener components are packed separately. Amine-cured system are suitable for marine and maintenance coatings where corrosion resistance is required. The working pot life of amine-epoxy resins systems depends on the curing agent, solvent, accelerators, and temperature. High solid epoxy resins are used in industrial coatings when maximum resistance to solvents and corrosives is needed.

Properties of epoxy resins are influenced by factors at the molecular level, such as backbone structures of epoxy resins and curing agent; nature of the covalent bond developed between the epoxy resins and the curing agent during the cross-linking, and density and extent of cross-linking, i.e., degree of cure. The ratio of resin to hardener was shown to have a strong effect on the structure and the properties of the cured resins **[Bauer 1980]**. Normal stoichiometry employs equivalent weight of amino hydrogen per equivalent weight of epoxy resins, but in practice, the best performance may be given by other ratios. It is usually

a major good in epoxy coatings to maximize pot life and minimize cure time at ambient temperature. In this respect, the curing and application of our prepared epoxy resins and hardener based on rosin at ambient temperature are another goals of this work.

3.6.1.1 Relationships between cured epoxy resin structure and their mechanical properties

Cured thermoset polymers are more difficult to analyze than cured thermoplastic. They are insoluble and generally intractable. However, their properties are influenced by factors at the molecular level, such as backbone structures of epoxy resin and curing agent; nature of covalent bond developed between the epoxy resin and the curing agent during the cross- linking and density of cross linking, i.e., degree of cure. Epoxy resins have a wide and increasing use in industry owing to their unique combination of properties. The absence of volatile by products and low shrinkage during cure results in good molding characteristics, and the minimization of internal stresses give the thermoset excellent mechanical properties. Furthermore, the cured resins possess outstanding chemical resistance and they have high adhesive strength due mainly to the generation of polar hydroxyl groups during cure. Although epoxy resins are used as adhesives, they suffer from a lack of flexibility, and hence reduce shear strength and low peel, when cured with conventional "small molecule" reagents. The increasing of epoxide contents of resins leads to a densely cross-linked structure. Improvements in flexibility can be obtained by incorporating long chain aliphatic compounds into the resin before cure. These may either remain uncured during curing when they act as plasticizers, or they may be linked chemically into the system by the cure process when they may be

described as flexibilizers. In this respect, we have designed both epoxy binders and hardeners based on aliphatic and cycloaliphatic systems to produce cured epoxy resins have good durability with excellent mechanical properties. For these purposes, the mechanical properties of cured resins have tested by determining the impact, adhesion bending and hardness.

The curing experiments, reported here, were formulated as solvent-based liquid coatings with different ratios of curing agent. In all the investigated samples 1% of $(ET)_3N$ (wt% based on weight of epoxy binder) was added as catalyst. For curing tests, epoxy resins based on GTE and GDE were mixed with curing agents AEP at ratios 1:1, 2:1, 3:1 and 4:1 (wt of epoxy: wt of hardener), the mixed ratios are dissolved in 10% of xylene (wt% based on hardener) to ease application of the formulated resins. Then, these samples were sprayed (by using air spray gun) with wet film thickness, WFT, 350μ m on blasted steel panels.

The tests for measuring the mechanical properties were evaluated after 24h at ambient temperature (25°C). The data of mechanical properties (adhesion, impact, bending and hardeners) for cured epoxy resins based on GDE and GTE with curing agents were listed in ***Tables (3.14)*** and ***(3.15).*** The data reported on adhesions indicate that all cured epoxy resins based on GDE have superior adhesion properties with steel. This can be attributed to the high epoxy functionality of resins and presence of terminal glycol groups as indicated from hydroxyl numbers of the prepared epoxy binders based on GDE. It has been demonstrated that the presence of small controlled amounts of terminal glycol groups can have beneficial effects on adhesion **[Adams et al. 1986].** It was also

noted that the mixing ratios between epoxy resins and AEP hardener have affected the impact of coatings films. This was observed by deformation of coating films when the mixing ratio between epoxy and AEP hardener was 1:1 (wt: wt). Moreover, the films were deformed when mixing ratios were 1:1 and 2:1 (wt: wt) for GTE. While the mixing ratios of epoxy: hardener is 3:1 and 4:1 give the best results with impact and T-bend tests. These behaviors indicate that the ratios of cross-linking agent affect the mechanical properties of coatings. This behavior leads to speculate that the high cross-linking density networks decreases the mechanical properties of the formed network. The variation of hardness results (by pencil test) from soft (minimum cross-links) to hard coatings (maximum cross- link- density) indicate that the best results are determined at mixing ratio 4:1 for epoxy: hardener systems.

Table (3.14): Coating tests of GDE Oligomers Cured with Hardener as Curing Agent at Different Mixing Ratios

Sample no.	GDE: AEP (wt: wt%)	Adhesion	Impact	T-bend	Hardness
GDE1	4:1	+	+	+	HB
GDE2	3:1	+	+	+	H
GDE3	2:1	+	+	+	2H
GDE4	1:1	+	_	_	2H

+ PASS

- FAIL

Table (3.15): Coating tests of GTE Oligomers Cured with Hardener as Curing Agent at Different Mixing Ratios

Sample no.	GTE: AEP (wt: wt%)	Adhesion	Impact	T-bend	Hardness
GTE1	4:1	+	+	+	H
GTE2	3:1	+	+	+	HB
GTE3	2:1	+	-	-	B
GTE4	1:1	+	-	-	B

+ PASS

- FAIL

3.6.1.2 Evaluation of chemical resistance for cured resins

Durability of coats may be defined as the capacity of paint to endure; that is, to remain unchanged by environment and events. Effects of environmental conditions have an enormous effect on durability, and test methods for developing and monitoring the performance of coating systems are always designed to simulate conditions of usage. They are usually designed to accelerate the degradative processes to which coatings are subjected. The reason for this acceleration of the degradation processes is to provide early warning of coatings failure.

There are two types of test methods to evaluate the durability of coatings chemical resistance test and mechanical tests. In the previous section, we have evaluated the mechanical tests of the present types of cured epoxy based on GTE and GDE. In the present section, we have discussed the chemical resistance test as described in experimental section. In this respect, the coated panels have subjected to chemical environments (alkali, acid, solvent and salt spray) to study the durability of coats. The data of alkali-, acid-, solvent- resistance and water resistance were determined for cured epoxy systems (based on both GDE and GTE) and listed in ***Tables (3.16)-(3.17)***. The sign (-) indicates failure of tests, while (+) sign indicates the coatings pass the tests. The failure of test indicates that the coating films losses their adhesion with panels and show cracking and flaking of the film. The reason for coating failure are legion nevertheless some reasons for failure are readily identifiable, and attempts can be made to compact them.

Table (3.16): Chemical Resistance Tests of GTE oligomers Cured with Hardener as Curing Agent at Different Mixing Ratios

Sample no.	GTE: AEP (wt: wt %)	Acid resistance	Alkaline resistance	Water resistance	Acetone rub test
GTE1	4:1	-	-	-	+
GTE2	3:1	+	+	+	+
GTE3	2:1	+	+	+	+
GTE4	1:1	+	+	+	+

+ PASS

- FAIL

Table (3.17): Chemical Resistance Tests of GDE oligomers Cured with Hardener as Curing Agent at Different Mixing Ratios

Sample no.	GTE: AEP (wt: wt %)	Acid resistance	Alkaline resistance	Water resistance	Acetone rub test
GDE1	4:1	+	+	+	+
GDE2	3:1	+	+	+	+
GDE3	2:1	+	+	+	+
GDE4	1:1	+	+	+	+

+ PASS

- FAIL

Solvent resistance may be tested for different reasons. Tests of resistance to petrol and diesel fuel are carried out on compositions that may be expected to encounter contact or intermittent splashing with these liquid, e.g. motor vehicle finishes, storage tanks, etc. The use of polar solvents such as ketones is often used to assess the degree of cure of a cross-linked composition for solvent resistance, methyl isobutyl ketone or acetone is recommended. In addition to immersion testing, solvent resistance may be assessed by a solvent rub test. In this respect, acetone has used to determine the degree of curing of the present coating systems by both immersion and rub methods.

The failure of tests was determined either by disruption or dissolution of the coating films from panels. Generally, solvent resistance depends primarily on polarity of cured network resins. Non-polar polymers show solvent resistance to water, acetone and other polar solvents, whereas polymers containing sites for hydrogen bonding are most affected by moisture humidity and polar solvent **[Howard 1977]**. Moreover, the molecular weight and crosslink density of polymer networks are directly related to its resistance to solvent attack. This is due to the thermodynamic relation between polymer network structures and solvent **[Meyersen, 1966]**.

Cross-linking is the ultimate structural factor in preventing a polymer from dissolving in a solvent. Although this cannot eliminate the effects of polarity and hydrogen bonding, it raises molecular weight to the size of an infinite network, preventing "individual "polymer chains from dissolving in the solvent. The higher the degree of cross-linking indicates the less free volume and segmental mobility remain available

in the polymer. So that solvent molecules can hardly penetrate the cross-linked network at all. The cross-link density can be controlled by change type of curing agents and functionality of epoxy resins **[Dima et al. 1993]** , In this respect, it was found that all the prepared epoxy resins based on both GDE have good solvent resistance with all mixing ratios with AEP. It was also noted that the increasing of epoxy functionality from 1.8 to 2 for GTE and GDE resins enhances solvent resistance for all epoxy resins / curing agents mixing ratios. This can be attributed to increasing of crosslink density by increment of epoxy functionalities, although the epoxy polarity is increased by increment of epoxy functionalities **[Tess 1988]**. The high solvent resistance of the cured epoxy systems based GDE indicates that the xylene solvent is not trapped in the cured system **[Dibenedetto 1980]** and **[Helloan 1983]**.

Whereas, most conventional structural materials are subjected to severe attack by many aqueous acids and bases, most organic polymers are relatively resistant to these corrosive environments. Only specific functional groups in the polymer may cause sensitization to such reagents. The acidic hydroxyl group in phenolic resins remains sensitive to alkali even after final cure **[Oldring 1998]**. The acetal group in cellulosics, polyformaldehyde and polyvinyl acetals is very sensitive to hydrolysis by aqueous acid **[Lupinsky 1982]**. Polyesters, polyamides, and polyurethanes may be hydrolyzed by acid or alkaline catalysis.

In the present systems, the structure of network based on GDE and GTE as epoxy binders and AEP as curing agent, have aliphatic ester groups, which are sensitive to both aqueous acidic and alkaline solutions. The data of acid and alkali chemical resistance for cured GDE and GTE

epoxy resins indicates that these networks posses high resistance to alkaline and acidic aqueous solutions, although they have ester groups. The high alkaline and acidic resistance can be referred to high crosslink density of networks due to high epoxy functionalities. This can be attributed to high crosslink density of network decreases their exposure to environment **[Masashi et al. 1997]** and **[Dibenedetto 1980]**. This can be observed for fails of chemical resistance of cured epoxy based on GTE at mixing ratios (4:1, wt: wt). This can be attributed to the decreasing of hardener content, which decreases cross-link density of network and increase the attack of ester groups of network to acidic and alkaline solutions.

3.6.1. 3 Testing corrosion resistance of coating

Salt spray tests are probably the most common tests applicable to corrosion resistance and the most controversial **[Capp 1914]**. It was well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrates, and it is useful to have information and the behavior of a particular system in protecting such substrate from corrosion both with intact and damaged coating films **[Sample 1943]** and **[La Que 1951 and 1952]**. However, they are well established, and, despite the problem of reproducibility, are quite useful guides to performance in the absence of longer term corrosion data. They are this unlikely to be discarded. They are considered unrealistic by some workers because of the degree of acceleration of the corrosion process that they achieve and the variability of the extent of damage that is inflicted in some of the tests.

There are two tests: the continuous salt spray test and the intermittent. In the present work, the continuous salt spray test was used, as described in experimental section, to study the effect of salts on the properties of coating films. The duration times of tests were determined for all cured epoxy systems based on GDE and GTE and listed in ***Tables (3.18) – (3.19).*** The test was stopped when the films show poor adhesion.

The results of salt spray indicate the strong adhesion of coatings by increase of epoxy functionalities. This was observed from the improvement in coating performance from 75 to 95% for GDE after 646h of exposure to the salt spray environment. Coating performance was consistently improved for each exposure time for both coatings. This can be attributed to relationships between coating properties and performance.

In this respect, the adhesion of substrate with coat is the main problem for coating failure **[Bullett et al 1969]**. Cracking, flaking scaling or blistering due to under rusting (the latter often being accompanied by brown discoloration of the film) is due to mechanical action by the products of corrosion. The most familiar corrosion of this type is the rusting of iron exposed to moist atmosphere or water **[Slabaugh et al. 1966]**. The initial penetration of rust through the protective coating film is based on the coating constituents **[Mayne 1957]**. The coating constituents must be able to resist the transfer of ions through the coating and be able to expand and contract with the underlying surface over which it is applied. These ions are chloride, sulfate carbonate, or similar ions, which on penetrating the film, would start under film corrosion. So the coatings must be highly adherent to the substrate and must have excellent resistance to water, ionic passage, osmosis,

chemical weather and electroendosmosis **[Gelfer 1958]**, **[Panl 1973]**, **[Meldrum 1993]** and **[Mansfeld 1981]**..

Table (3.18): Salt Spray Resistance of Cured GTE Epoxy Resins

Sample no.	GTE: AEP (wt: wt %)	Exposure TIME (h)	Disbanded area (I)		ASTM RATING*
			mm^2	%	
GTE1	4:1	300	67.4	58.1	2.5
GTE2	3:1	400	35.9	31	3
GTE3	2:1	500	5.2	4.4	7
GTE4	1:1	500	13	11	6

*ASTM METHOD. D 1654-92

Table (3.19): Salt Spray Resistance of Cured GDE Epoxy Resins

Sample no.	GTE: AEP (wt: wt %)	Exposure TIME (h)	Disbanded area (I)		ASTM RATING*
			mm^2	%	
GDE1	4:1	646	2.33	2	8
GDE2	3:1	646	3.38	2.9	7.7
GDE3	2:1	646	5.2	4.4	7.2
GDE4	1:1	646	12.9	11	6

*ASTM METHOD. D 1654-92

Resistance to osmosis and electrondosmosis greatly affect coating life. In this respect water or dilute salt water are directed to the coating, they are semipermeable membranes, to which the principle of osmosis definitely applies. If the steel surfaces contain chlorides, sulfates or other ions (on which the coating is applied) will increase water penetration through the coating and leads to blistering and coating failure. So the strong adhesion is required to overcome the physical action of osmosis and electrondosmosis. Strong adhesion also prevents moisture vapor from passing through the coating and condensing in a poor area of adhesion, leading to a blistering of coating.

This is of particular significance when it comes to the choice of suitable coating systems. In our epoxy systems, it was observed that increasing of epoxy functionality increases the adhesion of coat with steel. This can be referred to the curing of epoxy groups with AEP hardener produce hydroxyl groups. It has been shown that the concentration of resultant hydroxyl group has a deleterious effect on the adhesion of the epoxy coating to the steel metal **[Bullett et al. 1968]**. The high salt spray resistance of cured epoxy resins can be attributed to the alicyclic structure of AEP that have high resistance to osmosis and electroendosmosis by comparing to aliphatic amines **[Wallington 1974]**.

Essentially four types of epoxy materials are used in petroleum pipeline, tanker and marine coatings:

- The epoxy coal tar type coating,
- The amine catalyzed ambient temperature cure coating,
- The polyamide epoxy coating, and

- The epoxy ester type coating.

Furthermore, an unlimited number of combinations can be formulated that are still called epoxy. In the present system of cured epoxy polyamine resins, based on both GDE and GTE have excellent alkali, acid and solvent resistance and provide a dense hard coating with good adhesion. From these points, epoxy resins based on both GDE and GTE can be used in linings for petroleum tanks and tankers, salt barges and ships, general chemical tankers, as well as exterior coatings for the bottoms, boot-topping, and decks.

3.6.2 Evaluation of UP/VE Systems for Construction Applications

Unsaturated polyesters are extremely hard when cured. Alternatively, they can be made to be permanently flexible and rubber-like. They can be highly chemical-and water-resistant, or they can be water-tolerant. They can have good electrical insulation, and dielectric properties, or they can have poor electrical characteristics. They can be tough and impact-resistant, or they can be made to shatter readily. Polymer Concrete (PC) is a composite material in which the entire binder is polymeric in replacement of the cement.

It has a large material modification, but much selective control on properties. Although initially studied for its excellent mechanical properties, PC is now widely used in electrical applications. Polymer concrete, as the name suggests, is a composite material consisting essentially of a mixture of careful graded aggregates and fine fillers bound together by means of an organic resin system. In the ordinary

cement concrete, the gravel is the aggregate, sand is the filler and Portland cement is used as the binder. Because of this similarity in composition, the polymer composite is termed as polymer concrete. In the polymer concrete, the inorganic portion of the composite is usually very high ranging from about 82% to about 90% by weight. Therefore, the resin binder used should have low viscosity to facilitate good wetting of the particles.

The polymer may be dispersed in the non-polymer phase as well. There are three types of polymer based concrete systems as:

- Polymer Impregnated Concrete (PIC).
- Polymer Cement Concrete (PCC).
- Polymer Concrete (PC).

PIC is produced by monomer impregnation of normal hardened concrete followed by in-situ polymerisation. A typical impregnating monomer is methyl methacrylate. In this type of concrete, the simultaneous improvement of large number of features makes it impossible to control one feature selectively. This process is mainly used for repairs in civil structures and is less applicable for electrical requirements.

PCC is produced by adding a polymer or its precursor during the mixing of fresh ordinary concrete with the curing taking place after placement of the materials. It has moderate material modification efficiency. PCC is used for repairs to runways, roads and wherever there is need for rapid curing.

PC is prepared by mixing a monomer or resin with an aggregate and polymerising or curing the material after its placement. This system is cement free. It also has a large material modification but much more selective control on properties. As already mentioned, PC finds many applications in the electrical industry.

Polymer concrete is a mixture of different components in the proper ratios, which can be casted into any desired shape. The main ingredients of polymer concrete are based on resin, fillers and catalyst. The polymer resin acts as binder for the filler particles and the strength of polymer concrete then depends on bond between filler and resin and the degree of compactness achieved. For optimum strength / cost results, the resin content should be sufficient to coat all the filler particles and just fill the voids between them. If the resin content is not sufficient to fill the voids then the strength of polymer concrete falls. There are four main characteristics, which a polymer concrete must satisfy to be suitable for rapid placement:

- Rapid Cure
- High Strength
- Durability
- Rapid placement in all weather conditions

3.6.2.1 Mechanical properties of cured UP/VE systems

In low temperature composite manufacturing processes, a major concern is how to control the resin gel time and cure time and how to achieve a high resin conversion with low residual volatile organic chemicals. Each polyester oligomer contains a number of internal maleate and fumarate double bonds to co-polymerize with cross-linking agents (i.e. styrene),

forming three-dimensional networks. A post-curing step is often needed to reach high conversion for better mechanical strength, high corrosion resistance and good thermal properties. After being launched at ambient conditions, an increase of the resin temperature caused by the reaction exotherm may occur **[Dow Chemical 1989]** and **[Li L et al. 1999]**. When the temperature rise is sufficiently high, the thermal decomposition of un-catalyzed initiators or even the self-initiation of the monomers may take place, which accelerates the curing reaction of UP resins **[Li L et al. 2001]**. Although the temperature rise can enhance the curing reaction and increase the final conversion, a fully cured polymeric composite part is still difficult to achieve when processed at room temperature stability of molded composites. Therefore, a major concern for fabricators is how to control the curing process, achieving a high final resin conversion with low residual volatile chemical content in low temperature composite manufacturing processes. In this respect the cured rods based on PU/VE/styrene systems were subjected to post curing at temperature 105°C for 24 h to ensure complete conversion of both styrene and vinyl ester monomer in the cross-linked networks of UP. The total conversion of monomers to cross-linked polymers was estimated using ***equation (3.4):***

$$\textbf{Total conversion (\%)} = W \times 100 / W_0 \qquad \textbf{(3. 4)}$$

Where, W and W_0 are total weights of cross-linked polymers after post curing at 105°C and weight of reactants, respectively.

Small molecules carrying functional groups (monomers) or preformed larger molecules carrying functional groups serve as polymer network *precursors*. The functionality of precursors is important because it

determines the conversion or time window of processability of the reacting material (pot-life). High-functionality precursors, like primary chains in vulcanization, gel at quite low conversions. Low-functionality precursors can be blended in such a way that the gel point can be adjusted as close to 100% conversion as desired. Even more important than the precursor functionality is the type of the cross-linking reaction: step-wise or chain with fast propagation step. For instance, polycondensation (step-wise reaction) of a blend of tetra- and bifunctional monomers will gel above 50% conversion, whereas the equivalent blend of monovinyl and divinyl monomers polymerized by free-radical mechanism gels in the range of several per cent conversion or lower. Moreover, the structure of the product is different as a result: of the difference in polymerization mechanisms. The cross-linking of UP/VE and styrene systems leads to nearly instantaneous curing by the formation of radicals starting both polymerization and cross-linking. A wide variety of vinyl cross-linkers has been used to form cross-linked networks. The choice of the cross-linkers is quit broad in bulk polymerization. The Flory-Stockmayer theory has been used to predict the gel network buildup of a cross-linking polymerization **[Flory 1953]** and **[Stockmayer 1945]** Many side reactions, such as interchain cyclization, decrease the efficiency of the cross-linking reactions. This can be significant at high cross-linker levels, such as used in styrene divinylbenzene copolymers where intramolecular cyclization is believed to occur. At very high levels of cross-linker and at high conversion, pendant vinyl groups were found to be less reactive and not utilized in forming the network. Local steric effects and lack of chain mobility were proposed for their lack of reactivity **[Malinsky et al. 1971]**. Okay et al. **[Okay et al. 1995]** determined that, almost half of pendant

double bonds in a mixture of methacrylate cross-linkers were consumed by internal cyclization reactions when the mole fraction of cross-linkers was ranged from 0.126 to 0.256 (Wt%). However, Landin and Macosko **[Landin et al. 1984]** showed that the rate of intramolecular cyclization was very low at low levels of cross-linker. To understand the distribution of cross-links in the network, the reactivity of the various double bonds in the system must be determined. This includes the reactions between double bonds of UP and VE with styrene, the initial double bonds of the cross-linker, and the various double bonds that are pendant to the polymer chain after incorporation of the cross-linker. In the present work, the reactivity of VE and styrene cross-linkers towards UP was investigated from polymerization conversion (oven recovery). In this respect, the data of total conversion percentage (%) for cross-linking of UP in presence and absence of cross-linkers were determined and listed in ***Tables (3.20) & (3.21).*** It was found that the conversion percentage (%) increases as the amount of VE increases and it have much pronounced effect on conversion percentage (%). The increment of conversion percentage (%) with increasing contents of both GTA and GTM cross-linkers suggests that the obtained networks contain either highly cross-linked copolymer or more of the linear copolymer chains are linked into the gel network. This can explained on the basis that when the weight percentage of VE increased the molar number of monomers of styrene and VE became larger and larger, and as a result, the conversion increased due to increased probability of cross-linking. Otherwise, VE has two double bonds, so the higher VE level makes graft polymerization and chemical cross-linking easier. Conversion data indicates that UP1 has greater conversion percentage than UP2. This can be referred to the presence of more curable maleic double bonds in UP1

structure than UP2, which increases the probability to react with VE and styrene. It was also observed that UP/GTM has a low conversion (%) values than that determined for cross-linked copolymers with GTM. This can be attributed to the differences in the reactivity ratios of both cross-linkers with the produced polymer **[Atta et al. 2001]**. This can explained on the basis that reactivity of GTM towards UP may promote the reaction rate initially due to a cross-inking. Facilitated gel effect but may retard the diffusion of reactants and leave un-reacted vinyl groups (trapped free monomers or pendants) within the system at the later stage. The effect of temperature and post curing on conversion values was observed from data listed in ***table (3.20).*** The increase of temperature is expected to increase the conversion values. With an increase in temperature, however, the rates of copolymerization and homopolymerization also increase **[Park et al. 1998]**.

Table (3.20): Conversion Values of Cured UP/GTA Having Different Composition

VE (%Wt)	Type of UP	Conversion (%) of Cross-linked gels at temperature				
		25°C	35°C	45°C	55°C	105°C
0	UP1	84.7	87.3	90.4	92.5	96.2
	UP2	81.1	83.4	87.6	90.2	95.5
5	UP1	88.5	92.5	94.6	95.7	99.0
	UP2	85.2	87.9	91.5	94.8	98.2
10	UP1	89.9	94.4	95.6	97.1	99.2
	UP2	87.4	89.1	93.2	95.6	98.8
15	UP1	91.2	96.5	98.1	98.9	99.6
	UP2	89.2	90.7	94.7	96.1	98.9
20	UP1	93.5	97.6	98.8	99.1	99.8
	UP2	90.5	91.5	95.6	96.7	99.0

Table (3.21): Conversion Values of Cured UP/GTM Having Different Composition

VE (%Wt)	Type of UP	Conversion (%) of Cross-linked gels at temperature				
		25°C	35°C	45°C	55°C	105°C
0	UP1	84.7	87.3	90.4	92.5	96.2
	UP2	81.1	83.4	87.6	90.2	95.5
5	UP1	85.3	87.5	91.4	93.7	96.5
	UP2	82.5	83.9	88.5	90.8	96.2
10	UP1	86.8	88.4	92.6	94.1	96.8
	UP2	83.4	84.1	89.2	91.6	96.4
15	UP1	88.2	90.5	94.1	95.9	97.6
	UP2	85.2	87.7	90.7	92.1	96.9
20	UP1	90.5	91.6	95.8	97.1	98.8
	UP2	89.5	90.5	92.6	94.7	97.2

✓ ***Preparation and characterization of PC***

The PC samples were prepared from the CUP resin and RUP obtained from recycling of PET. The molding technique and the equipment used for casting the PC specimens were described in detail in the experimental chapter.

The PC mix design was optimized for workability, strength, and economy as suggested by Rebeiz et al. **[Rebeiz et al. 1991]**. The optimum aggregate composition was 50% 10-mm pea gravel, 35% sand, and 15% fly ash (fly ash makes the mix both more workable and stronger). The optimum aggregate-to-resin ratio was 9:1. The mix design for polymer mortar (PM) consisted of 20% resin, 60% oven-dried sand, 20% fly ash according to the recipes recommended by Paul and his collaborators **[Rebeiz et al. 1992]**. It has been reported that UP composites with low styrene residue can be obtained with the use of a high level of peroxide when cured at room temperature **[Roskott et al. 1978]**. However, a high initiator concentration may result in low molecular weight and inferior mechanical properties of the cured composites. It may also shorten the gel time, resulting in poor mold filling and fiber wetting during molding. Many studies on UP resins **[Yang et al. 1987]** and **[Newman et al. 1996]** have demonstrated that the type of initiator has a profound effect on the residual amount of UP unsaturation and styrene monomer. Some effort has been made to improve the curing agent systems for better performance at low temperature cure, i.e. high final resin conversion, long pot life, and short cycle time **[Li L et al. 2002]** and **[Fujii 2002]**.

✓ **Mechanical properties**

It is of interest to measure the mechanical properties of the cured resins to decide potential the applications. The mechanical properties are quantified easily, since the test methods are standardized and are easily related. The derived values of the Youngs modulus (E_Y) in GPa and compression strength (σ_{max}) in MPa for cured CUP and RUP are given in ***Tables (3.22) – (3.25)***. The values of Young's modulus, E_Y, in GPa and compressive strength, σu, in MPa were derived from the stress-strain curves for different cured resins. PCs made from virgin material **[Rebeiz et al. 1991]** have compressive strength ranging from 40 to 130 MPa. Thus, the properties of PCs made with resins using recycled PET are comparable to those using virgin resins. With respect to the polymer mortars, PMs, the measured values of σu seem to be in a good accord with the values reported by paul and his collaborators **[Rebeiz et al. 1992].** These authors have reported the mechanical properties of the PM prepared using virgin resins. The obtained values of σu for PMs prepared in the present investigation are comparable to that reported **[Rebeiz et al. 1992]** for PM using virgin resin.

Data shows that the σu values for CUP cross-linked with GTA and GTM are ranged between 135 MPa and 240 Mpa. The corresponding values, for RUP being in the range 106 MPa – 186 MPa. The range of the measured values of σu for PCs is slightly higher than the value obtained by Rebeiz et al. (91.8 MPa) **[Rebeiz et al. 1992]**. Accordingly, the UP resins designed from recycled PET may be used for making PMs. The following sections will discuss the effect of chemical structure of both UP and VE on mechanical properties of cured resins. On the

other hand, effect of VE concentration and reaction temperature will be discussed here in after.

a. ***The effect of molecular structure on the curing and mechanical properties***

The effect of the structure of the resin on its mechanical and curing behavior has been investigated. The molecular weights of the prepared polymers were determined by the end group analysis. Since methods of end group analysis count the number of molecules in a given weight of sample, they yield the number-average molecular weight for polydisperse materials. The method become insensitive at high molecular weight (above 25000); as the fraction of end groups becomes too small to be measured with precision **[Billmeyer 1971].** End group analysis in condensation polymers usually involves chemical methods of analysis for functional groups. Carboxyl and hydroxyl groups in polyesters **[Pohl 1954]** and **[Conix 1958]** are usually titrated with a standard reagent. In the present study, the resultant molecular weight of RUP is 3310 g/mol, as tabulated in ***Table (3.3),*** in conjunction with the acid number of the prepared polyesters. While, the molecular weight of CUP is 6720 g/mol. The reason to that can be attributed to the effect of the molecular weight of the repeating unit difference initial initiator concentration, as well as to the effect of the oligoester diols for UP1 and UP2. The former exhibits on average a higher molecular weight and thus it contains more terephthalate repeating units. The presence of more terephthalate repeating units between the cross-links results in the existence of harder domains and better separation between the cross-links in the packed cross-linked structure and as a result the mechanical properties are improved **[Farahat et al. 2002].**

Table (3.22): Mechanical Parameters of Cured UP1 with GTA at Different Temperatures

GTA (wt %)	Curing parameters at different temperatures							
	Compressive strength (σ_{max}) MPa				Young's modulus (E_Y) GPa			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	135.231	137.351	158.689	161.234	21.134	22.541	25.364	26.545
5	151.132	153.159	161.231	166.211	21.121	22.403	23.511	25.101
10	170.947	175.947	180.325	186.421	18.603	19.415	21.811	23.031
15	179.652	183.897	187.213	192.310	15.531	17.705	18.233	19.854
20	182.641	204.871	235.214	243.221	14.024	16.265	16.852	18.621
GTA*	185.412	209.231	255.451	264.145	12.214	14.251	15.324	17.651

*:55%GTA, 45% styrene

Table (3.23): Mechanical Parameters of Cured UP1 with GTM at Different Temperatures

GTM (wt %)	Curing parameters at different temperatures							
	Compressive strength (σ_{max}) MPa				Young's modulus (E_Y) GPa			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	135.231	137.351	158.689	161.234	21.134	22.541	25.364	26.545
5	136.637	145.740	154.497	163.201	18.343	19.501	20.012	21.212
10	138.878	152.897	160.312	170.121	16.083	17.543	18.232	20.011
15	152.431	155.544	168.512	181.312	15.012	15.202	16.562	18.253
20	171.774	177.604	180.322	210.352	14.113	14.433	15.203	16.312
GTM*	180.213	182.213	186.642	189.561	13.214	14.253	15.013	15.782

*:55%GTM, 45% styrene

Table (3.24): Mechanical Parameters of Cured UP2 with GTA at Different Temperatures

GTA (wt %)	Curing parameters at different temperatures							
	Compressive strength (σ_{max}) MPa				Young's modulus (E_Y) GPa			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	106.123	114.231	137.821	153.241	20.247	21.547	23.478	25.478
5	105.235	112.450	123.012	159.124	18.012	20.231	22.012	24.369
10	104.213	106.147	110.243	161.432	16.023	19.012	20.258	21.587
15	100.102	102.123	108.243	168.142	14.258	16.587	17.859	18.789
20	95.310	97.142	100.145	162.214	12.364	14.258	14.369	15.680
GTA*	110.147	116.213	140.154	160.247	10.254	12.369	13.987	14.258

*:55%GTA, 45% styrene

Table (3.25): Mechanical Parameters of Cured UP2 with GTM at Different Temperatures

GTM (wt%)	Curing parameters at different temperatures							
	Compressive strength (σ_{max}) MPa				Young's modulus (E_Y) GPa			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	106.123	114.231	137.821	153.241	20.247	21.547	23.478	25.478
5	110.012	116.124	142.014	155.217	17.001	18.021	20.022	23.259
10	118.247	124.845	152.452	160.745	15.897	16.147	18.358	20.952
15	145.387	159.852	161.659	180.674	13.964	15.820	16.800	17.701
20	152.248	161.021	173.274	186.956	12.005	13.050	13.978	14.091
GTM*	160.214	169.147	178.123	190.147	10.024	11.007	12.047	13.267

*:55%GTM, 45% styrene

The choice of saturated acid (aliphatic or aromatic) and glycols offers great latitude in the design of polymer backbones. The cross-linking density of the cured product depends to a great extent to the type of the glycol and the percentage of the unsaturated dibasic acid used in constructing the resin. In this respect, CUP backbone is based on PG while, RUP is based on GDA which have long chain length than PG. Accordingly, the structure of RUP has low number of double bond as compared with CUP and that will increase the flexibility of RUP than CUP. The flexibility of this resin may be attributed to the effect of the chain length of the glycol molecules (GD) which, have been used in constructing the UP resin.

The increase in the length of the glycol molecules certainly leads to an increase in the length of the polymer segments. This in turn reflects on the intra- and intermolecular interactions and yields lower energy barriers for rotation, which enhances the flexibility of the resin. Accordingly, increasing the molecular weight of the utilized glycol or dibasic acid causes a decrease in the cross-linking density. Consequently, the mobility of the polymer segment increases, and hence an increase in flexibility is detected as manifested by a reduction in Young's modulus.

The reduction in E_Y may be attributed to an increase in the length of the polymer segments. The previous argument may lead to speculation that increasing the molecular weight of the glycols decreases the cross-linking density. Consequently, the mobility of the polymer segment increases and hence an increase in flexibility is manifested by a reduction in Youngs modulus.

b. The effect of molecular structure and content of VE on the curing and mechanical properties of UP

The mechanical properties of the UP resins produced were studied in relation to the effect of the VE concentration, as well as to the effect of the oligoester diols structure used. There are different mechanical data observed when GTA and GTM were used as cross-linkers. On the other hand, the mechanical properties are changed when CUP are replaced with RUP. It was observed that the compressive strength σu values increased with increasing of VE content from 0-20%. This indicates that the flexibility of resins was decreased with incorporation of VE in network structure. The increase in σ_{max} on increasing the VE content can be attributed to the increased content of curable double bonds, thus greatly increasing the crosslink density. This resulted in the cured UP/ VE resins being harder and more resistant to deformation upon the application of external stresses. The net effect is that the mechanical strength was significantly improved as a result; of the more chemically bonded structures.

The data listed in ***Table (3.24)*** shows different mechanical properties when GTA was used as cross-linker for RUP. It was found that the compressive strength values were reduced with increasing concentrations of GTA. This can be explained on the basis that the reactivity of GTA with RUP is more reactive than RUP with styrene. The wide difference in reactivity between GTA and GTM during the cross-linking of the UP's may be explained by the stabilization caused by the inductive effect of the methyl group present in the GTM structure. This behavior demonstrates the effect of the bulky phenyl group, afforded by styrene monomer, on the flexibility of the cured

resins. It can be seen that the decrease of the amount of styrene in the network leads to decrease in the number of phenyl groups.

Careful inspection of data indicates that the compressive strength values of UP are reduced when GTM replaces GTA. This can be explained on the different reactivity between UP, GTA, GTM and styrene radicals. The data indicates that, the rate of reaction of the UP radical with GTA is faster than with GTM, and the GTM radical reacts faster with its own monomer than does the GTA radical **[Kucharski et al. 1997]**. Accordingly, all GTM cross-linker radicals are used up before a significant number of styrene molecules can be incorporated in the cross-linked UP **[Lai 1997]**.

So the probability that homopolymerisation of styrene occurs during cross-linking is higher with GTM than GTA. It is well established that E_Y decreases with homopolymerisation of the monomer **[Lai 1997]**. This finding is in good agreement with that reported by Urban et al. **[Urban et al. 1991].** These authors sated that the spectroscopic evidence indicates that during the cross-linking reaction, styrene monomer homopolymerizes, forming atactic polystyrene, which is an integral part of the polyester/styrene network. They concluded that the atactic polystyrene may form physical cross-links along which chemical reaction between C=C bonds of polyester and styrene when styrene content exceeds 40%. Bucknall et al. **[Bucknall 1991]** used blends containing unsaturated polyester resin, poly(vinyl acetate), and styrene monomer in various proportions. The blends were cured by benzoyl peroxide as initiator. They reported that the peak temperature reached a maximum at 40% styrene. The Young's modulus measured by these

authors was found to decrease with decreasing styrene content and increasing concentration of poly (vinyl acetate) in the blend. It is obvious that their finding runs in harmony with the present results. This speculation agrees with the data listed in ***tables (3.23) and (3.25)***, which indicates that E_Y decreases on incorporation of GTM in a network of cross-linked UP. The fact that the σ_{max} values were higher for cross-linked UP's in presence of GTA than GTM indicate the formation of a denser cross-linked network in presence of GTA than with GTM cross-linkers. This can be attributed to the higher reactivity of GTA towards UP radicals. Careful inspection of data listed in ***Tables (3.22) and (3.25)***, it is indicated that the high compressive strength values were obtained when 55% of GTA and GTM cured with 45% of styrene monomer. This shows that highly cross-inked networks were obtained due to high reactivity of GTA or GTM with styrene.

c. ***The effect of temperature on the curing and mechanical properties***

The data demonstrates that, the value of E_Y increased as the temperature of reaction increased. This is due to a decrease of the molecular weight with an increase in the polymerization temperature. In radical polymerization induced by thermal decomposition of an initiator, generally, as the polymerization temperature increases, the dissociation rate of initiation, propagation, and termination are enhanced **[Odian 1991].**

All these factors except the rate of termination increase the rate of polymerization. However, a further increment in the polymerization temperature reduces the molecular weight of the polymer, due to an increase of the rate of termination and chain transfer, and increases the

relative amount of the polymer chain end, which affects the mechanical properties of polymers. Accordingly, an increase in the reaction temperature forms a denser network of the cured polymers and reduces the average molecular weight between cross-links **[Flory et al. 1943]**. Therefore, the increasing the polymerization temperature results in increase of both σ_{max} and E_Y values.

3.6.2.2 Chemical resistances of cured UP/VE systems

It is common practice in the laminating industry for composite parts to be cured at room temperature or to receive only a low-temperature post cure **[Grentzer et al. 1992]**. Under-cure of the resin will not generally produce optimal tensile properties **[Hunay et al. 2001]** and in applications where corrosive environments are experienced by the material, further degradation of the mechanical properties can occur. The loss of strength or stiffness over time can produce unexpected material failure resulting in, at the very least, costly downtime or hazardous spills. It was thought that the initial cure of the resin might affect the extent of degradation in the mechanical properties during exposure, yet little in the literature examines this aspect of current industrial practice **[Liao et al. 1998]**. Applications requiring corrosion resistant composite materials usually use vinyl ester resin as the composite matrix because these thermosets have high resistance to chemical attack.

In this respect, the resistance to the corrosive environments was assessed using the procedure outlined in **[ASTM C581-94]** as explained in experimental section. Specimens were immersed in four separate environments: 5 wt% NaOH, 32 wt% HCL, 25 wt% H_2SO4, and uncut

Kerosene, each at 66°C (150°F). The initial appearance of the panels was affected by the cure conditions. With exposure to the media, the appearance of all the panels changed to show color changes, and blistering. The observations at 3 months are summarized in ***table (3.26)*** the data indicates that there is no change on color and weight when plaques are subjected to sodium hydroxide and HCl or H_2SO4. This can be referred to high cross-linking density of resins decreases the exposure of polar groups of network to environments.

Table (3.26): Chemical Resistance Tests Of UP1 and UP2 Cured With GTA and GTM at Different Mixing Ratios

Cured Network (%)	Acid resistance				alkali resistance				Water resistance				Solvent resistance	Acetone Test
	5	10	15	20	5	10	15	20	5	10	15	20	(5-20)*	(5-20)*
UP1/GTA	+	+	+	+	+	+	+	+	+	+	+	+	+	+
UP1/GTM	+	+	+	+	+	+	+	+	+	+	+	+	+	+
UP2/GTA	+	+	+	+	+	+	+	+	+	+	+	+	+	+
UP2/GTM	+	+	+	+	+	+	+	+	+	+	+	+	+	+

* GTA or GTM Contents