RESULTS AND DISCUSSION

3. RESULTS and DISCUSSION

Rosin, exudates of pine trees, has been developed as a feedstock for synthesis of various chemicals and intermediates for polymers. It is often used in the formulation of adhesives, paints, varnishes and printing inks. Some authors have shown the possibility of its use in the synthesis of polyester imides [128] and polyamidimide [129]. It is also incorporated in some formulations of unsaturated polyester, but in small quantities [130]. A large majority of organic coating films in the end-use state exist in the form of a three-dimensional 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.

Unsaturated polyester resins, UP, have firmly established themselves as important matrix materials in the field of reinforced plastics and coatings, although phenol formaldehyde type resins are preferred when specific fire and smoke resistance qualities are required. 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 [131-135]. 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. However, their properties are influenced by factors at the molecular level, such as backbone structures of UP resin and curing agent; nature of covalent bond developed between the UP resin and the curing agent during the cross- linking and density of cross linking, i.e., degree of cure. UP 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. Although UP resins are used as organic coatings, they suffer from rigidity, low acid and alkali resistances and low adhesion with steel when cured with conventional "small molecule" reagents. The increasing of unsaturation contents of UP resins leads to a densely cross-linked structure. Improvements in flexibility can be obtained by incorporating long chain aliphatic compounds into the chemical structure of UP resins. In this respect, we have designed both UP resins and hardeners based on aliphatic and cycloaliphatic systems to produce cured UP resins have good durability with excellent mechanical properties. It is well known that vinyl ester, VER, resins are the addition products of UP resins [136, 137]. 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 [138, 139].

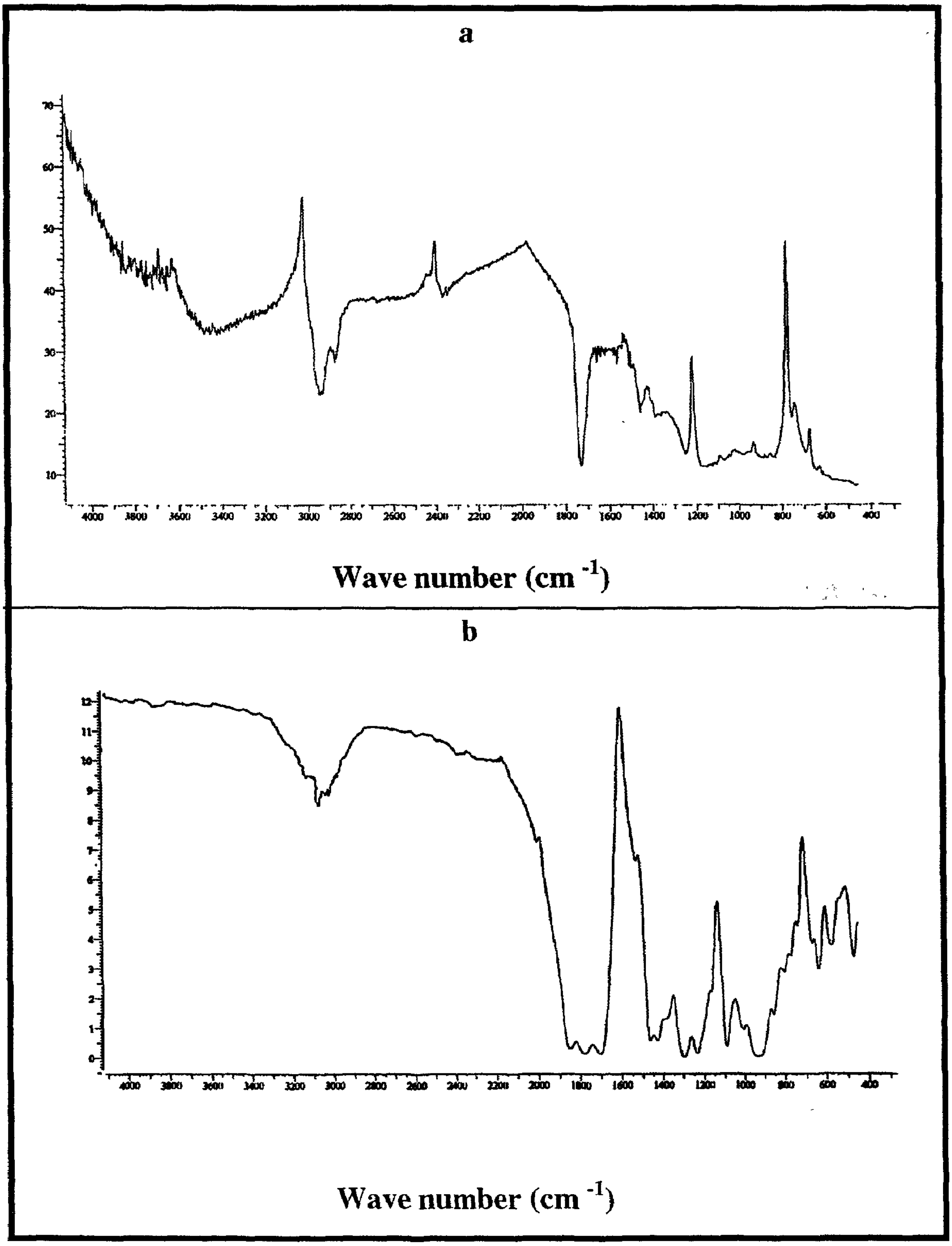
The aim of this work was to use the rosin as potential raw materials for the production of UP and vinyl ester resins as coatings. In order to fulfill these goals, three steps were distinguished. The first step includes the preparation of Diels Alder adducts of rosin acid to be used as dibasic acid material in manufacture of UP resins using ethylene or propylene glycol as diol. On the other hand the produced adducts were used to prepare vinyl ester resin which used as hardener for the prepared UP resins. In the second step, the curing behavior of UP resins and vinyl ester resins used for the production for ambient temperature coatings was investigated by manipulating the amounts of the initiators used. In the final step, the cured resins were evaluated as organic coatings for steel.

3.1 PREPARATION OF DIELS ALDER ADDUCT OF ROSIN

The Diels-Alder adduct of rosin and maleic anhydride, for example, has been extensively used as a raw material for polymers such as polyester imides, polyamide imides, etc. [140-145]. In the synthesis of the rosin maleic anhydride Diels-Alder adduct, MPA, rosin in its levopimaric acid form acts as the diene and maleic anhydride as the dienophile. Similarly, acrylic acid, acrylonitrile, acrylates and methacrylate may act as the dienophile with rosin. There have been some reports regarding the use of rosin acrylic acid in polymer synthesis [146, 147], a mixture of rosin and acrylic acid along with some other chemicals were reacted together to obtain a polymer, or the acrylic acid modified rosin was used and not the pure adduct of rosin acrylic acid [146]. Penezek and other workers reported the use of rosin acrylic acid adduct (APA) in the preparation of

UP derivatives. This adduct was used for the production of alkyd resins or as a paper sizing agent [147]. However, there was no detailed report about the synthesis and characterization of APA and the polyester and polyamides obtained from the adduct. We therefore report now the synthesis and characterization of APA and a polyester and a polyamide obtained by the reaction of this diacid adduct with 1, 6-hexanediol and 1, 6- hexanediamine, respectively. A very interesting reaction, involving the double bonds of rosin acid, as diene permits their coupling with unsaturated carboxylic substances as dienophiles and transformation into organic poly basic acids in accordance with the Diels-Alder mechanism. The synthesis of maleopimaric acid (MPA) and acrylopimaric acid (APA) from rosin acids has already been reported [101, 102]. The present work describes the condensation of EG with MPA to produce hydroxymethylated derivative. In this respect, the MPA was separated from diethyl ether solutions of the reaction mass by precipitation with petroleum ether. The removal of unreacted MA was made by repeated washing with distilled water. The purification of crude MPA was performed by recrystallization from acetone (as described in experimental part). The levopimaric adducts of high purity have been obtained by dehydration of the crystals at 180°C for 2h. This adduct was subjected to react with EG at 140°C. The produced resin is soluble in toluene, xylene, $CHCl_3$ and CCl_4.

The structures of APA, MPA, and MPE were confirmed by IR spectroscopy. IR spectra of APA and MPA compounds were represented in ***Figure 3.1 (a-b)***. While IR spectrum of MPE was represented in ***Figure(3.2)***. The characteristic bands in the IR spectra of APA and MPA (***Figure 3.1 a-b***) are observed at 1700 cm^{-1} (γ C= O



Figure(3.1) : IR spectra of a)-APA and b)MPA.

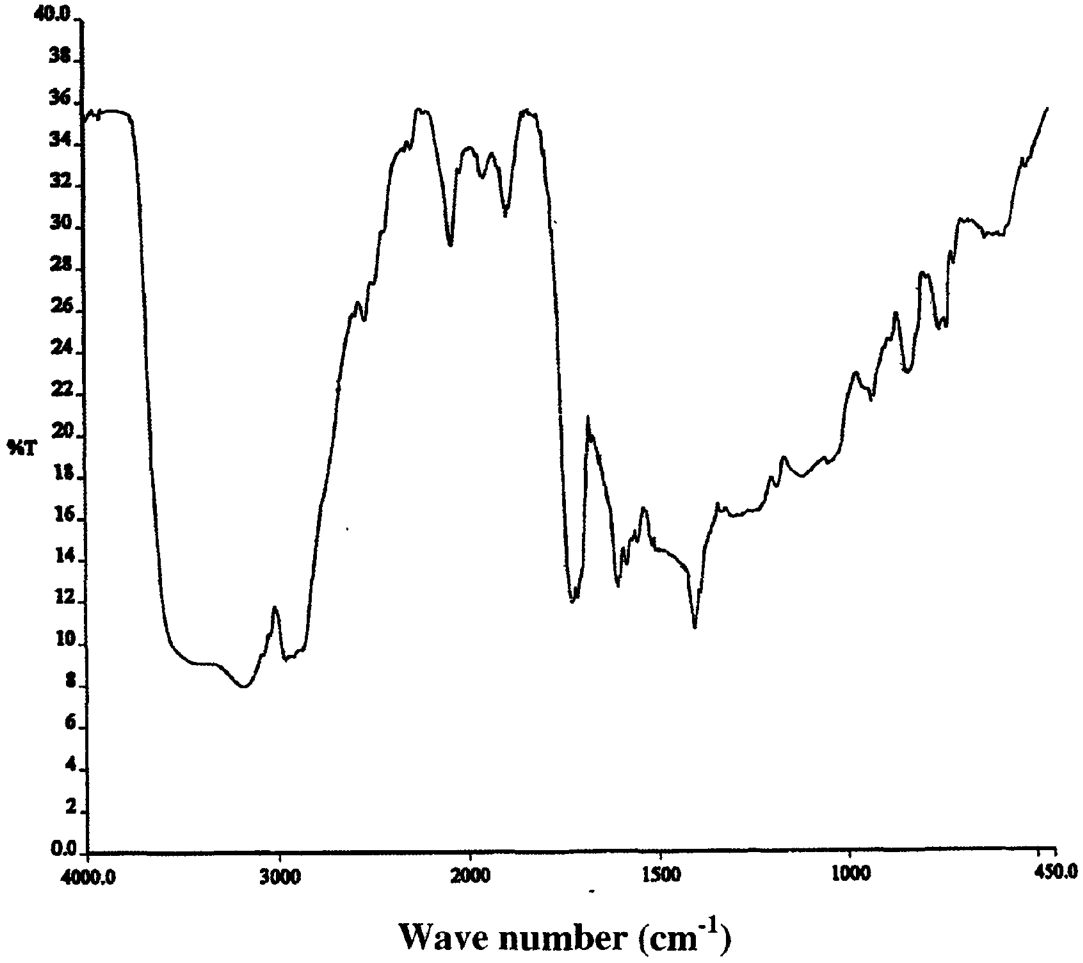


Figure (3.2): IR spectrum of MPE.

in COOH group), 1470 cm $^{-1}$ (double bond in hydrophenanthrene moiety), 1780 and 1850 cm $^{-1}$ ($\gamma_{C=O}$ of cyclic anhydride group). In the IR spectrum of MPE ***(Figure 3.2)*** shows the characteristic bands at 1730 cm $^{-1}$ and 1110 cm $^{-1}$ ($\gamma_{C=O}$,sym and γ_{C-O}, sym in ester) and at 3420 Cm $^{-1}$ (γ_{O-H}). The disappearance of the bands characteristic of cyclic anhydride group of MPA and the appearance of bands at 1730 cm $^{-1}$ ($\gamma_{C=O}$ sym in ester), 1700 cm $^{-1}$ ($\gamma_{C=O}$, sym of COOH) indicate that the esterfication of MPA was completed by reaction of carboxylic groups of levopimaric acid and one of carboxylic group of MA with OH group of EG.

3.2 SYNTHESIS OF DIVINYL ESTER CROSS-LINKERS

Epoxy resins are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrine (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. In the present work, the formation of glycidyl ether of rosin acids was prepared through reaction of hydroxymethyl derivatives of MPE with EC in presence (50 % by weight) NaOH as catalyst. The produced glycidylether with MPE have designated here as EMPE. The liquid epoxy resin was mainly characterized by epoxy content (EP). It was noted that the epoxide functionality of EMPE epoxy is 1.8. This indicates that only difunctional hydroxyl groups were reacted with EC. The higher viscosity values for the prepared epoxy, 4553 CP, indicate that no side reaction can be occurred [148]. This side reaction is based on the formation of terminal glycol groups due to hydrolysis of epoxy end groups.The presence of terminal glycol groups can give lower viscosity resin [149]. The proposed structure of EMPE was elucidated by using IR spectroscopy.IR spectrum of EMPE was represented in **Figure (3.3).** IR spectrum, figure 3.3, show appearance of new strong peak at 815 cm^{-1} and 780 cm^{-1}, $\gamma_{c\text{-}o}$ of epoxy ring, which indicate the presence of epoxid rings in structure of EMPE.

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[150-157]. 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 UP resins, especially the studies on the formation-structure-properties of vinyl ester resins.

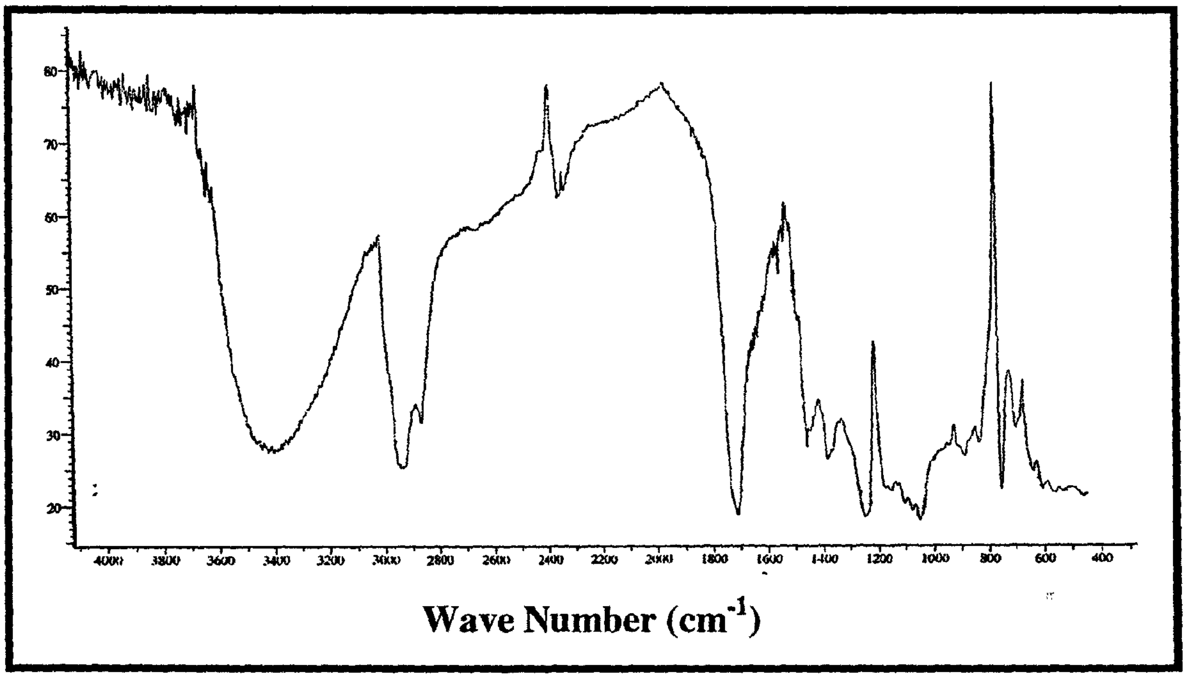
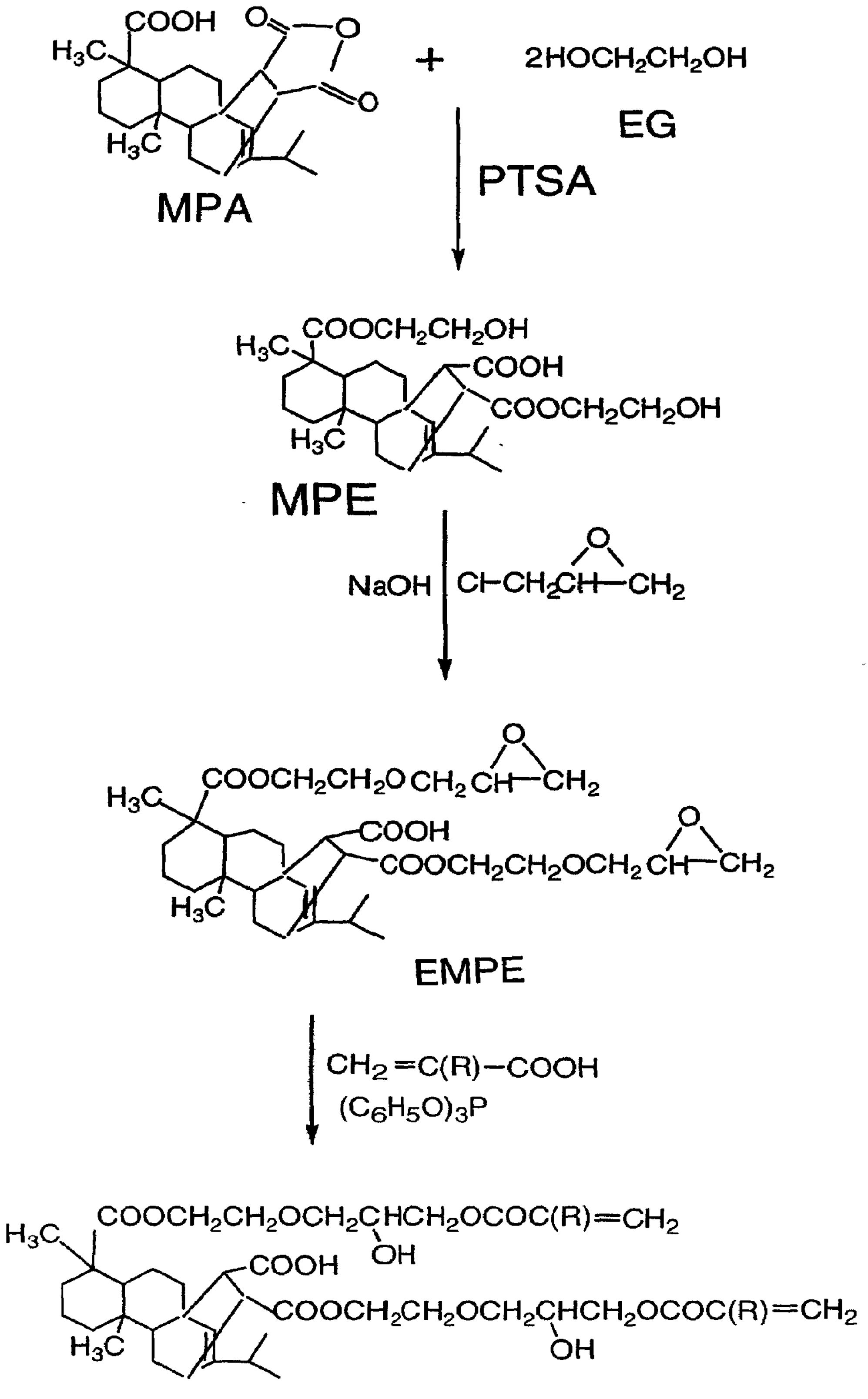


Figure (3.3): IR spectrum of EMPE.

Commercial vinyl ester resins are a mixture of styrene with a methacrylated epoxy compound based on bisphenol-A. Using rosin offers the possibility of a lower cost source for the latter component. Vinyl ester resins are usually produced from reaction of epoxy resins with unsaturated monocarboxilic acid. This reaction is usually catalyzed by tertiary amines, phosphites, and alkalis or ammonium salts. Triphenyl phosphite is a more effective catalyst as compared to other catalysts. The vinyl ester resins can also be prepared by the reaction of glycidyl methacrylate with multifunctional phenol [158]. The present study was intended to prepare vinyl ester resin from rosin acid. The first step includes the esterification of MPA and EG and the reaction of their products with EC to produce epoxy resin. The second part of the synthesis was based on the reaction between the epoxy resin and acrylic or methacrylic acid in presence of p-toluene sulphonic acid to produce vinyl ester resins having acrylate or methacrylate end groups. Schulze et al. [159] 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) mono methyl 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, vander Waals interactions are dominant. Accordingly, we presumed that the incorporation of EG 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 EMPE and acrylic or methacrylic acids. The produced vinyl esters of EMPE with acrylic and methacrylic acid are coded as AVEMPR and MAVEMPR, respectively. The reaction scheme was illustrated in ***figure (3.4).*** The chemical structure of the vinyl ester resins AVEMPR and MAVEMPR was confirmed by ^{1}HNMR analysis. In this respect, ^{1}HNMR spectra of vinyl ester resins AVEMPR and MAVEMPR were represented in ***Figure (3.5 a and 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 rosin adduct. 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 EMPE derivative.

3.3 SYNTHESIS OF UNSATURATED POLYESTER RESINS

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. The preparation of unsaturated polyester is based on condensation reaction between acids, APA, MPA, PA, AdA or MA, and glycol such as EG and PG. In this respect, APA or MPA adduct was reacted with ethylene glycol (EG) and



AVEMPR (R=H)
MAVEMPR (R=CH_3)

Figure (3.4): Scheme of synthesis of MPA vinyl ester resins

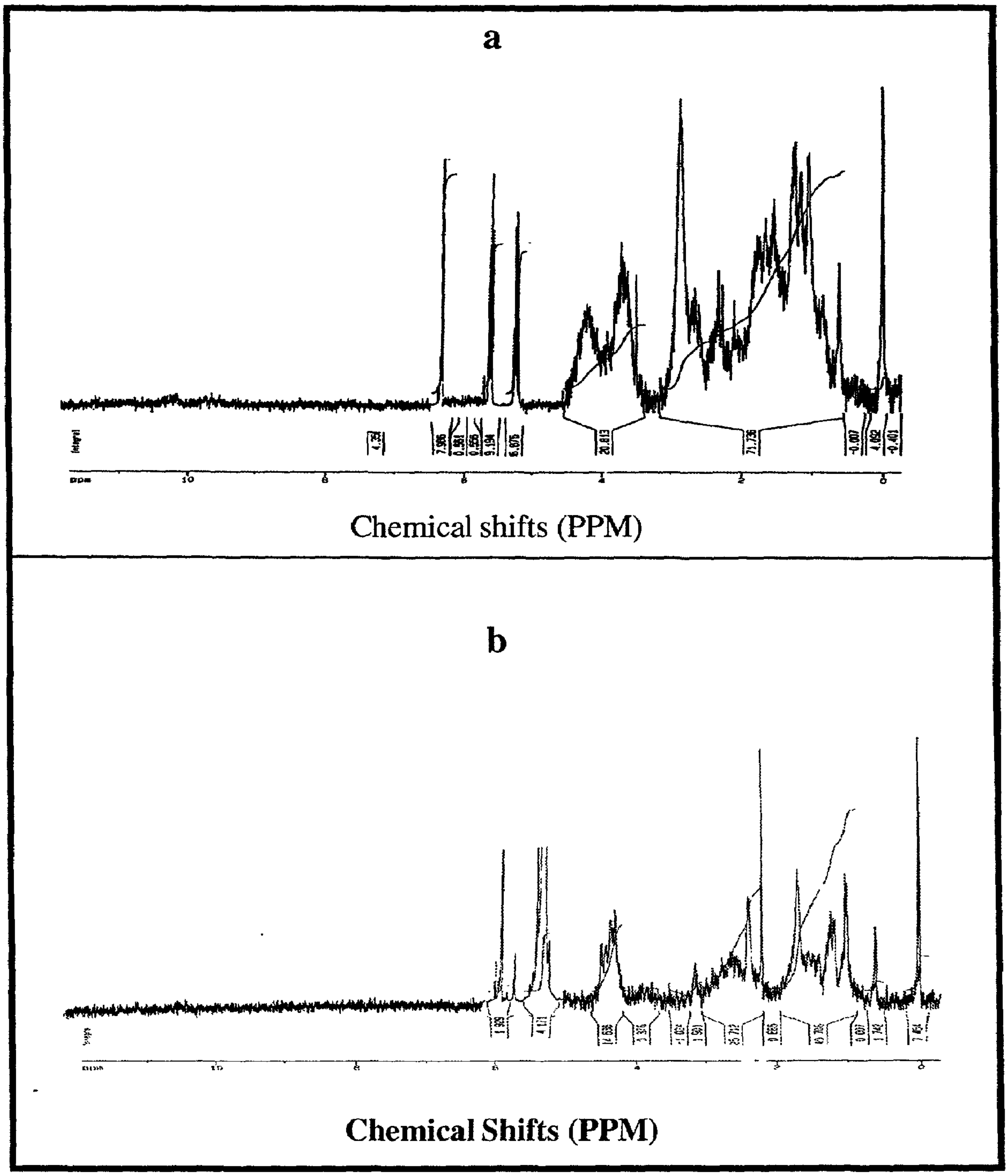


Figure (3.5): ^{1}HNMR spectra of a)- AVEMPR and b)-MAVEMPR.

maleic anhydride (MA) by solvent method as reported in the experimental section. The unsaturated polyesters under investigation are composed mainly of three categories being, saturated dibasic acids, unsaturated dibasic acids and glycols. The resin is then diluted with vinyl or divinyl monomers. The possible combinations of unsaturated polyester and vinyl monomer permit a wide range of properties to be obtained. In the industrial manufacture of polyester resins, however, the choice of raw materials will be determined by availability and cost, and by the particular characteristics required in final result. In the present investigation, two different UP resins were prepared. The unsaturated diacid used in all cases is MA. The first type of UP is based on APA while the second is based on MPA glycol esters. The variable materials were saturated acid and glycols. The selected resins were designated as UP1, UP2, UP3, UP4, UP5 and UP6 for which EG, EG-PA, EG-AdA, PG, PG-PA and PG-AdA were used as glycols and saturated diacid. The polycondensation reaction to prepare UP was followed up from the measuring of water volume which collected during the course of reaction. It was observed that upon raising the temperature from 180 °C to 200 °C, about 70 % of the total quantity of water removed rapidly then reduces smoothly and slowly near to the end of reaction. This leads to speculate that the polycondensation reaction proceeds very fast up to certain limit, when the reaction exceeds this limit, the molecular weight of the growing molecules increases markedly. Consequently, the viscosity of the reaction mixture increases and the diffusion of the reactive groups decrease by the same factor. An obvious necessity for a reaction to occur is collision between the reactive groups.

The rate of the reaction is then proportional to the overall concentration of the reactive groups. As the polyesterification reaction proceeds, the number of the active groups was reduced. At the same time, each of the reactive molecules is surrounded by a set of neighboring polymer molecules which form a cage. The reactive molecule oscillates in the cage, suffering a series of collisions with its neighbors before being able to escape from the cage. The rate of escape is proportional to the diffusivity and inversely proportional to viscosity. Upon increasing the temperature to 200°C, the viscosity of the medium reduces and the thermal motion of the reactive molecule increases. Accordingly, the rate of escape and the collision probability of active molecules increase. This leads to a further increasing of water quantity which removed from the polyesterifcation reaction. However, the concentration of the reactive groups is decreasing with increasing the reaction time. Consequently, the number of collisions is reduced.

The molecular weights of the prepared UP resin were determined using end group analysis as described in the experimental section. 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 becomes insensitive at high molecular weight (above 25,000 g/mol) as the fraction of end groups becomes too small to be measured with precision [160]. End group in condensation polymers usually involves chemical methods of analysis for functional groups. Carboxyl and hydroxyl groups in polyester are usually titrated with a titrable reagent [161]. In the present study the resultant molecular weights were listed in **table (3. 1)** in conjunction with the acid number of the prepared polyesters. The degree of polymerization of the prepared UP were calculated and listed in **table (3. 1)**. Careful inspection of data indicate that the degree of polymerization was increased with using PA and MPA as dibasic acids and EG as glycol. On the other hand, the degree of polymerization was decreased with using AdA and APA as dibasic acids and PG as glycol. This observation indicates that the degree of polymerization values was reduced with decreasing the molecular weight of the used dibasic acid. This observation runs in harmony well with the conclusion drawn in the work based on polycondensation of saturated dibasic acid with EG [162].

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 w% UP. 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 the prepared UP was confirmed by IR and ^{1}HNMR analyses. In this respect, the IR spectra of MPAUP1 and APAUP1 were selected and represented in ***figure 3.6 and 3.7,*** respectively. While ^{1}HNMR spectra of were selected as representative samples and given in ***figures (3.8 -3.12),*** respectively. The characteristic bands in the IR spectra of UP(***Figures 3.6 -3.7*** are observed at 3450 cm $^{-1}$ as sharp strong band (γ OH end group), 1730 cm $^{-1}$ as sharp strong band (γ C= O in COO ester group), 1470 cm $^{-1}$ as sharp medium band (double bond in hydrophenanthrene moiety) and 1110 cm $^{-1}$ as broad strong band (γ_{C-O} of ester group). The disappearance of the bands characteristic of cyclic anhydride group of MPA at 1780 and 1850 cm $^{-1}$ ($\gamma_{C=O}$ of cyclic anhydride group) and

Table (3. 1): Molecular Weight of the Produced UP and Their Hydroxyl Numbers and Carboxylic Values.

Designation	OH Number mg KOH/g	COOH value mg KOH/g	Mn g/mol	n
MPAUP1	10.1	17.6	4050	7
MPAUP2	12	7.5	5753	8
MPAUP3	8.5	10	6064	8
MPAUP4	17	13	3740	6
MPAUP5	10.8	12.8	4754	6
MPAUP6	13.1	8.5	5194	7
APAUP1	3.5	27.5	3619	6
APAUP2	26	8.3	3271	5
APAUP3	10	11.2	5292	7
APAUP4	14	18	3506	6
APAUP5	9	13.5	4986	6
APAUP6	15	9.5	4579	5

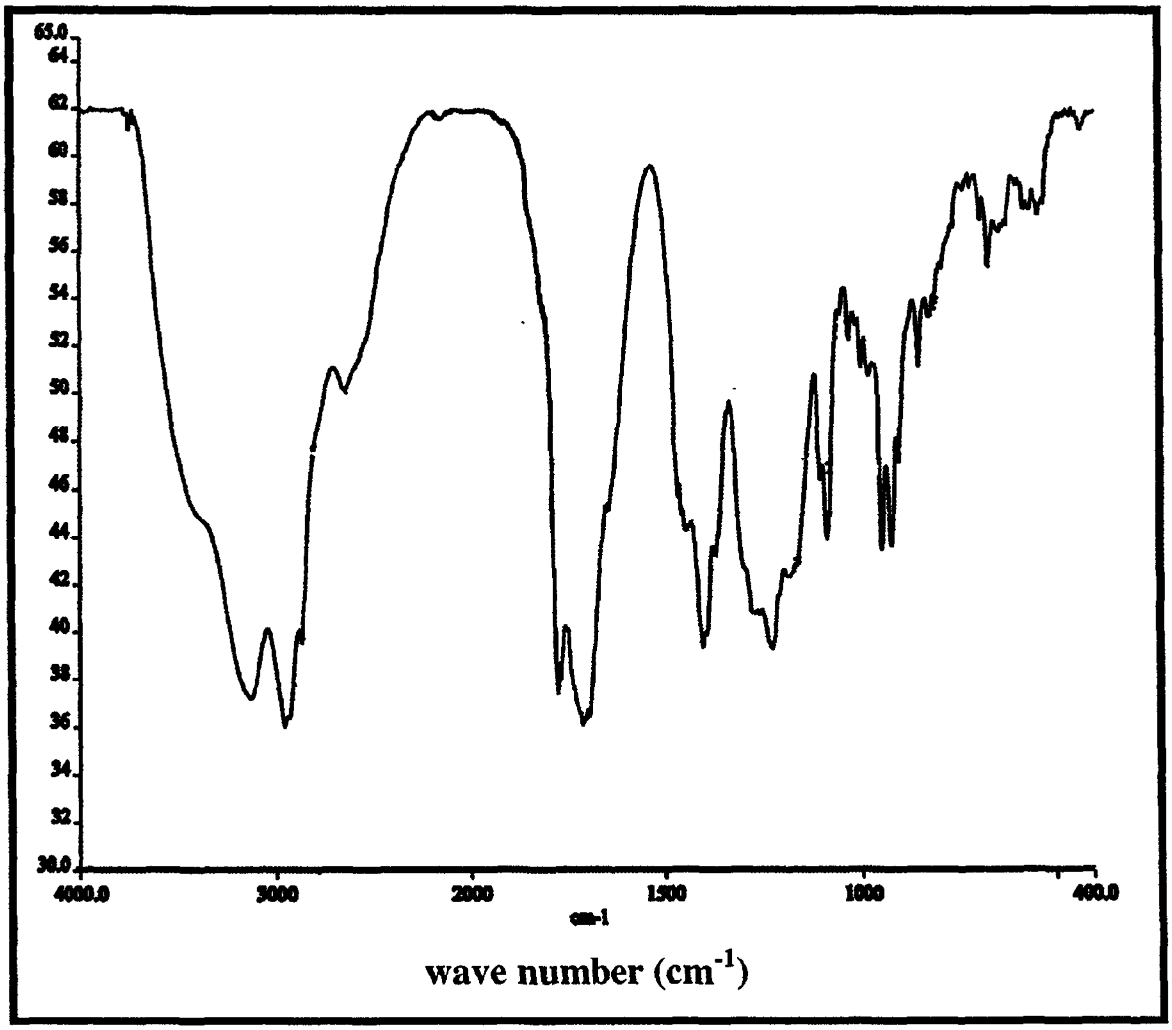


Figure (3.6): IR spectrum of MPAUP1.

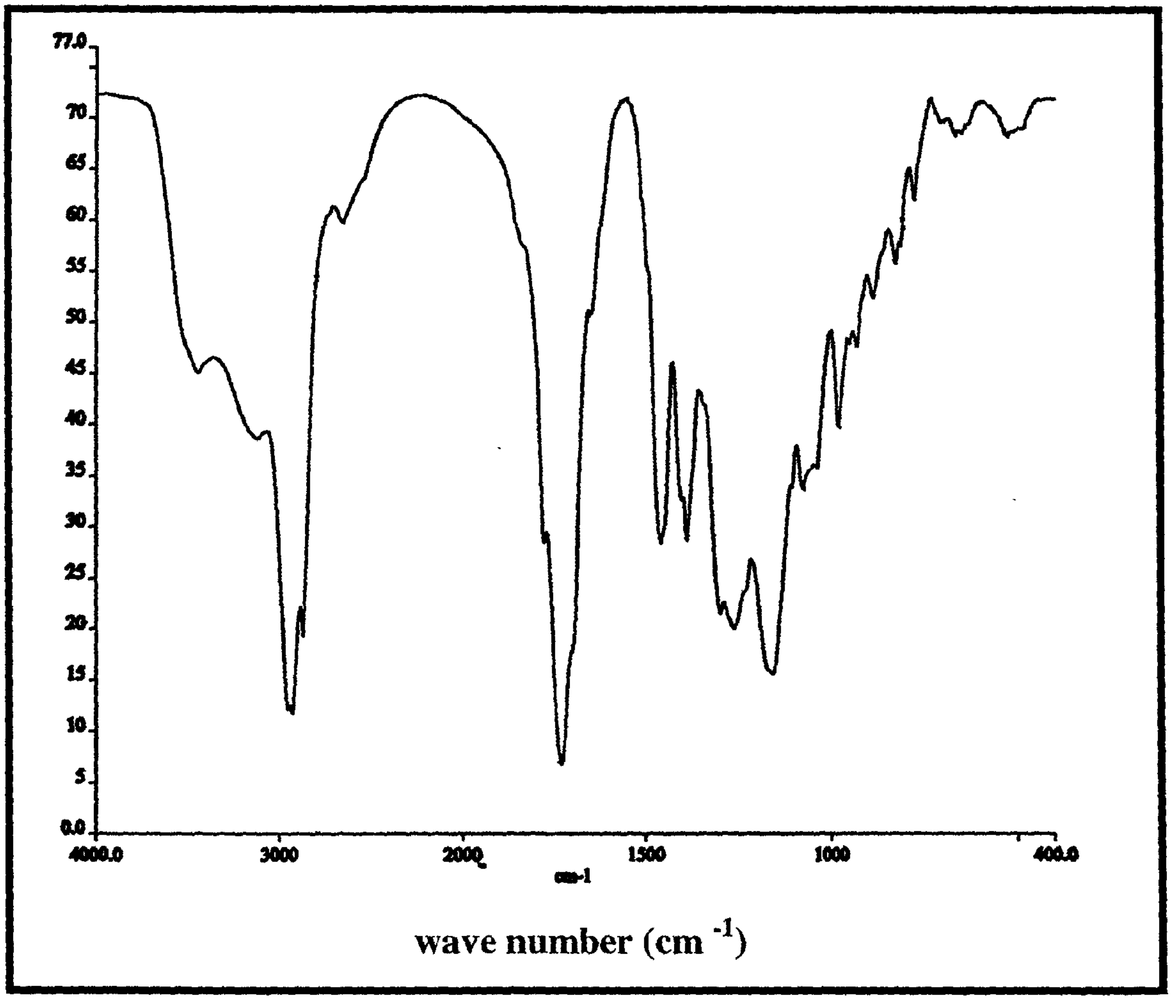


Figure (3.7): IR spectrum of APAUP1.

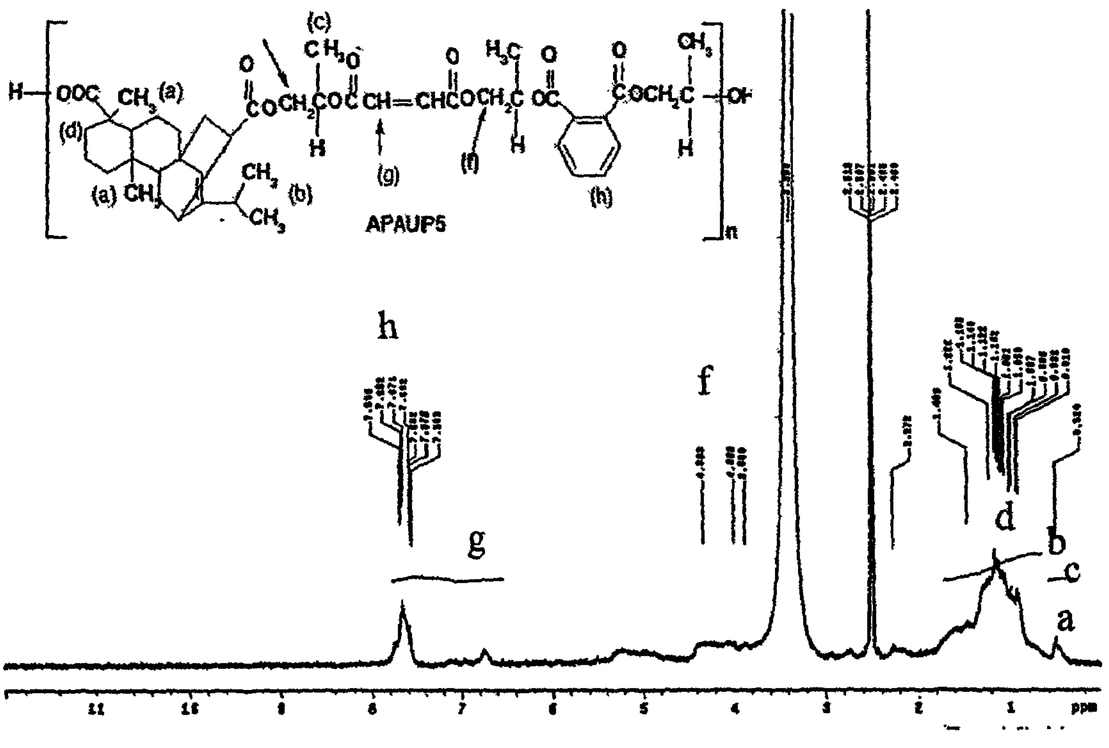


Figure (3.8): ^{1}HNMR Spectrum of APAUP5.

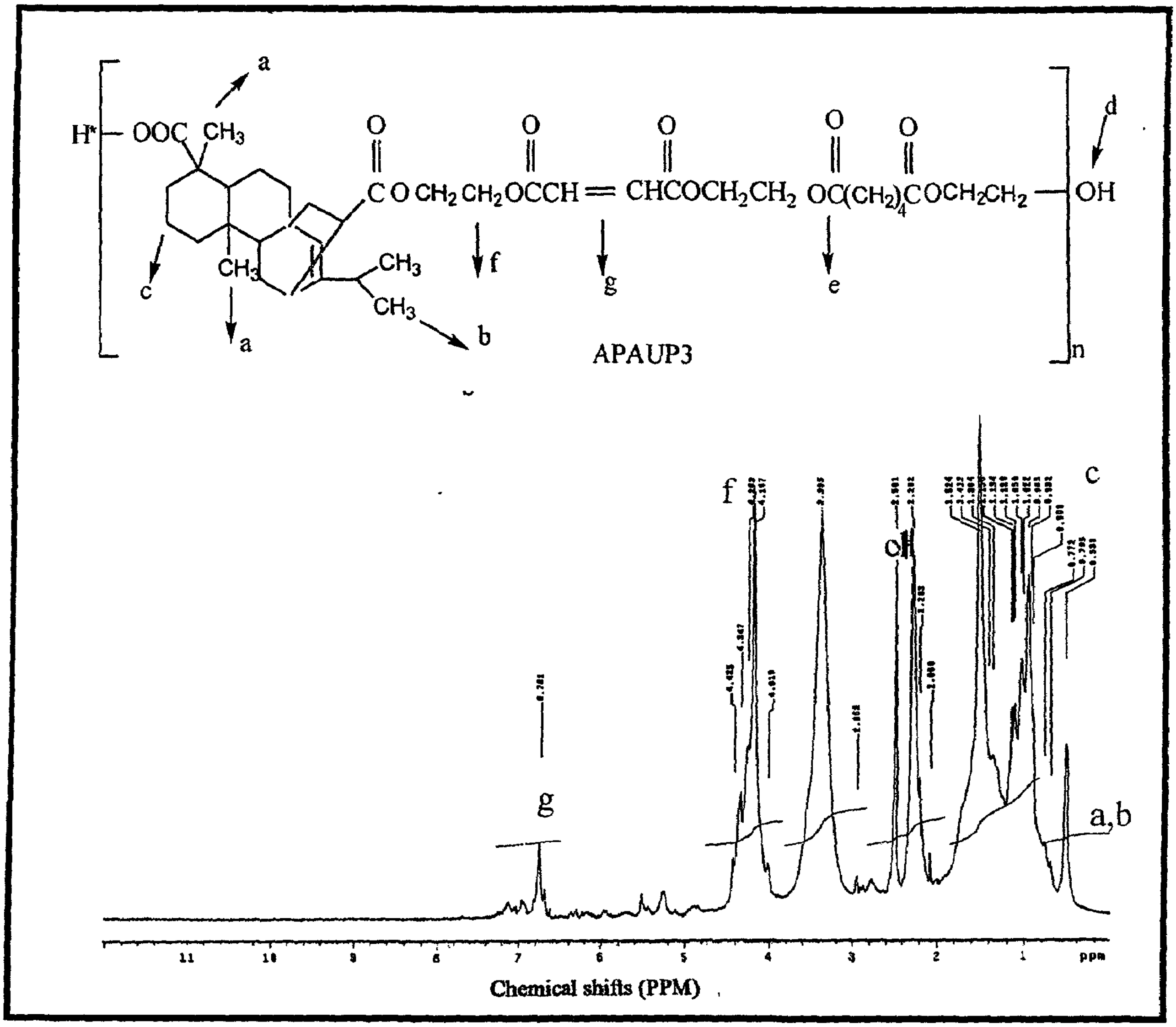


Figure (3.9): ^{1}**HNMR Spectrum of APAUP3.**

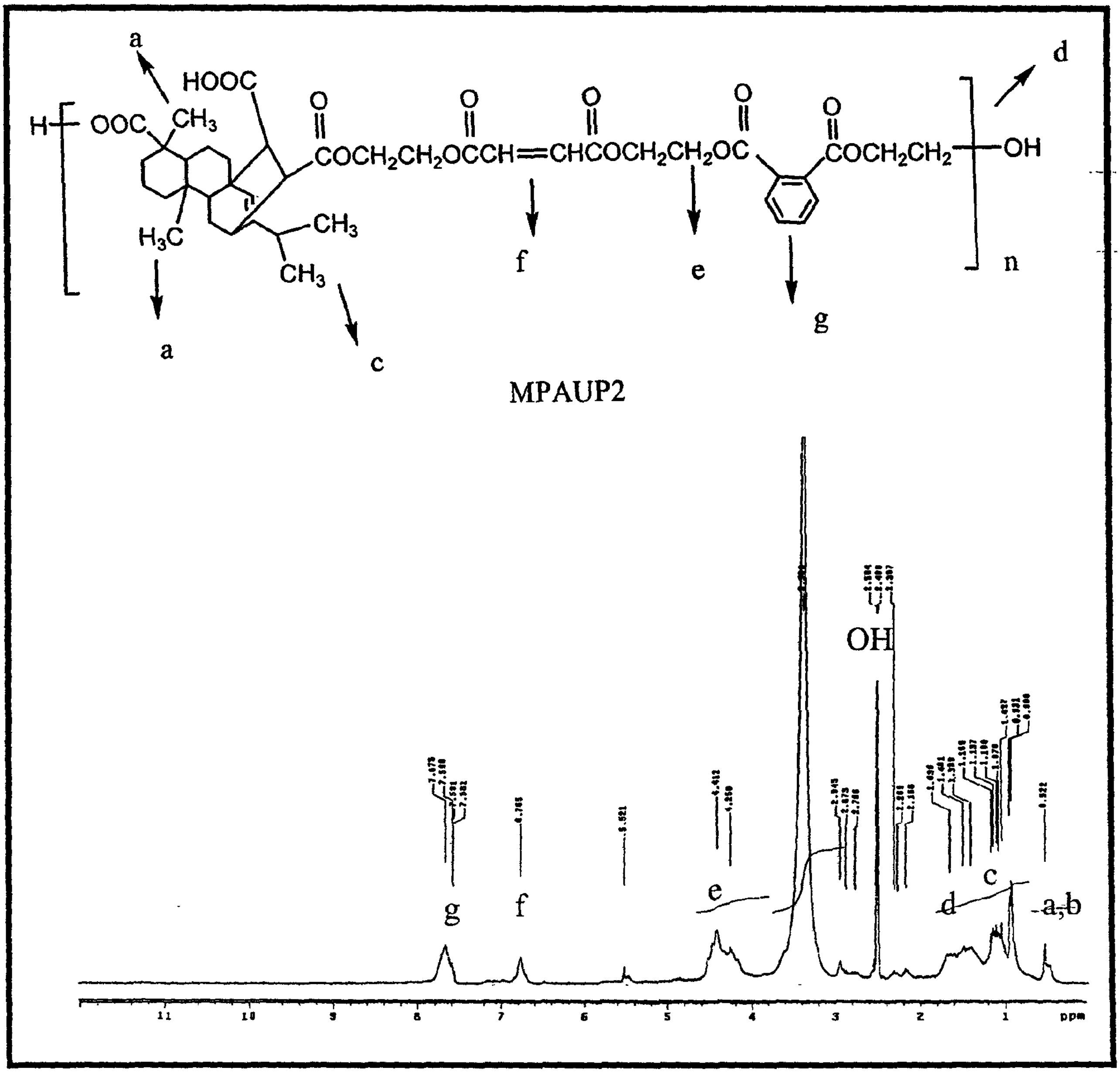


Figure (3.10): ^{1}**HNMR Spectrum of MPAUP2**

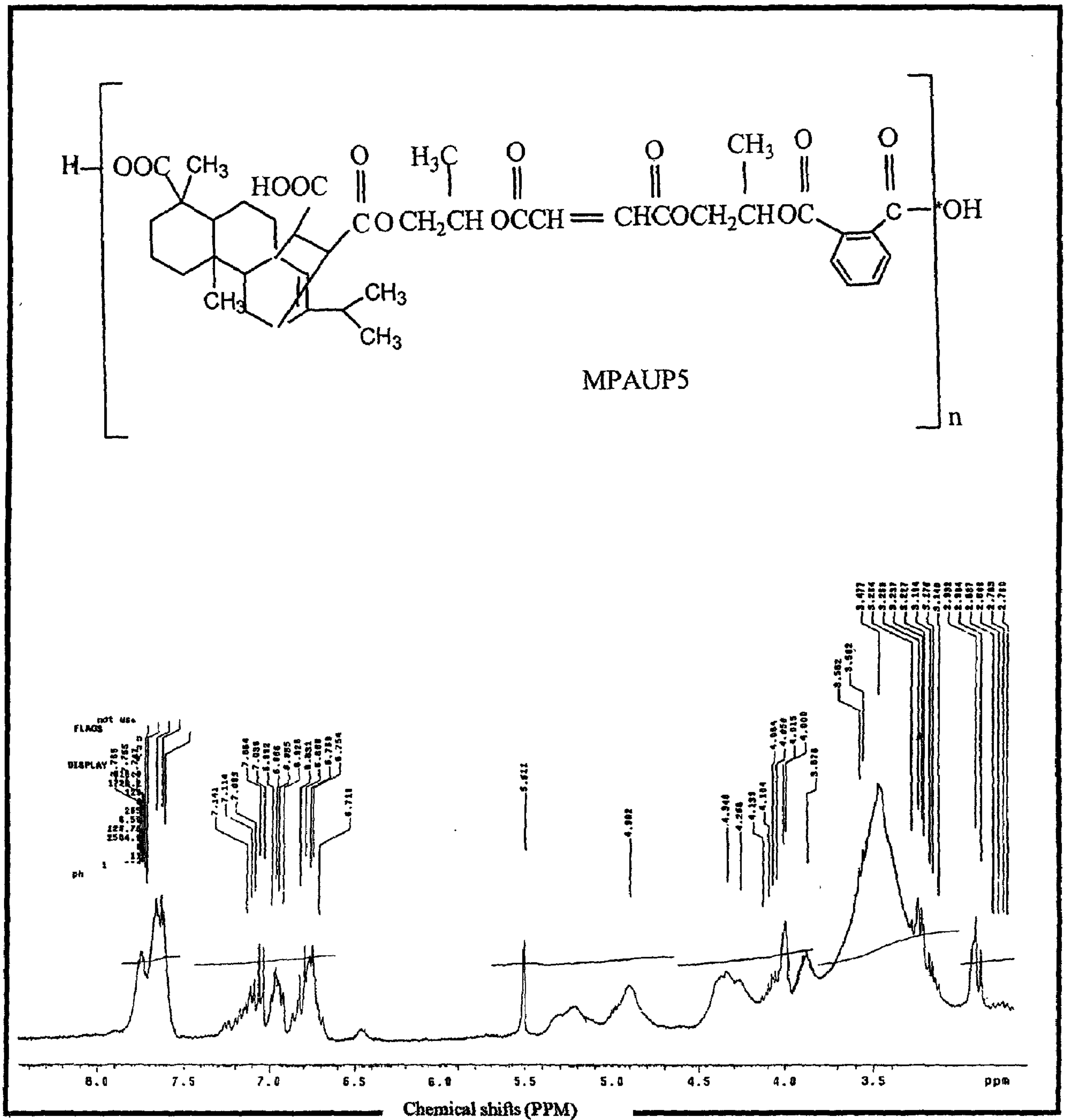


Figure (3.11): ^{1}**HNMR Spectrum of MPAUP5.**

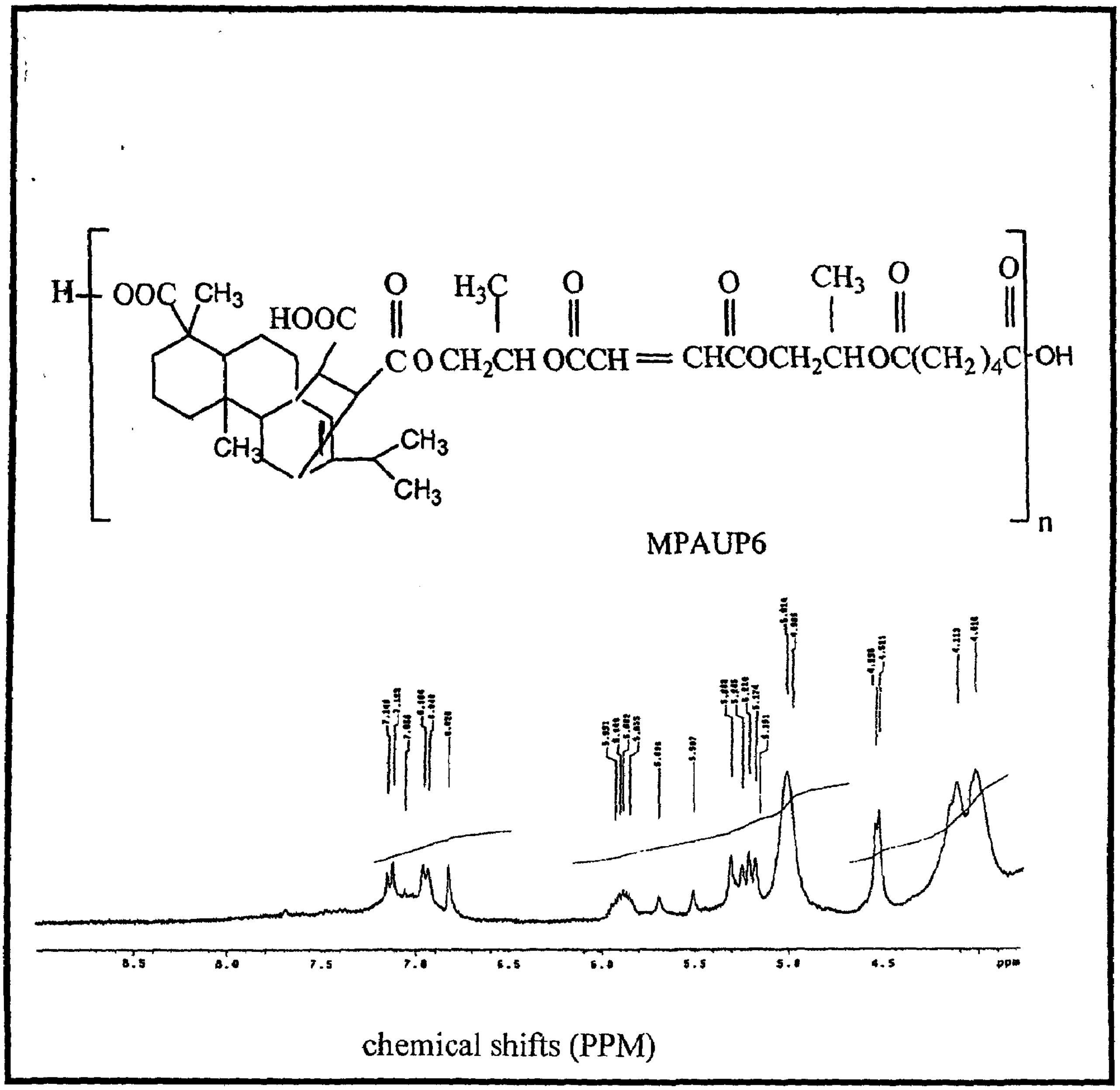


Figure (3.12): ^{1} HNMR spectrum of MPAUP6.

the appearance of bands at 1735 cm $^{-1}$ ($\gamma_{C=0}$ sym in ester), 1710 cm $^{-1}$ ($\gamma_{C=0}$, sym of COOH) indicate that the esterfication of MPA was completed by reaction of carboxylic group OH group of EG or PG. The IR spectra of all UP based on PA show bands at 1580 and 1555 cm $^{-1}$ correspond to aromatic $\gamma_{C=C}$ stretching vibrations.

The ^{1}HNMR spectra of UP, show signals at δ 6.8 and 2.5 ppm which assigned to unsaturation system of MA(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. The spectra of UP containing PA show a complicated aromatic proton signals multiplet at 7.8 ppm. The spectral data for all UP derivatives are illustrated in brief **Tables (3. 2 and 3.3)**.

Table (3.2): Spectral Data of UP Resins Based on MPA.

Assignment	MPA UP1	MPA UP2	MPA UP3	MPA UP4	MPA UP5	MPA UP6
Infrared Data (cm^{-1})						
O-H	**3350**	**3400**	**3350**	**3400**	**3450**	**3350**
C=O (ester)	**1735**	**1730**	**1733**	**1730**	**1735**	**1735**
C=O (acid)	**1700**	**1690**	**1700**	**1695**	**1700**	**1695**
C=C (MA)	**1650**	**1645**	**1650**	**1645**	**1650**	**1645**
C-O (ester)	**1175**	**1120**	**1150**	**1170**	**1150**	**1180**
C-H(Ph)	-	**750**	-	-	**760**	-
^{1}HNMR Chemical Shift (ppm)						
O-H (end glycol group)	2.5	2.5	2.5	2.5	2.5	2.5
H-C= (MA)	6.5	6.6	6.5	6.7	6.5	6.6
Aromatic H	-	7.6	-	-	7.6	-
O=CO-CH_2	4	3.9	3.9	3.8	3.85	3.9
ROSIN (=CH	5.36	5.4	5.4	5.32	5.34	5.42
CH3	**0.67-1.1**	**0.56-1.1**	**0.67-1**	**0.67-1**	**0.67-1.1**	**0.65-1**
CH_2)	**1.8**	**1.7**	**1.8**	**1.8**	**1.8**	**1.9**

Table (3.3): Spectral Data of UP Resins Based on APA.

Assignment	APA UP1	APA UP2	APA UP3	APA UP4	APA UP5	APA UP6
Infrared Data (cm^{-1})						
O-H	3450	3450	3450	3400	3450	3450
C=O (ester)	1735	1730	1733	1730	1735	1735
C=C (MA)	1650	1645	1650	1645	1650	1645
C-O (ester)	1185	1160	1170	1175	1170	1175
C-H(Ph)	-	760	-	-	760	-
^{1}HNMR Chemical Shift (ppm)						
O-H (end glycol group)	2.5	2.5	2.5	2.5	2.5	2.5
H-C= (MA)	6.5	6.6	6.5	6.7	6.5	6.6
Aromatic H	-	7.7	-	-	7.7	-
O=CO-CH$_2$	4	3.9	3.9	3.8	3.85	3.9
ROSIN =CH	5.36	5.4	5.4	5.32	5.34	5.42
CH3	0.67-1.1	0.56-1.1	0.67-1	0.67-1	0.67-1.1	0.65-1
CH$_2$	1.8	1.7	1.8	1.8	1.8	1.9

3.4 CURING EXOTHERMS

The curing stage is the second step in the preparation of thermoset polymers. The choice of resin and curing agent depends on the method of 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 acrylate or 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. Several methods based on data of dynamic mechanical analysis (DMA) [163] rheological measurement, near infrared analysis [164] and thermal differential scanning calorimetry (DSC) were used to study the curing kinetic mechanisms. In this respect, the present section concerns with studying the curing mechanisms of vinyl ester and unsaturated polyester resins at different conditions. In the present work, the curing exotherms of the prepared formulae were obtained by plotting the curing temperature as a function of time at different temperature ranged from 35°C to 55°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.

3.4.1 Curing Exotherms of UP with Styrene

The unsaturated polyesters, UP, 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 styrene content is very high or very low the obtained resins will have high shrinkage on curing or a tendency to form partial full cured resins, respectively. Vaidya and Nadkarni [165] proposed an effective range for the styrene percentage in a polyester resin from 30 to 40 w %. In this investigation, a 40 w % for the blank resin was used, in accordance also to other literature sources [166]. In this respect, styrene has been also used as solvent for UP resins. Accordingly, 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 [167]. 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 [168-173]. 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, 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 [174]. To prevent premature gelation and to inhibit the spontaneous polymerization of the resin, hydroquinone was added as an inhibitor [175].

The curing exotherms curves of the prepared UP cured with styrene as curing agents were selected as representative samples and plotted in figures **(3.13-3.24)**. The maximum heat evolved, T_{max}, upon curing and time required for complete curing, t_{max}, obtained from these plots are included in **tables (3. 4-3.27)**. The S-shaped gelation curve, **figures (3.13-3.24)**, and the vitrification curve divide the time-temperature plot into four thermosetting-cur process: liquid, gelled rubber, ungelled glass and gelled. 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 are 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

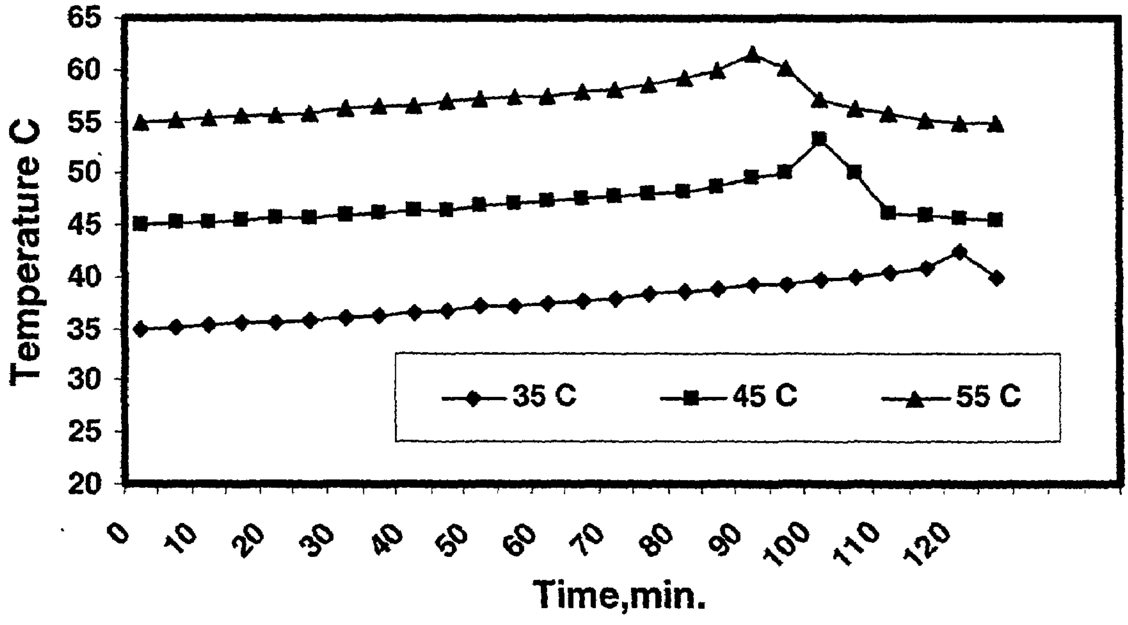


Figure (3.13): Curing exotherms of cured APAUP1 and styrene resins at different temperatures.

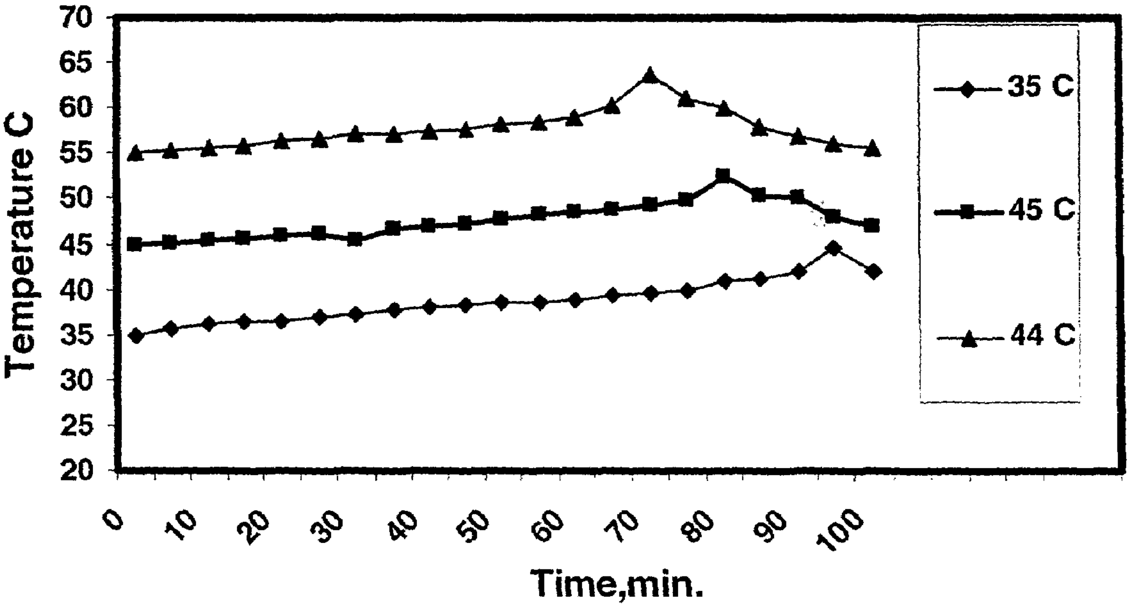


Figure (3.14): Curing exotherms of cured APAUP2 and styrene resins at different temperatures.

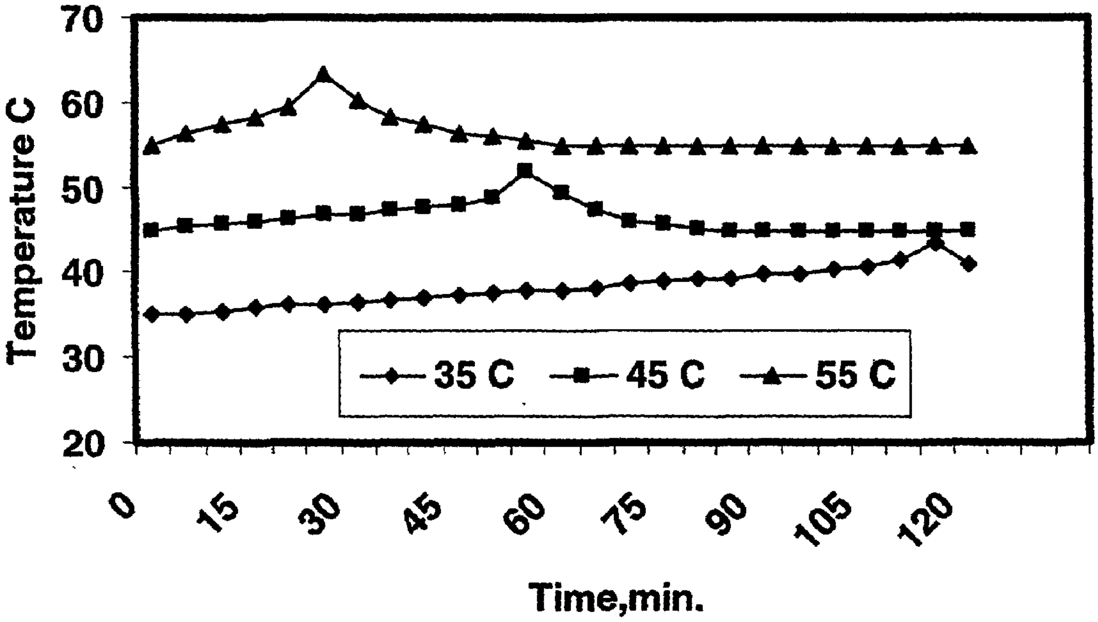


Figure (3.15): Curing exotherms of cured APAUP3 and styrene resins at different temperatures.

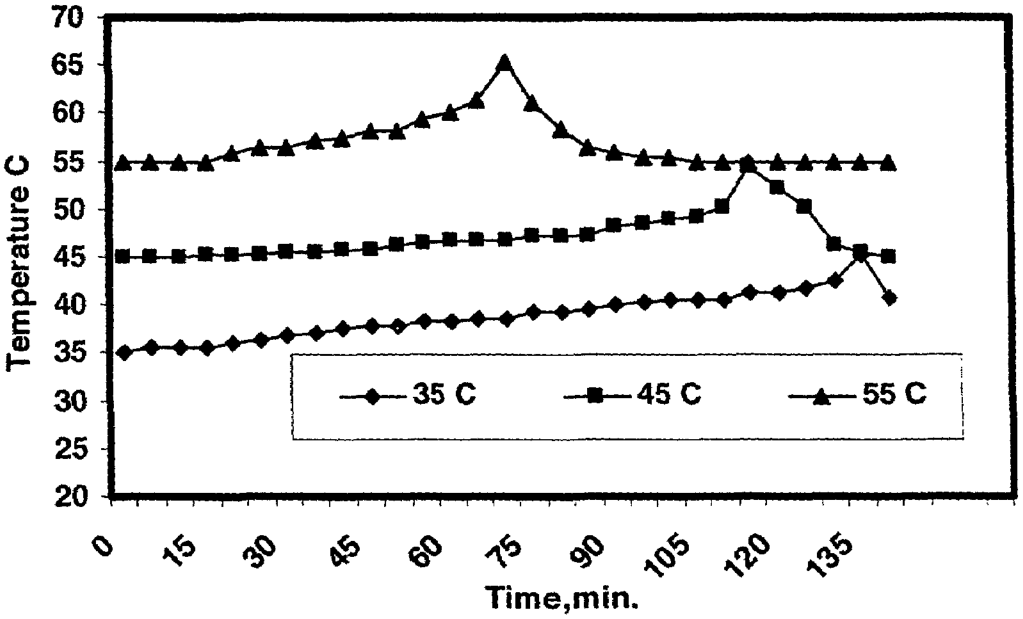


Figure (3.16): Curing exotherms of cured APAUP4 and styrene resins at different temperatures.

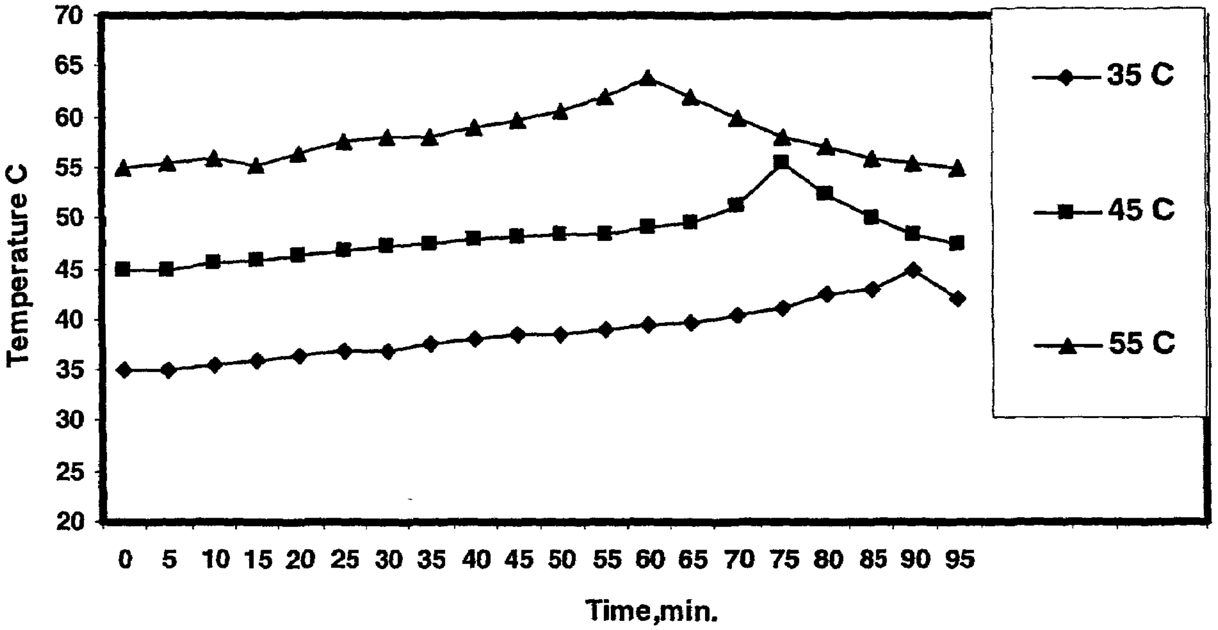


Figure (3.17): Curing exotherms of cured APAUP5 and styrene resins at different temperatures.

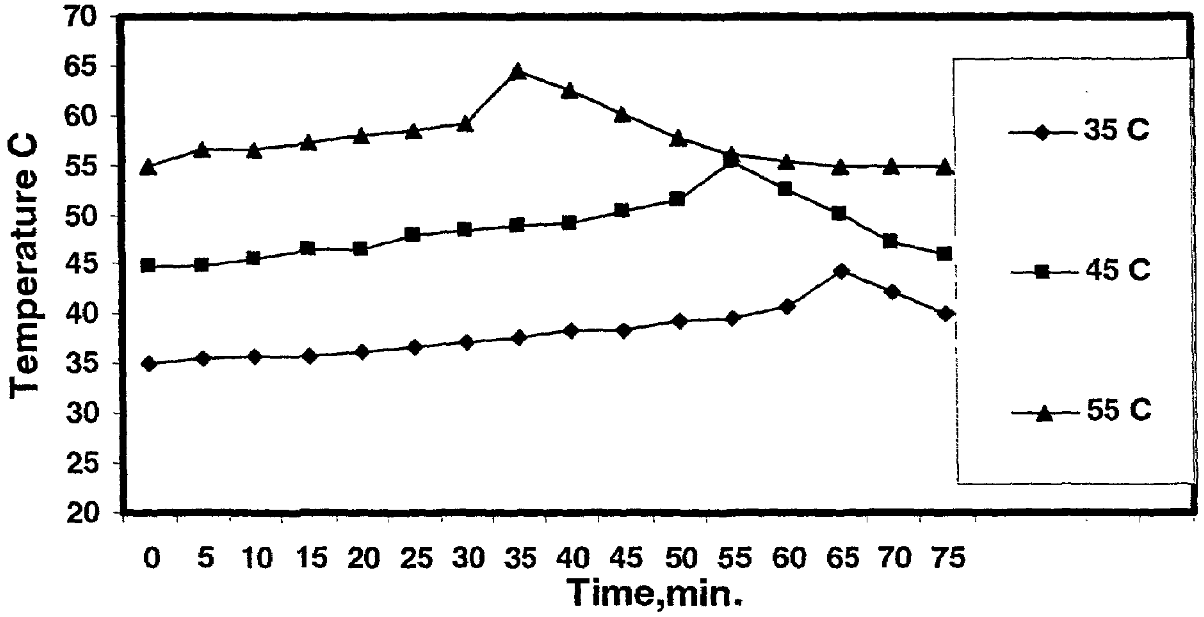


Figure (3.18): Curing exotherms of cured APAUP6 and styrene resins at different temperatures.

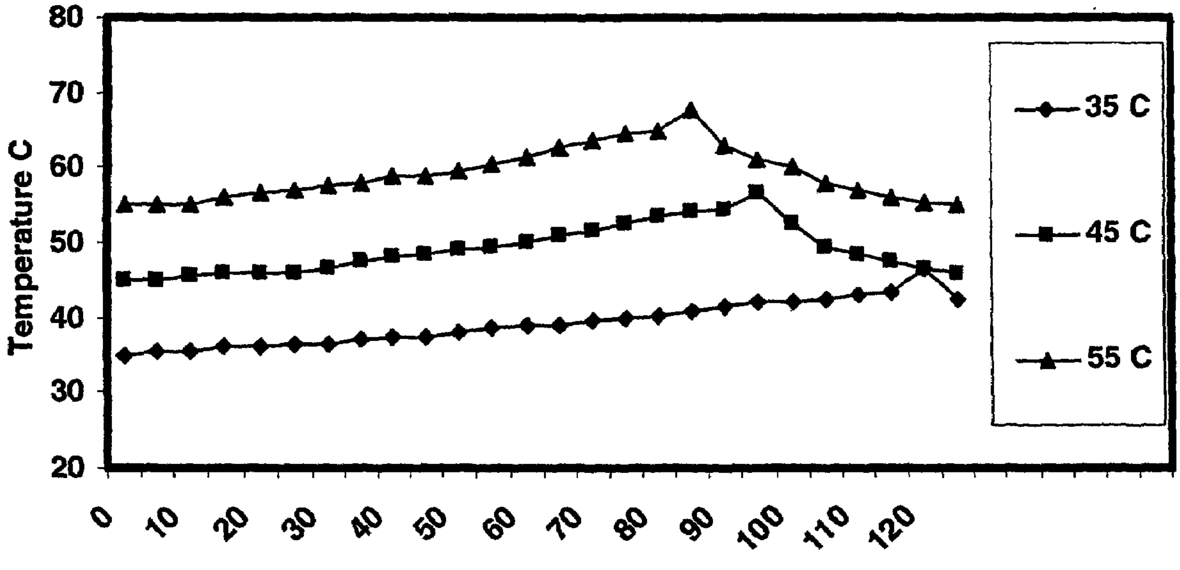


Figure (3.19): Curing exotherms of cured MPAUP1 and styrene . resins at different temperatures.

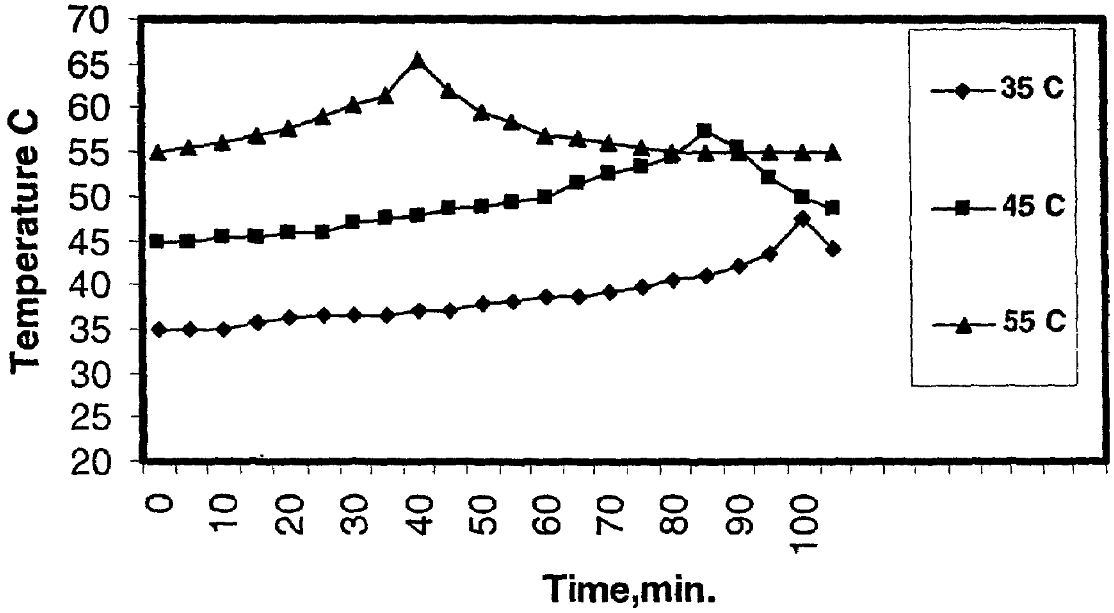


Figure (3.20): Curing exotherms of cured MPAUP2 and styrene resins at different temperatures.

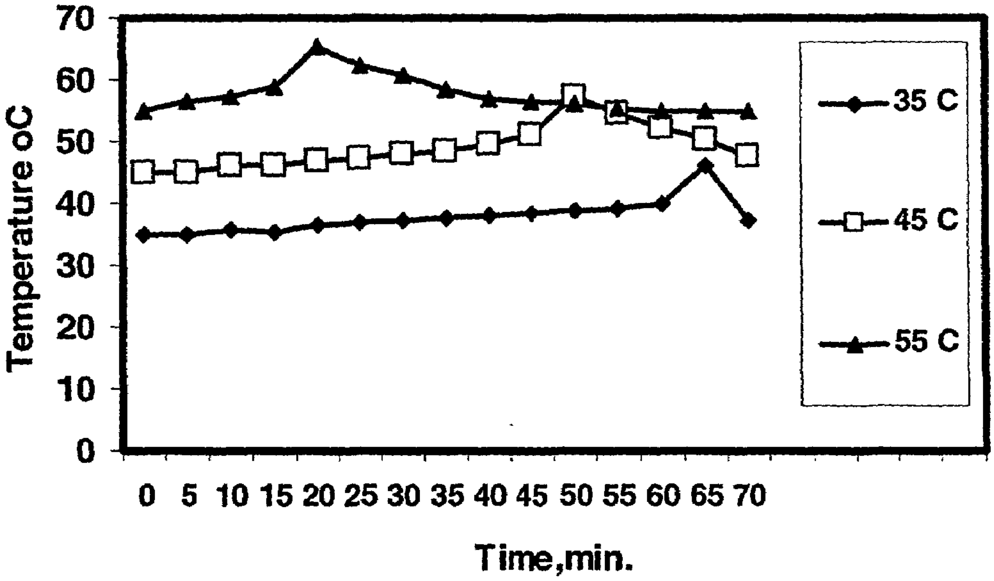


Figure (3.21): Curing exotherms of cured MPAUP3 and styrene resins at different temperatures.

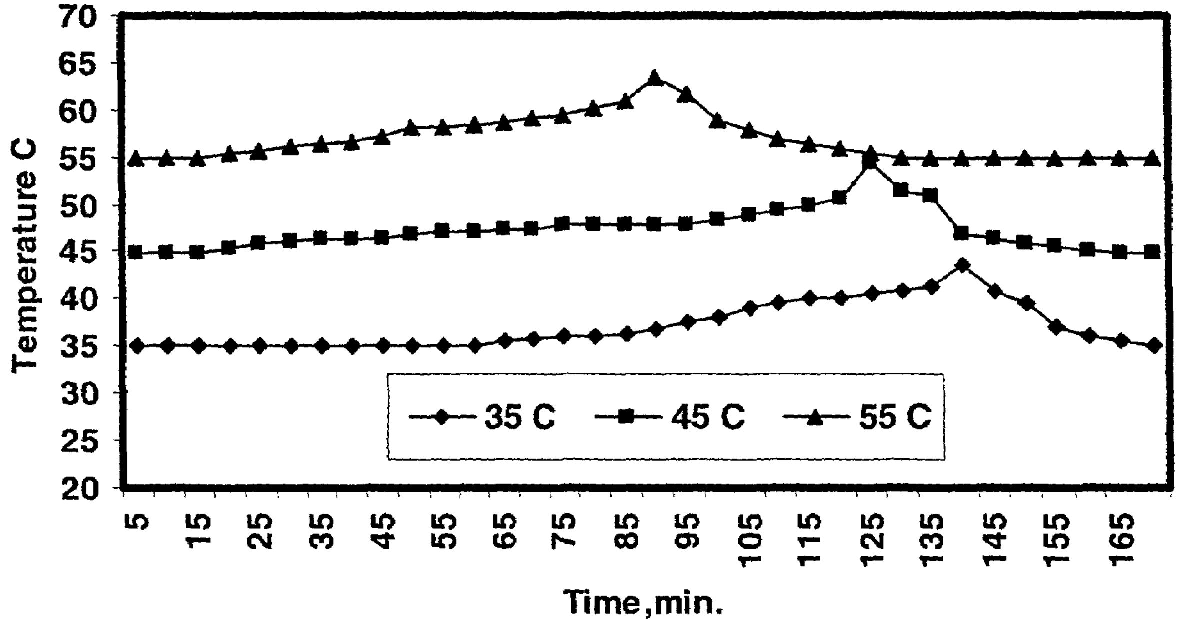


Figure (3.22): Curing exotherms of cured MPAUP4 and styrene resins at different temperatures.

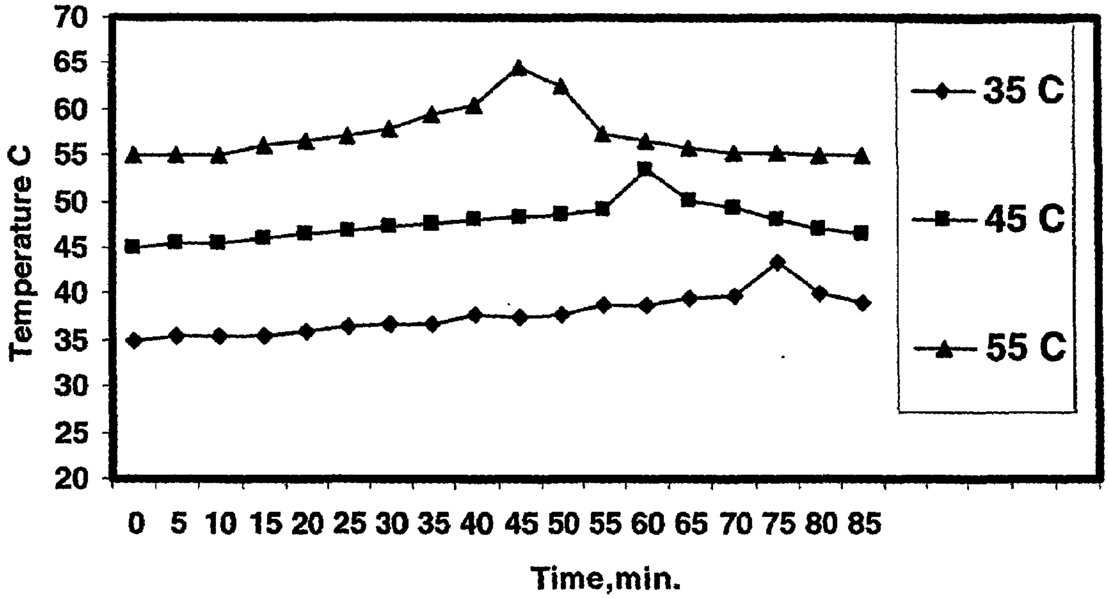


Figure (3.23): Curing exotherms of cured MPAUP5 and styrene resins at different temperatures.

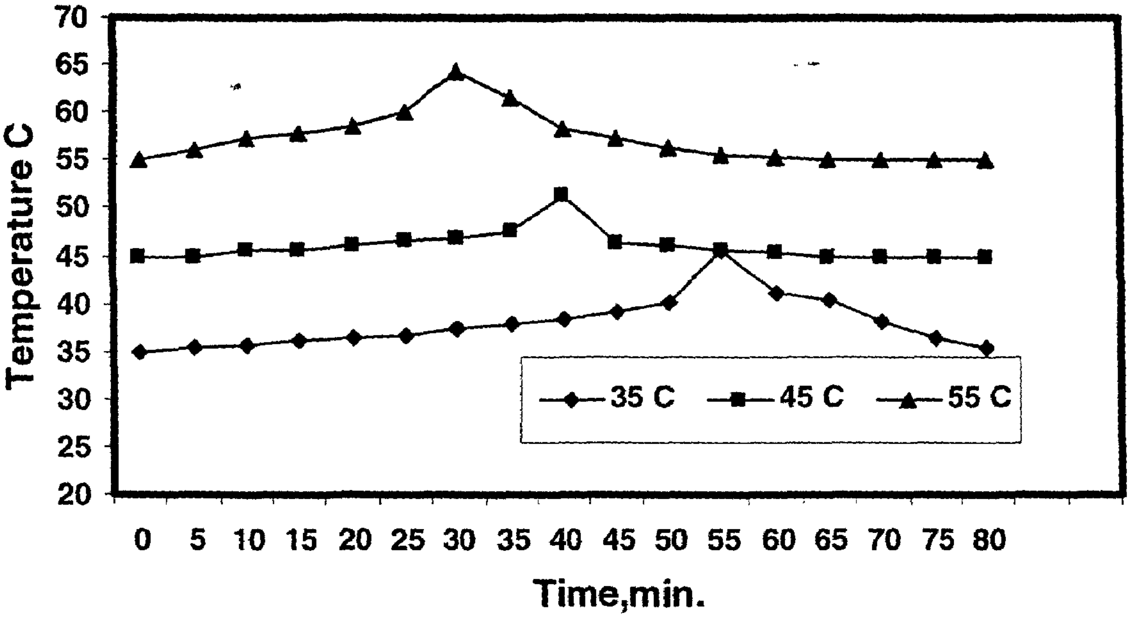


Figure (3.24): Curing exotherms of cured MPAUP6 and styrene resins at different temperatures.

Table (3.4): Curing Parameters of APAUP1 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	115	41	100	53	90	61
5	70	55.4	66	67.5	54	69.7
10	69	56.3	63	68.5	51	70.1
15	67	58.0	62	70	50	71.5
20	65	59.8	61	72.3	48	72.4
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

***:60%** AVEMPR, **40% styrene**

Table (3.5): Curing Parameters of APAUP1 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	115	41	100	53	90	61
5	74	53.4	72	66	57	68
10	73	55.4	70	67.1	56	69.2
15	72	57.2	68	69.2	54	70.1
20	70	59.3	66	70	53	71.0
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

***:60%** MAVEMPR, **40% styrene**

Table (3.6): Curing Parameters of APAUP2 with AVEMPR at Different Temperatures

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^{1}_{max} minute	T^{1}_{max} (°C)	t^{2}_{max} minute	T^{2}_{max} (°C)	t^{3}_{max} minute	T^{3}_{max} (°C)
0	95	44	80	52	70	63
5	65	57.8	60	69.5	50	71.7
10	60	59.1	57	71.5	46	72.1
15	55	62.0	52	73	42	74.5
20	52	63.5	49	75.1	40	77.4
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

***:60% AVEMPR, 40% styrene**

Table (3.7): Curing Parameters of APAUP2 with MAVEMPR at Different Temperatures

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^{1}_{max} minute	T^{1}_{max} (°C)	t^{2}_{max} minute	T^{2}_{max} (°C)	t^{3}_{max} minute	T^{3}_{max} (°C)
0	95	44	80	52	70	63
5	70	55.4	62	63	53	69
10	67	56.4	60	64.1	51	70.2
15	64	58.2	59	66.2	49	72.8
20	60	59.3	55	69	47	74.0
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C, 60% MAVEMPR, 40% styrene

Table (3.8): Curing Parameters of APAUP3 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	115	43	55	52	25	63
5	67	55.4	53	65	23	68
10	65	56.3	51	67	22	70
15	61	58.0	50	68	20	72
20	58	59.8	48	69	19	73
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.9): Curing Parameters of APAUP3 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	115	43	55	51	25	63
5	74	53.4	63	64	24	69
10	73	55.4	61	66	23	70
15	72	57.2	59	68	21	71
20	70	59.3	57	69	20	72
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C, *:60% MAVEMPR, 40% styrene

Table (3.10): Curing Parameters of APAUP4 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	135	45	115	54	70	65
5	87	52.4	82	65	67	67
10	83	54.4	80	66.1	64	68.2
15	82	56.2	78	68.2	62	70.5
20	80	58.3	76	70	59	71.4
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.11): Curing Parameters of APAUP4 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	135	45	115	54	70	65
5	94	53.4	88	66	68	68
10	91	55.4	85	67.1	66	69.2
15	82	57.2	80	69.2	65	70.1
20	80	59.3	78	70	63	71.0
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.12): Curing Parameters of APAUP5 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	80	42	75	55	60	64
5	60	58.8	55	69.5	53	72.7
10	57	60.1	52	72.5	49	73.1
15	52	63.0	50	74	46	74.5
20	45	64.5	43	76.1	40	78.4
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.13): Curing Parameters of APAUP5 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	80	42	75	55	60	64
5	63	56.8	58	68.5	55	70.7
10	60	58.1	54	70.5	53	72.1
15	58	60.0	51	71	49	73.5
20	54	61.5	45	72.1	42	75.4
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.14): Curing Parameters of APAUP6 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	65	44.5	55	55	35	65
5	50	59.8	45	69.5	33	73.7
10	47	61.1	42	73.5	32	74.1
15	42	64.0	40	75	30	74.5
20	40	65.5	38	75.1	28	75.4
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.15): Curing Parameters of APAUP6 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	65	44.5	55	55	35	65
5	55	59.2	48	69.1	34	73.2
10	49	60.1	45	73.2	33	73.1
15	45	63.0	43	74	32	73.5
20	43	64.5	41	73.1	30	74.4
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.16): Curing Parameters of MPAUP1 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	120	46.5	95	56.5	85	68
5	86	53	80	63	75	70
10	83	55	75	65	70	72
15	80	56	70	67	64	73
20	76	57	66	69	60	74
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.17): Curing Parameters of MPAUP1 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	120	46.5	95	56.5	85	68
5	96	52	88	62	80	69
10	90	54	85	64	75	70
15	86	55	82	65	71	71
20	82	56	76	68	68	73
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.18): Curing Parameters of MPAUP2 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	100	47.5	85	57.5	40	65.5
5	76	54	70	64	65	71
10	74	56	68	66	62	73
15	70	57	64	68	60	74
20	66	58	61	70	55	75
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.19): Curing Parameters of MPAUP2 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	100	47.5	85	57.5	40	65.5
5	78	52	73	62	68	69
10	75	53	70	64	66	70
15	72	55	68	66	63	71
20	69	57	65	69	59	72
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C, *:60% MAVEMPR, 40% styrene

Table (3.20): Curing Parameters of MPAUP3 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	65	46	50	57	20	65
5	56	59	50	66	45	73
10	54	60	48	67	42	74
15	50	61	44	68	40	74.8
20	46	61.5	41	71	38	76
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

***:60% AVEMPR, 40% styrene**

Table (3.21): Curing Parameters of MPAUP3 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	65	46	50	57	20	65
5	59	58	55	64	49	70
10	57	59	52	65	45	72
15	55	60	50	66	43	73
20	49	61	47	70	40	74
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.22): Curing Parameters of MPAUP4 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	140	43.5	125	54.5	90	63
5	96	48	90	60	85	65
10	93	50	85	62	80	66
15	90	52	80	63	74	68
20	86	53	76	65	70	70
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

***:60% AVEMPR, 40% styrene**

Table (3.23): Curing Parameters of MPAUP4 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	140	43.5	125	54.5	90	63
5	103	46	98	58	95	63
10	99	48	95	60	90	64
15	97	49	92	61	84	66
20	93	50	86	62	80	68
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.24): Curing Parameters of MPAUP5 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	75	43.5	60	53.5	45	64
5	60	57	55	63	40	67
10	58	58	53	64	38	68
15	55	60	48	65	35	70.8
20	52	60.5	45	68	33	72
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

*:60% AVEMPR, 40% styrene

Table (3.25): Curing Parameters of MPAUP5 with MAVEMPR at Different Temperatures

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^1_{max} minute	T^1_{max} (°C)	t^2_{max} minute	T^2_{max} (°C)	t^3_{max} minute	T^3_{max} (°C)
0	75	43.5	60	53.5	45	64
5	63	56	58	60	43	65
10	60	57	56	61	40	66
15	58	58	54	62	38	68.8
20	56	59.5	50	64	35	70
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

Table (3.26): Curing Parameters of MPAUP6 with AVEMPR at Different Temperatures.

AVEMPR (wt %)	Curing parameters at different temperatures					
	t^{1}_{max} minute	T^{1}_{max} (°C)	t^{2}_{max} minute	T^{2}_{max} (°C)	t^{3}_{max} minute	T^{3}_{max} (°C)
0	55	45.5	40	51	30	64
5	50	62	38	68	25	74
10	44	63	33	69	22	75
15	40	64	28	70	20	75.8
20	36	64.5	25	71	18	76
AVEMPR *	47	62	42	73	38	75.1

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C

***:60% AVEMPR, 40% styrene**

Table (3.27): Curing Parameters of MPAUP6 with MAVEMPR at Different Temperatures.

MAVEMPR (wt %)	Curing parameters at different temperatures					
	t^{1}_{max} minute	T^{1}_{max} (°C)	t^{2}_{max} minute	T^{2}_{max} (°C)	t^{3}_{max} minute	T^{3}_{max} (°C)
0	55	45.5	40	51	30	64
5	52	61	39	66	29	70
10	48	62	36	67	27	71
15	45	63	32	68	25	72.8
20	40	63.5	30	70	22	74
MAVEMPR *	50	60	48	71	42	73

1: at temperature 35° C 2: at temperature 45°C

3: at temperature 55°C , *:60% MAVEMPR, 40% styrene

polymer molecular weight rises steadily throughout the reaction:

$$\mathbf{R\text{-}OOH + Co^{2+} \longrightarrow RO^{\cdot} + OH + Co^{3+}}$$

$$\mathbf{R\text{-}OOH + Co^{3+} \longrightarrow R\text{-}O^{\cdot}O + H^{+} + Co^{2+}}$$

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 [176] after quenching, the yield can be increased by raising the temperature. In the present system Co (activator) and MEKP initiator) react to produce 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)*. 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.

The effect molecular weights of the prepared UP resins and their structure (determined by end group analysis), have been investigated. It was observed that the values of both T_{max} and t_{max}, which listed in **tables (3.4-3.27)**, are related to the structure of UP resins. In this respect, it was observed that the curing exotherms of UP based on APA have greater t_{max} and lower T_{max} values than that UP resins based on MPA when cured with styrene hardener at different temperatures. This can be related to the effect of molecular weight of the UP resin on the case of curing process. It is well known that the longer UP having high MA content is cured more easily than longer UP having low MA content. On the other hand, it can be observed that the structure of UP based on AdA shows high to low double bond temperature T_{max} and low curing time t_{max} than UP based on PA. Careful inspection of data of curing, **tables (3.4-3.27)**. This can be attributed content, polymerizable double bond, for UP, indicates that incorporation of PG in UP structure decreases curing times although UP resins based on PG have low MA content. This observation can be referred to fact that PG increases the miscibility between UP and styrene monomer. The increment of miscibity between UP and styrene increases the probability of curing of UP resins which decreases the curing time. It was also observed that the increase of temperatures for curing of all prepared UP in presence of styrene hardeners, from 35 to55°C decreases t_{max} of curing. This can be attributed to the increment of temperature strongly influences the ultimate crosslink density and increases molecular mobility resulting in higher cross-link density.

3.4.2 Curing Exotherms of UP with Vinyl Ester Resins

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 reactive diluents. 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. Commercial vinyl ester resins (VERs) consist of a bisphenol-A based dimethacrylate oligomers and styrene [177]. 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, it is generally recognized [178,179] that a lower concentration of styrene increases the rate of cure. As suggested [179], this is perhaps due to a decrease in the termination rate constant with increased the concentration of crosslinking species. (i.e. the dimethacrylate) that raises the polymerization rate [180] 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 methacrylyl radicals, as claimed by Rey et al. [181]. Due to the addition of bisphenol-A structure improves the rigidity of the polymer backbone and leads to improved mechanical properties [182,183]. In the present work VER are based on rosin adducts which 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. On the other hand, we shall describe the modification of an unsaturated polyester resin by the prepared vinyl ester resins, AVEMPR and MAVEMPR, 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. Blending a vinyl ester with an unsaturated polyester resin could lower the cure time, which would be an advantage in polymer coating applications. The curing exotherms of the prepared formulae based on UP 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 (AVEMPR and MAVEMPR) resins, UP dissolved in styrene monomer (60% both resins /40% styrene) cured by 2 wt% initiator in presence of 0.2 wt% activator were selected as representative samples and illustrated in ***figures (3.9 to 3.12).*** The formulae are based on UP and styrene in presence of 5%, 10%, 15% and 20% from VE (based on the total weight of UP and styrene). Styrene is reactive diluents, and VE serves as cross-linking agent. The cure of this resin proceeds via free radical bulk copolymerization. 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 (AVEMPR and MAVEMPR), 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 is also discussed. In this respect, the curing exotherms were determined at 35°C, 45°C and 55°C. 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 leads 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 [184], a weight fraction of MEKP 4% may be adequate in industrial use, when the curing must be completed fast. 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 show 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 [185]. Micro gels have been defined as domains of high cross-link density dispersed in a pool of un-reacted monomers. The crosslinking of such microgels 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 these subjects. It is also important to know exact chemical structure and molecular weight of UP.

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 (3.4 – 3.27)*** 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 unreacted 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 (3.4 -3.27)***, which indicate that AVEMPR have lower t_{max} and higher T_{max} values than MAVEMPR. This was clearly observed when AVEMPR or MAVEMPR resins was reacted with styrene with ratio 60:40 (w% : w%). This can be attributed to ability of styrene to react with divinyl monomers based on acrylates than that based on methacrylates.

3.4.2.1 Effect of cross-linking temperatures

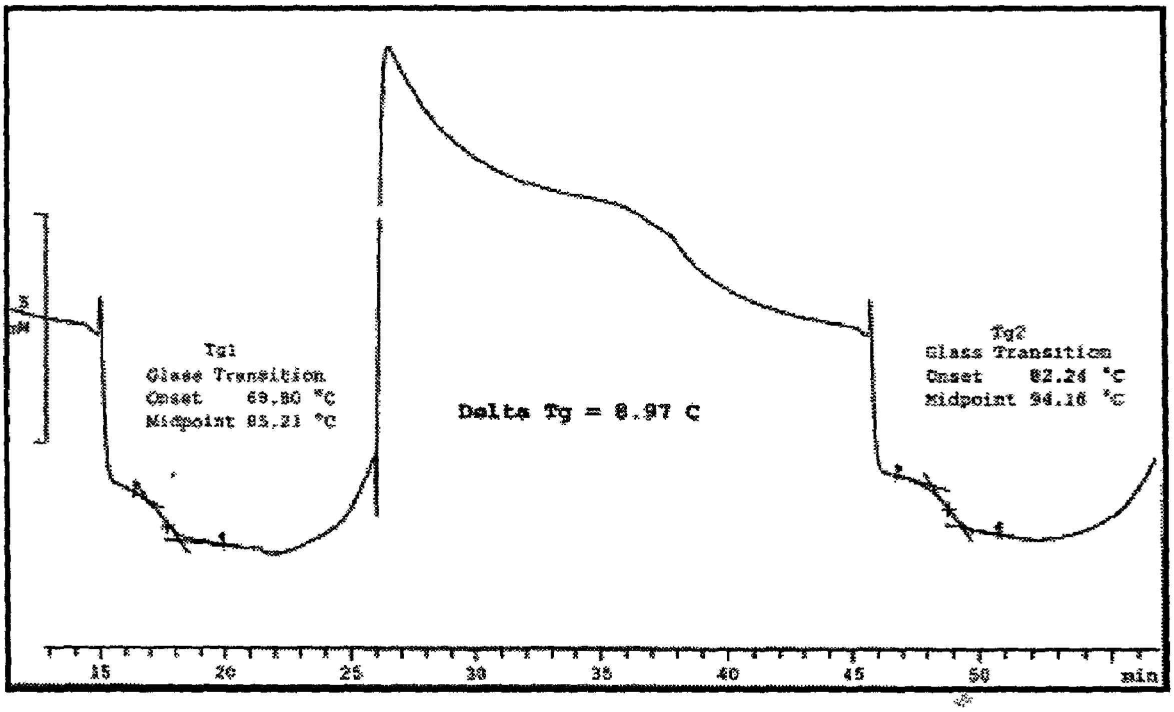
The nature of the formed networks based on vinyl ester, styrene and UP is difficult to understand and could be influenced by the reaction conditions such as temperature of reaction. The effect of the cross-linking temperature on the curing was investigated. In radical polymerization induced by thermal 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 [186]. 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 35 to 55 °C. The data of curing at these temperatures were listed in ***tables (3.4 -3.27)***. 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 decreases the viscosity of reactants and consequently affects the diffusion and reactivity ratios between reactants. In this respect, curing kinetics of styrene VE resins was studied at different temperatures. Ziaee et al. [187] reported that the reactivity ratios of VE to styrene affected by curing temperature. The data of ***figures (3.13 -3.24)*** show different behaviors as the reaction temperature increase. For low curing temperatures at 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 [188, 189] 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 (3.13 -3.24)*** when the curing temperature is between 45 and 55°C, the final degree of cure is increased because the material can be polymerized further before the T_g rises above T_{cure}. As indicated in ***figures (313. -3.24)***, the curves were too flat when the curing temperature was 45 and 55°C. This indicates that the final degree of curing was high [190].

3.4.2.2 Effect of UP and VE chemical structures

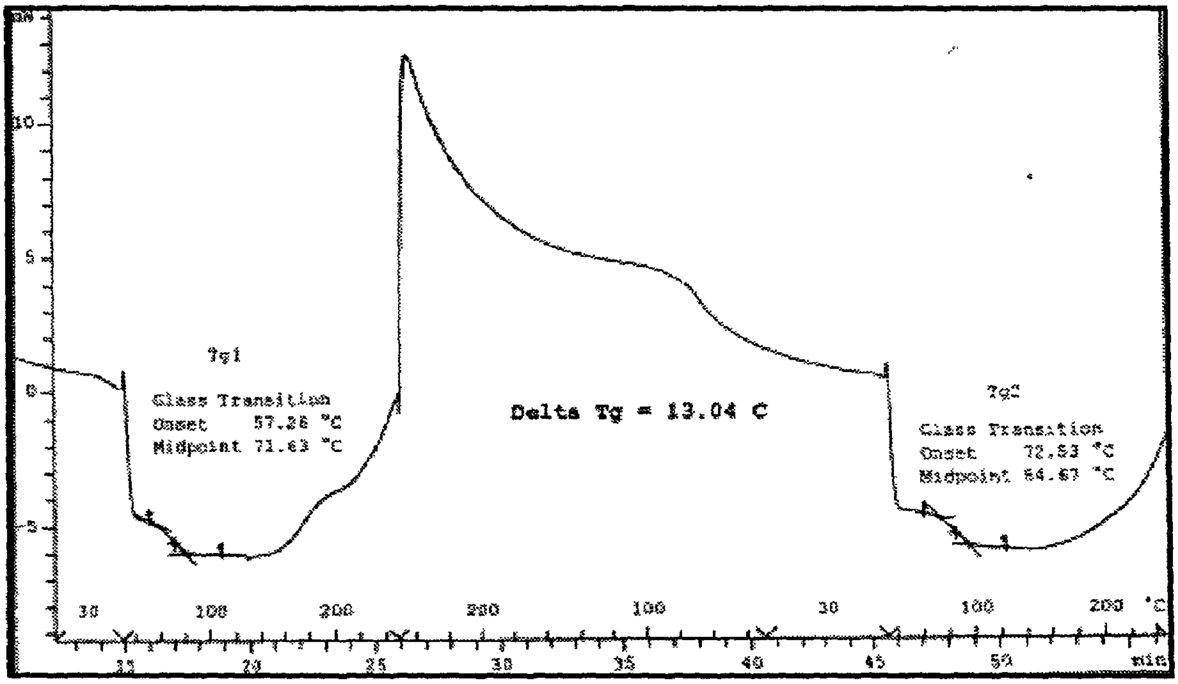
There is now great scientific and technological interest in the structure property relationships in the field of thermosets. However, several problems were related with the cure reaction and were not completely elucidated, which justifies the relative abundance of literature on all aspects of the cure and production of these resins. Unsaturated polyesters become insoluble and infusible by crosslinking with a monomer, usually styrene. 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 [191]. However, some researchers accept that the copolymerization of unsaturated polyester with styrene, UP/ST, results in the formation of a heterogeneous structure through strong intramolecular reactions and phase separation [192]. Abdel-Azim et al. [193]evaluated the effect of the resin microstructure on its cure behavior concluding that the maximum cure temperature is related to the molecular weight of the glycol segment incorporated in the resin . The influences of the molecular weight and the chain termination groups have 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 [194]. Kinetic models have been reported for the cure of UP/ST and mechanisms have been proposed for the microstructure formation [195]. 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 MPA, AdA and PA which includes long chain length having both aromatic moieties and aliphatic moieties. On the other hand, the length of dibasic acids and glycol moieties affect the molecular weight of UP and number of polymerizable double bond of maleic anhydride group in UP structure. Accordingly, the number of polymerizable double bond in UP based on MPA is higher than UP based on APA. So the curing time of UP based on MPA should be lower than UP based on APA.

3-5. CURING DSC MEASUREMENTS:

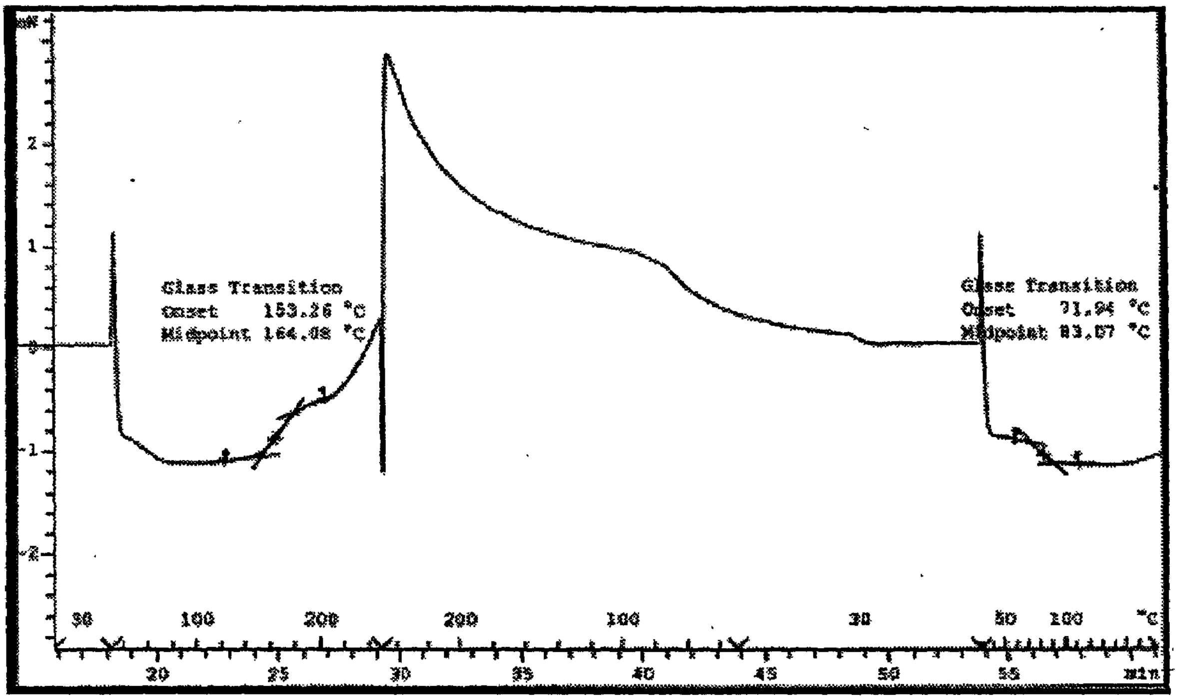
Several methods based on data of dynamic mechanical analysis (DMA) [209] rheological measurement, near infrared analysis [166] and thermal differential scanning calorimetry (DSC) were used to study the curing kinetic mechanisms. The reactivity of resins to be cured, and the properties of the end products, affects 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 resins. In the present work we have used DSC measurements to evaluate the curing exotherms of the prepared UP resins with styrene as curing agents. In this respect, the cured UP resin samples were heated and scanned from 25 to 150 °C and then immediately cooled at 25 °C. Tg values are reported as Tg1. While the temperatures of the heated resins from 25 to 285 °C followed by cooling to 25 °C are reported as Tg2. The change in Tg value was determined as the differences between Tgl and Tg2. DSC thermograms of some representative cured UP / styrene resins were plotted in **figures (3.25-3.30)**. The glass transition of these UP resin systems were measured by DSC as indicated in **Table (3.28).** The initial scan was performed to 150°C and the Tg was taken as the onset of the baseline change. The second scan was conducted to 280°C and was used to check for possible increases in Tg. Using this method, we were able to determine that the glass transition temperatures of the resin systems before and after



Figures (3.25): DSC Thermal Characteristics of Cured MPAUP1.

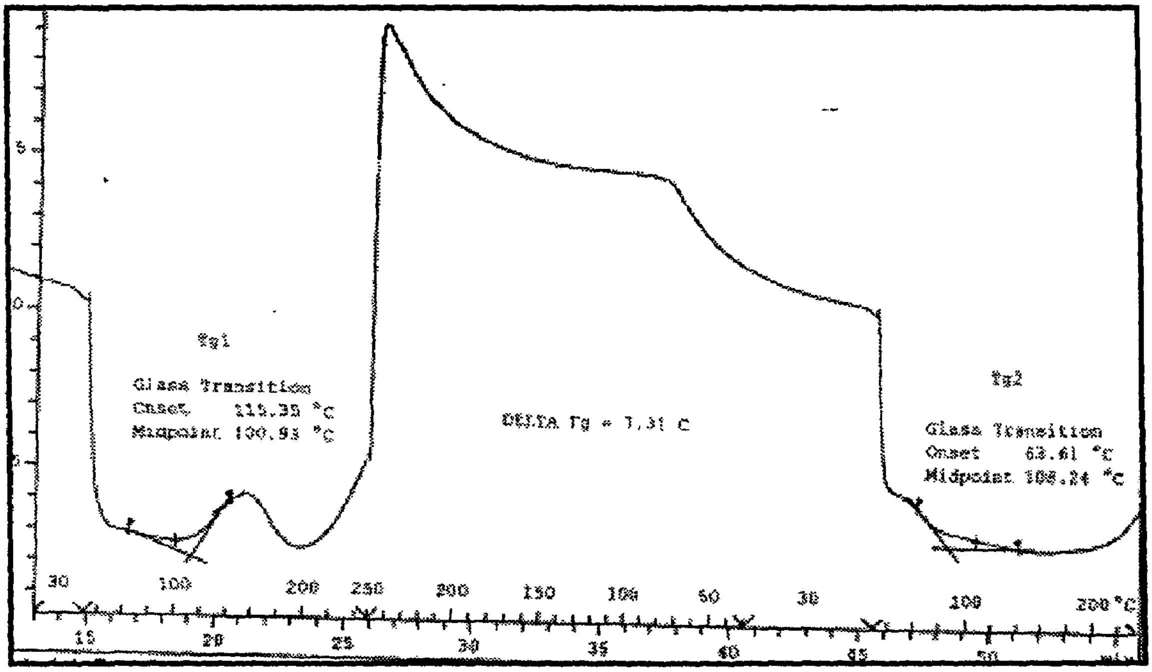


Figures (3.26): DSC Thermal Characteristics of Cured APAUP4



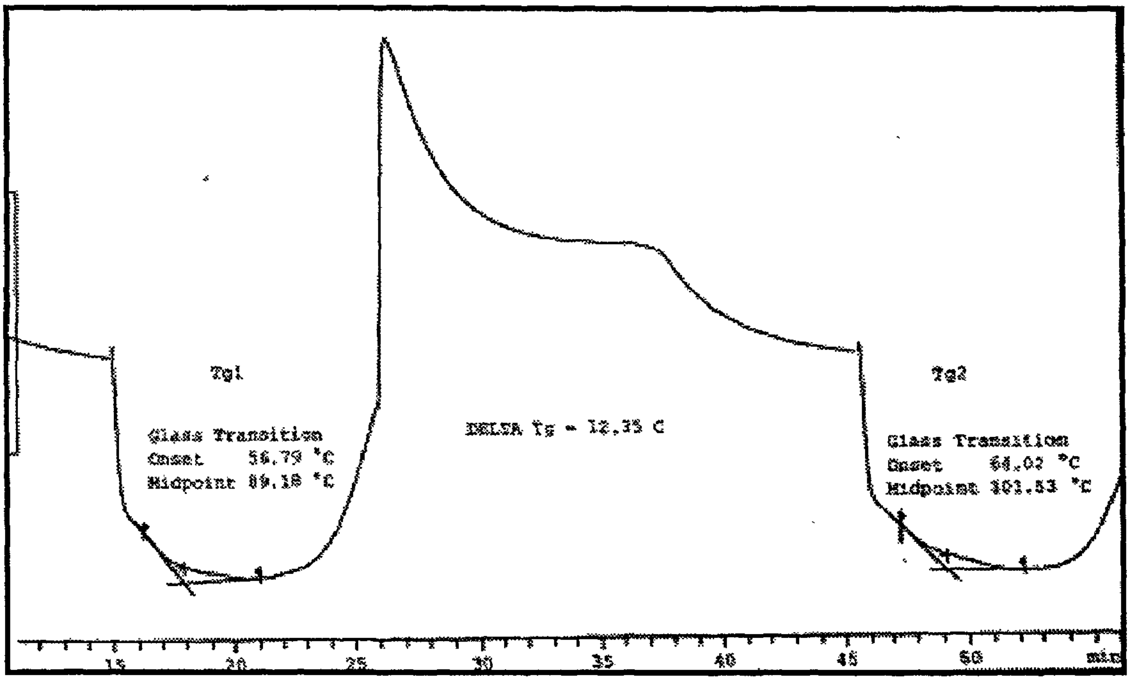
Temperature (° C)

Figures (3.27): DSC Thermal Characteristics of Cured APAUP1.

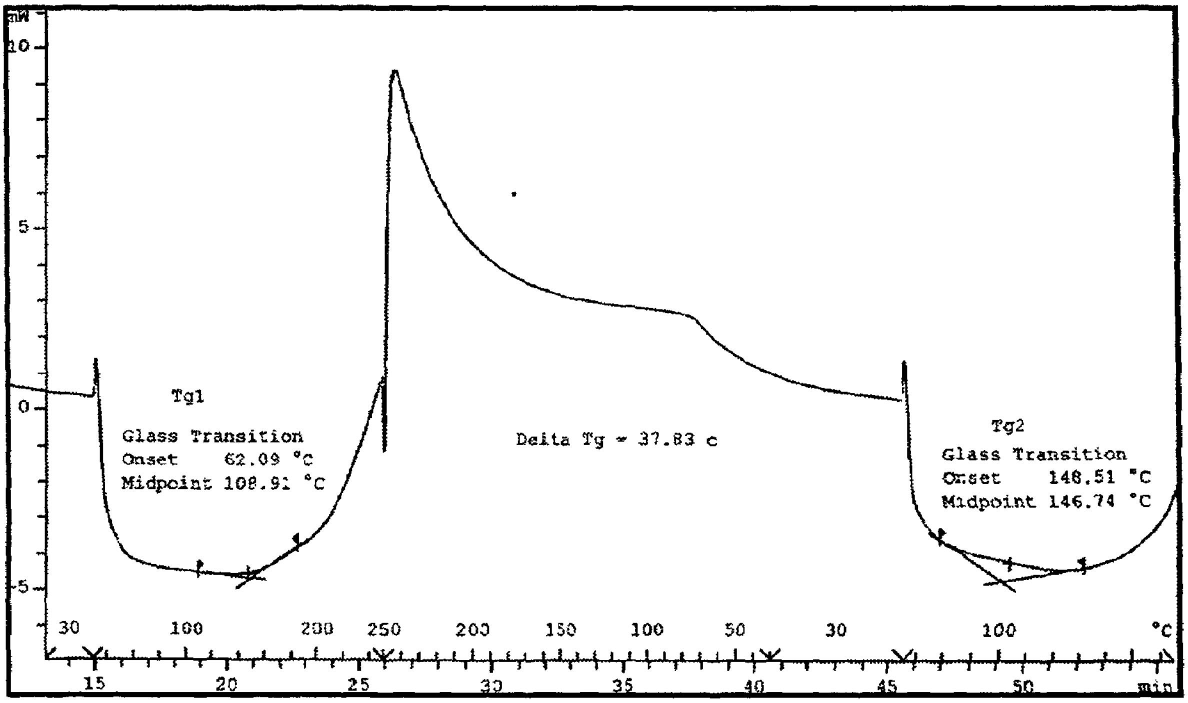


Temperature (°C)

Figures (3.28): DSC Thermal Characteristics of Cured MPAUP5.



Figures (3.29): DSC Thermal Characteristics of Cured APAUP6.



Temperature (°C)

Figures (3.30): DSC Thermal Characteristics of Cured MPAUP3.

Table (3.28): DSC Thermal Characteristics of Cured UP Resins with Styrene.

Designation	Tgl (°C)	Tg2 (°C)	ΔTg (°C)
MPAUP1	85.21	94.18	8.97
MPAUP2	115.5	130.3	14.8
MPAUP3	108	146	38
MPAUP4	80.12	86.62	6.5
MPAUP5	100.93	108.24	7.31
MPAUP6	95.3	110.3	15
APAUP1	83.07	146.08	63
APAUP2	112.3	142.3	30
APAUP3	94.3	116.6	22.3
APAUP4	71.63	84.67	13.04
APAUP5	106.4	118.9	12.5
APAUP6	89.18	101.53	12.35

[1] glass transition temperature of first run (from 25 to 150 °C).

[2] glass transition temperature of second run (from 25 to 285 °C).

Post-cure. It was observed that the data of Tg of the UP resins also increased during post-cure. This phenomenon was observed and has attributed it to an increase in molecular weight due to uncontrolled chain extension, and to the removal of solvent [196].

Tg of the polymer is important for the intended application. This transition temperature is defined as being the temperature or range of temperature at which the polymer passes from a hard and often brittle stage (glass) to a resistant stage of the rubber type. The applicable Tg values were determined from the points of intersection of the extrapolated baseline at the low temperature end and the tangents to the curve at the inflection point and determine the applicable exothermic heats of reaction (Δ H). Careful inspection of Tg data of the prepared UP resins reveals that the cured resins have low values than 100 °C except UP resins based on PA. This can be referred to introducing of PA groups will induce some rigidity in the resin backbone.The Tg of polymeric system has multifunctional dependence on the micro- structural characteristics of high molecular weight macromolecules[196-198]. The higher Tg values are related to strong dipolar interaction between side substituents of the polymeric chain. While, the glass transition temperature of low molecular weight compounds depends on the intermolecular interaction of individual molecules exclusively, being controlled by the molar volume and dipolar connectivity, hydrogen bonds, and Vander Waals interactions between molecules. This was observed in the UP resins based on AdA that posses lower Tg values. This was refereed to the introduction of AdA as aliphatic group will introduce some flexibility as well as PG in the structure of UP resins. On the other hand, almost UP resins have high Tg2 values more than 100 °C which indicate that the probability for formation of highly crosslinked polymers was increased with increasing the temperature. Increasing Tg2 above 100 °C indicates that polystyrene, PS, can be obtained as homopolymer. The probability for formation of PS was decreased with introducing of PG in the structure of both APAUP4 and MPAUP4.

Careful inspection of data listed in **Table (3.28)**, reveals that the UP resins possess different ΔTg values. It is well known that low ΔTg indicates higher curing of resins. The lower ΔTg values were observed when MPA, PG were incorporated with UP instead of APA and EG. This indicates that the reactivity of the ST towards prepared UP resins based on MPA and PG is much higher than UP resins based on APA and EG at higher temperatures. On the other hand UP resins based on MPA have higher Tg2 than that UP resins based on APA. This indicates that the cured UP/styrene resins based on MPA have a tendency to form dangling styrene chains which are not complete cured. It was also observed that the cured UP resins with PG have lower Tg2 values than that based on EG. This can be attributed to the higher crosslink density resulting from reaction of UP resins based on PG with styrene curing agent [189]. These observations agree to the results obtained for curing exotherms of UP/styrene resins at different temperatures. Accordingly, we can concluded that the cured UP/styrene resins have high crosslink densities when PG, APA and AdA were incorporated in UP resins.

3.6. EVALUATION OF CURED RESINS FOR COATING APPLICATIONS:

Organic coatings are prepared from one or more types of precursors of the final crosslinked 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 crosslinking chemistry but also their architecture can be tailored. Through the architecture, the processing properties, particularly the viscosity buildup 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 crosslinking 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. 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 [199] and [200] 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 [201]. Okay et al. [202] 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 [203] showed that the rate of intramolecular cyclization was very low at low levels of cross-linker.

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 [178]. 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 [204]. 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 UP/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 resins to cross-linked polymers was estimated using equation (Total conversion (%) = W x100/ W_0). Where, W and W_0 are total weight of cross-linked polymers after post curing at 105°C and weight of reactants, respectively. 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 (%) for cross-linking of UP in presence and absence of cross-linkers were determined and listed in ***tables (3.29 –3.31)***. It was found that the conversion (%) increases as the amount of VE increases and it have much pronounced effect on conversion (%). The increment of conversion (%) with increasing contents of both AVEMPR and MAVEMPR 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 as dangling chains. This can be 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 indicate that the presence of more curable maleic double bonds in UP structure which increase probability to react with VE and styrene. It was also observed that UP/MAVEMPR has a low conversion (%) values than that determined for cross-linked copolymers with AVEMPR. This can be attributed to the differences in the reactivity ratios of both cross-linkers with the produced polymer [205]. This can be explained on the basis that, the reactivity of AVEMPR towards UP may promote the reaction rate initially due to a cross-inking.

Table (3.29): Conversion Values of Cured UP/styrene having Different Compositions.

Type of UP	Conversion (%) of Crosslinked gels at temperature		
	35 °C	45 °C	55 °C
APAUP1	87.3	90.4	92.5
APAUP2	82.1	88.2	90.4
APAUP3	90.1	92.3	94.5
APAUP4	85.4	89.4	91.4
APAUP5	87.1	88.6	90.2
APAUP6	86.2	88.1	89.4
MPAUP1	88.3	90.3	92.3
MPAUP2	84.1	86.5	89.4
MPAUP3	92.1	94.5	96.1
MPAUP4	89.2	91.4	93.4
MPAUP5	85.1	87.9	90.5
MPAUP6	93.42	95.6	97.2

Table (3.30): Conversion Values of Cured UP resin having Different Crosslinkers Concentrations.

crosslinker (w %)	Type of UP	Conversion (%) of Crosslinked gels at temperature[1]			Conversion (%) of Crosslinked gels at temperature[2]		
		35 °C	45 °C	55 °C	35 °C	45 °C	55 °C
5	APAUP1	92.3	93.4	95.5	90.3	91.4	93.5
	APAUP2	90.1	92.2	94.4	89.1	90.2	92.4
	APAUP3	95.1	96.3	97.5	92.1	93.3	95.5
	APAUP4	91.4	93.4	95.4	90.4	91.4	93.4
	APAUP5	95.1	97.6	98.2	92.1	94.6	96.2
	APAUP6	94.2	98.1	99.4	91.2	96.1	97.4
10	APAUP1	94.3	95.4	97.5	92.3	93.4	95.5
	APAUP2	92.1	94.2	96.4	91.1	92.2	94.4
	APAUP3	97.1	97.3	98.5	94.1	95.3	97.5
	APAUP4	93.4	95.4	97.4	92.4	93.4	95.4
	APAUP5	97.1	98.6	98.9	94.1	96.6	98.2
	APAUP6	96.2	98.9	99.8	93.2	97.1	99.4
15	APAUP1	95.3	96.4	98.5	93.3	94.4	95.8
	APAUP2	93.1	95.2	97.4	92.1	93.2	94.7
	APAUP3	98.1	98.4	98.8	95.1	96.3	97.8
	APAUP4	94.4	96.4	97.9	93.4	94.4	95.7
	APAUP5	98.1	98.8	98.9	95.1	97.6	98.8
	APAUP6	98.2	99.1	99.5	94.2	98.1	99.5
20	APAUP1	95.9	96.4	98.9	93.3	94.8	96.8
	APAUP2	93.8	95.7	97.7	92.8	93.7	95.7
	APAUP3	98.7	98.9	99.3	95.9	96.8	98.4
	APAUP4	94.6	96.8	98.4	93.8	94.8	96.7
	APAUP5	98.4	99.4	99.7	95.6	97.9	99.2
	APAUP6	98.6	99.7	99.8	94.7	98.7	99.8

[1] AVEMPR [2] MAVEMPR

Table (3.31): Conversion Values of Cured UP resin having Different Crosslinkers Concentrations.

crosslinker (w%)	Type of UP	Conversion (%) of Crosslinked gels at temperature[1]			Conversion (%) of Crosslinked gels at temperature[2]		
		35 °C	45 °C	55 °C	35 °C	45 °C	55 °C
5	MPAUP1	91.3	92.4	93.5	88.3	90.4	92.5
	MPAUP2	89.1	91.2	92.4	87.1	89.2	91.4
	MPAUP3	93.1	95.3	95.5	90.1	92.3	94.5
	MPAUP4	90.4	92.4	93.4	88.4	90.4	91.4
	MPAUP5	93.1	96.6	97.2	90.1	93.6	94.2
	MPAUP6	92.2	97.1	98.4	89.2	95.1	96.4
10	MPAUP1	93.3	94.4	95.5	90.3	92.4	94.5
	MPAUP2	91.1	93.2	95.4	89.1	91.2	93.4
	MPAUP3	95.1	96.3	97.5	92.1	94.3	96.5
	MPAUP4	92.4	94.4	95.4	90.4	91.4	94.4
	MPAUP5	95.1	97.6	97.9	92.1	95.6	97.2
	MPAUP6	94.2	97.9	99.2	91.2	95.1	97.4
15	MPAUP1	94.3	95.4	97.5	91.3	92.4	94.8
	MPAUP2	92.1	94.2	96.4	90.1	91.2	93.7
	MPAUP3	97.1	97.4	97.8	93.1	94.3	95.8
	MPAUP4	93.4	95.4	96.9	91.4	92.4	93.7
	MPAUP5	97.1	97.8	97.9	93.1	95.6	96.8
	MPAUP6	96.2	98.1	98.5	92.2	96.1	97.5
20	MPAUP1	94.9	95.4	96.9	91.3	92.8	94.8
	MPAUP2	92.8	94.7	95.7	90.8	91.7	93.7
	MPAUP3	97.7	97.9	98.3	93.9	94.8	96.4
	MPAUP4	93.6	95.8	96.4	91.8	93.8	94.7
	MPAUP5	97.4	98.4	98.7	93.6	96.9	97.2
	MPAUP6	97.6	98.7	98.8	92.7	97.7	98.8

[1] AVEMPR [2] MAVEMPR

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 [206].

3.6.1 Evaluation of Mechanical Properties for cured UP resins

Cured thermoset polymers are more difficult to analyze than cured thermoplastic. They are insoluble and generally intractable. However, properties are influenced by factors at the molecular level, such as backbone structures of resin and curing agent; nature of covalent bond developed between the UP resin and the curing agent during the cross-linking and density of crosslinking, i.e., degree of cure. UP resins have a wide and increasing use in industry owing to their unique combination of properties. The absence of volatile byproducts 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 low adhesive strengths. Although UP resins are used as organic coatings, they suffer from rigidity, and hence they have low peel, when cured with conventional “small molecule” reagents. The increasing of unsaturation 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. In this respect, we have designed both UP resins and VE hardeners based on cycloaliphatic systems to produce cured UP resins have good durability with excellent mechanical properties. For these purposes the mechanical properties of cured resins have been tested by determining the impact, T-bend and adhesion pull off tests. In this respect, UP resins were sprayed (by brush) with wet film thickness, WFT, 300 μm on blasted steel panels. The tests for measuring the mechanical properties were evaluated after post curing at 105 °C for 24h and stand for another 24h at ambient temperature (25°C). The data of mechanical properties (adhesion, impact, and T-bending) for cured UP resins based on APA and MPA with VE as curing agents were tabulated in ***Tables (3.32 - 3.40).*** The data reported on adhesions indicate that all cured UP resins based on APA and MPA with AVEMPR and MAVEMPR have superior adhesion properties with steel. This can be attributed to the presence of polar group in the structure of both UP and VE resins. It has been demonstrated that the presence of small controlled amounts of terminal glycol groups can have beneficial effects on adhesion [148]. The effect of the structure of the resin on its mechanical properties 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. In the present study, the resultant molecular weights of UP were tabulated in ***table (3.3),*** in conjunction with the acid number of the prepared polyesters. The reason to introduce AdA, PA, EG and PG in the structure of UP is mainly to study the effect of these groups on

Table (3. 32): Coating tests of UP resins Cured with Styrene as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	2	4	-
APAUP2	3	6	+
APAUP3	2.5	5	+
APAUP4	2	5	+
APAUP5	3	7	+
APAUP6	3. 5	8	+
MPAUP1	1. 5	3	-
MPAUP2	2. 5	5	+
MPAUP3	2. 5	4	+
MPAUP4	2.5	6	+
MPAUP5	3	7	+
MPAUP6	3	5	+
AVEMPR 60/STYRENE40	8	15	+
MAVEMPR 60/STYRENE40	10	12	+

+ PASS

- FAIL

Table (3. 33): Coating Tests of UP Resins Cured with 5% AVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	2	3. 5	+
APAUP2	3.5	6	+
APAUP3	3.5	9	+
APAUP4	2.5	6	+
APAUP5	4	10	+
APAUP6	3	10	+
MPAUP1	1.5	3	+
MPAUP2	2	5	+
MPAUP3	3	8	+
MPAUP4	3	4	+
MPAUP5	3.5	7. 5	+
MPAUP6	3	10	+

+ PASS

- FAIL

Table (3. 34): Coating Tests of UP Resins Cured with 5% MAVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	2. 5	6	+
APAUP2	4	10	+
APAUP3	3. 8	10	+
APAUP4	3. 5	6	+
APAUP5	4	10	+
APAUP6	5	10	+
MPAUP1	2. 5	5	+
MPAUP2	3	8	+
MPAUP3	3	9	+
MPAUP4	3	6	+
MPAUP5	3. 5	10	+
MPAUP6	4. 5	10	+

+ PASS
- FAIL

Table (3.35): Coating Tests of UP Resins Cured with 10% AVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	2. 5	5	+
APAUP2	3. 5	9	+
APAUP3	3. 5	10. 5	+
APAUP4	3	7	+
APAUP5	4	11	+
APAUP6	4. 5	13	+
MPAUP1	2. 5	4. 5	+
MPAUP2	2. 5	8	+
MPAUP3	3	9. 5	+
MPAUP4	3	6. 5	+
MPAUP5	4	9	+
MPAUP6	4	12	+

+ PASS

- FAIL

Table (3. 36): Coating Tests of UP Resins Cured with 10% MAVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	2	9	+
APAUP2	4	10	+
APAUP3	3. 8	12	+
APAUP4	3. 5	8	+
APAUP5	4	15	+
APAUP6	4	15	+
MPAUP1	2	6	+
MPAUP2	3	10	+
MPAUP3	3	11	+
MPAUP4	3	7. 5	+
MPAUP5	3. 5	10	+
MPAUP6	3. 5	15	+

+ PASS
- FAIL

Table (3. 37): Coating Tests of UP Resins Cured with 15% AVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	3	8	+
APAUP2	4	10	+
APAUP3	4	12. 5	+
APAUP4	3. 5	9	+
APAUP5	5	13	+
APAUP6	5	15	+
MPAUP1	3	5	+
MPAUP2	3	9	+
MPAUP3	3. 5	10	+
MPAUP4	3. 5	7	+
MPAUP5	4. 5	10	+
MPAUP6	4. 5	13	+

+ PASS
- FAIL

Table (3.38): Coating Tests of UP Resins Cured with 15% MAVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	2. 5	10	+
APAUP2	4. 5	11	+
APAUP3	4. 5	13	+
APAUP4	5	9	+
APAUP5	4. 5	15	+
APAUP6	4. 5	15	+
MPAUP1	2. 5	7	+
MPAUP2	3. 5	11	+
MPAUP3	3. 5	12	+
MPAUP4	3. 5	9	+
MPAUP5	4	11	+
MPAUP6	4	15	+

+ PASS

- FAIL

Table (3. 39): Coating Tests of UP Resins Cured with 20% AVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	3	8	+
APAUP2	4. 5	10	+
APAUP3	4	11	+
APAUP4	3. 2	10	+
APAUP5	4. 5	13	+
APAUP6	4. 8	15	+
MPAUP1	2. 5	7	+
MPAUP2	4. 3	10	+
MPAUP3	4	11	+
MPAUP4	3	9	+
MPAUP5	4. 5	11.5	+
MPAUP6	4. 5	14.5	+

\+ PASS

\- FAIL

Table (3. 40): Coating Tests of UP Resins Cured with 20 % MAVEMPR as Curing Agent.

UP Resins	Pull-Off resistance (MPa)	Impact (J/mm)	T-bend
APAUP1	4	10	+
APAUP2	5	15	+
APAUP3	5	16	+
APAUP4	4. 5	12	+
APAUP5	5	15	+
APAUP6	5	15	+
MPAUP1	3. 5	7.5	+
MPAUP2	4. 5	12	+
MPAUP3	4. 5	15	+
MPAUP4	4	9	+
MPAUP5	5	13	+
MPAUP6	5	15	+

+ PASS
- FAIL

properties of cured films. 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 [207]. 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. It was also noted that increasing ratios of VE hardeners increases the impact of UP coatings films. This behavior leads to speculate that the high crosslinking density networks posse's good mechanical properties of the formed network. It was also noted that, the mechanical properties of cured UP styrene films was increased when APA replaced MPA in structure of UP resins. These results agree with data of curing exotherms of UP resins which indicate that UP resins based on MPA has a great tendency to form dangling chain. It is well known that, dangling chain affects the mechanical properties of crosslinked polymers [208]. On the other hand, it was observed that the cured UP/styrene resins based on PG posses good mechanical properties than that based on EG. This can be referred to fact that PG modifies mechanical properties of cured UP resins. The flexibility of this resin may be attributed to the effect of CH_3 group of PG and length of AdA on 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. Consequently, the mobility of the polymer segment increases, and hence an increase in flexibility. The data listed in tables (3.32-3.40) indicate that the data of pull-off resistances for cured UP resins with styrene and VE systems agree with the data of bending tests. This observation indicates that the cured film with good adhesion, high pull off resistance values, have good result with bending tests.

The mechanical properties of resin systems can also be used to estimate the degree of cure [209, 210]. The mechanical properties of the UP resins produced were studied in relation to the effect of the VE types and concentrations [202].There are different mechanical data were observed when AVEMPR and MAVEMPR were used as cross-linkers. It was observed that the impact resistance and pull-off resistance 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. This observation 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. ***Tables (3.33-3.40)*** show different mechanical properties when AVEMPR was used as cross-linker for UP. It was found that the mechanical properties were improved with increasing concentrations of AVEMPR. This can be explained on the basis that the reactivity of AVEMPR with UP is more reactive than UP with styrene. The wide difference in reactivity between AVEMPR and MAVEMPR 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 MAVEMPR 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 impact and pull-off resistance values of UP are reduced when AVEMPR replaces MAVEMPR. This can be explained on the different reactivity between UP, AVEMPR, MAVEMPR and styrene radicals. The data indicate that, the rate of reaction of the UP radical with AVEMPR is faster than with MAVEMPR and the MAVEMPR radical reacts faster with its own monomer than does the AVEMPR radical [211]. Accordingly, all MAVEMPR cross-linker radicals are used up before a significant number of styrene molecules can be incorporated in the cross-linked UP [212]. So the probability that homopolymerisation of styrene occurs during crosslinking is higher with MAVEMPR than AVEMPR. It is well established that mechanical properties of UP decreases with homopolymerisation of the styrene monomer [212]. This finding is in good agreement with that reported by Urban et al. [213]. 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., [214] 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 mechanical properties measured by these authors were 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 (3.33-3.40)***, which indicate that impact and pull off resistance decreases on incorporation of MAVEMPR instead of AVEMPR in a network of cross-linked UP. The fact that the mechanical properties were higher for cross-linked UP's in presence of AVEMPR than MAVEMPR indicate the formation of a denser cross-linked network in presence of AVEMPR than with MAVEMPR cross-linkers. Careful inspection of data listed in ***table (3.32)***, indicates that the high impact and pull off resistance values were obtained when 60% of AVEMPR and MAVEMPR cured with 40% of styrene monomer. This indicates that highly cross-inked networks were obtained due to high reactivity of AVEMPR or MAVEMPR with styrene.

3.6.2 Chemical Resistances of Cured UP/VE Systems:

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 evaluate the mechanical tests of the present types of cured UP resins. 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.

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 [215]. Under-cure of the resin will not generally produce optimal tensile properties [216] 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 [217]. 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. 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 ***tables (3.41-3.45)***. The data of alkali-, acid-, solvent- resistance and water resistance were determined for cured 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

Table (3. 41): Chemical Resistance Tests of UP Resins Cured with Styrene as Curing Agent.

UP Resins	Acid resistance (day)	Alkaline resistance (day)	Water resistance	Acetone rub test
APAUP1	2	1	+	+
APAUP2	2	1	+	+
APAUP3	2	1	+	+
APAUP4	2	2	+	+
APAUP5	2	2	+	+
APAUP6	2	2	+	+
MPAUP1	2	1	+	+
MPAUP2	2	1	+	+
MPAUP3	2	1	+	+
MPAUP4	2	2	+	+
MPAUP5	2	2	+	+
MPAUP6	2	2	+	+

+ PASS

- FAIL

Table (3.42): Chemical Resistance Tests of UP Cured with AVEMPR at Different Mixing Ratios.

Cured Network (%)	Acid resistance (day)				alkali resistance (day)				Water resistance				Solvent resistance	Acetone Test
	5	10	15	20	5	10	15	20	5	10	15	20	(5-20)*	(5-20)*
APAUP1	15	90	40	30	10	60	30	15	+	+	+	+	+	+
APAUP2	10	90	45	30	10	60	30	15	+	+	+	+	+	+
APAUP3	15	90	50	45	35	70	30	20	+	+	+	+	+	+
APAUP4	45	90	90	90	25	90	60	30	+	+	+	+	+	+
APAUP5	60	90	90	90	45	90	60	55	+	+	+	+	+	+
APAUP6	50	90	65	30	10	60	30	15	+	+	+	+	+	+

* Weight percentage of AVEMPR

Table (3.43): Chemical Resistance Tests of UP Cured with MAVEMPR at Different Mixing Ratios.

Cured Network (%)	Acid resistance (day)				alkali resistance (day)				Water resistance				Solvent resistance	Acetone Test
	5	10	15	20	5	10	15	20	5	10	15	20	(5-20)*	(5-20)*
APAUP1	7	45	20	15	3	30	10	5	+	+	+	+	+	+
APAUP2	5	45	15	10	3	30	10	5	+	+	+	+	+	+
APAUP3	7	60	20	13	5	45	15	7	+	+	+	+	+	+
APAUP4	30	90	70	90	10	60	30	17	+	+	+	+	+	+
APAUP5	30	90	70	90	15	90	45	35	+	+	+	+	+	+
APAUP6	15	60	25	19	2	30	10	3	+	+	+	+	+	+

* Weight percentage of MAVEMPR

Table (3.44): Chemical Resistance Tests of UP Cured with AVEMPR at Different Mixing Ratios.

Cured Network (%)	Acid resistance (day)				alkali resistance (day)				Water resistance				Solvent resistance	Acetone Test
	5	10	15	20	5	10	15	20	5	10	15	20	(5-20)*	(5-20)*
MPAUP1	10	60	20	15	5	30	10	5	+	+	+	+	+	+
MPAUP2	5	60	25	20	5	30	10	5	+	+	+	+	+	+
MPAUP3	10	60	30	30	7	40	10	10	+	+	+	+	+	+
MPAUP4	30	60	60	60	15	60	30	10	+	+	+	+	+	+
MPAUP5	45	60	60	60	30	60	40	30	+	+	+	+	+	+
MPAUP6	30	60	25	20	5	30	10	10	+	+	+	+	+	+

* Weight percentage of AVEMPR

Table (3.45): Chemical Resistance Tests of UP Cured with MAVEMPR at Different Mixing Ratios.

Cured Network (%)	Acid resistance (day)				alkali resistance (day)				Water resistance				Solvent resistance	Acetone Test
	5	10	15	20	5	10	15	20	5	10	15	20	(5-20)*	(5-20)*
MPAUP1	5	30	10	5	3	20	7	4	+	+	+	+	+	+
MPAUP2	4	30	10	5	3	20	7	4	+	+	+	+	+	+
MPAUP3	5	50	15	10	3	30	7	7	+	+	+	+	+	+
MPAUP4	20	50	40	40	7	40	20	15	+	+	+	+	+	+
MPAUP5	20	50	40	40	10	40	25	20	+	+	+	+	+	+
MPAUP6	15	40	20	15	2	20	7	2	+	+	+	+	+	+

* Weight percentage of MAVEMPR

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. Solvent resistance may be tested for very different reasons. 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 [121]. 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 [218]. 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 crosslink density can be controlled by change type of curing agents and functionality of UP resins [219], in this respect, it was found that the all prepared UP resins based on both APA and MPA have good solvent and hot water resistance with all mixing ratios with AVEMPR and MAVEMPR. This can be attributed to increasing of crosslink density of UP although the UP polarity is increased by increment of UP molecular weights [221]. The high solvent resistance of the cured UP systems indicates that all cured UP resins have high crosslink density networks [220,221].

Most conventional structural materials are subject 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 [222]. The acetal group in cellulosics, polyformaldehyde and polyvinyl acetals is very sensitive to hydrolysis by aqueous acid [223]. Polyesters, polyamides, and polyurethanes may be hydrolyzed by acid or alkaline catalysis [224]. The data of acid and alkali resistances indicate that there is some change on color and weight when plaques are subjected to sodium hydroxide, HCl or H_2SO_4 during period of 90 days. In the present systems, it was observed that the cured UP resins show low acid and alkali resistance when cured with styrene monomer as indicated in **table (3.41)**. This can be referred to low cross-linking density UP/styrene resins which increases the exposure of polar groups of network to environments. On the other hand incorporation of both AVEMPR and MAVEMPR as curing agent for UP/ styrene system increases acid and alkali resistances of cured resins. This can be attributed to high crosslink density of network decreases their exposure to environment [225] and [220]. It was also observed that UP resins based on APA, PG and AdA show good alkali and acid resistances than that based on MPA, EG and PA. This can be attributed to formation of high crosslink density networks when APA, PG and AdA were used to prepare UP resins. These data agree in harmony with the data reported from molecular weight, curing exotherms and DSC measurements. It was also noticed that, the acid and alkali resistances of cured UP resins were increased when AVEMPR used as crosslinker instead of MAVEMPR. This can be refereed to formation of dangling chains when MAVEMPR used as crosslinker for UP resins, as explained in curing exotherm measurements, which increase exposure of crosslinked network to acidic and alkaline media. Careful inspection of data, **table (3.41-3.45),** indicates that increasing MAVEMPR and AVEMPR crosslinker concentrations up to 10 (w%) increases acid and alkali resistance and decreases when the concentration increases from 15 to 20 (w %). This observation can be referred to formation of high percentages of dangling chains when the concentrations of both crosslinkers exceed 10 (w %) which increase exposure of networks to acid and alkali solutions and consequently increases the hydrolysis of cured UP resins [208].

Acid and alkali resistances were evaluated for cured materials without applying on the test panels as reported in experimental section. In this respect all cured resins show excellent resistances to immersion in acid and alkali for 90 days at temperature of 25 °C. The weight and color of the cured resins were not changed. These indicate that the cured resins posses excellent resistances to acid and alkali.

3.6. 3 Testing Corrosion Resistance of Coating

Salt spray tests are probably the most common tests applicable to corrosion resistance and the most controversial [226]. It is 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 [227-229]. 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 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. In this respect, the adhesion of substrate with coat is the main problem for coating failure [230]. 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 [231]. The initial penetration of rust through the protective coating film is based on the coating constituents [232]. The coating constituents must be able to resist the transfer of ions the coating and be able to expand and contract with the underlying through 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 [233-236]. Resistance to osmosis and electrondosmosis greatly affect coating life. In this respect, the duration times of tests were determined for all cured UP and 10 (w%) of AVEMPR or MAVEMPR styrene systems and listed in ***tables (3.46 –3.48).*** The weight percentage of 10 % was selected in this test according to previous section which indicates that percentage is the most applicable to produce cured resins without any deformation to mechanical damage and high alkaline and acidic resistances. On the other hand, photos of salt spray resistance of APAUP5/AVEMPR (10%)/styrene, APAUP5/MAVEMPR (10%)/styrene and MPAUP4 were selected as representative samples and shown in **figures (3.31-3.33).** The test was stopped when the films show poor adhesion. The results of salt spray indicate the strong adhesion of coatings by using APA, PG and PA in the structure of UP resins. On the other hand, incorporation of AVEMPR vinyl ester resins instead of MAVEMPR in UP networks improves the coating performance from 75 to 95% 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, water or dilute salt water are directed to the coating, they are semi permeable 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

Table (3.46): Salt Spray Resistance of Cured UP Styrene Resins

Sample no.	Exposure TIME (h)	Disbonded area		ASTM RATING*
		cm^2	%	
APAUP1	300	18.3	15.8	5
APAUP2	300	7.1	6	7
APAUP3	300	13	11	6
APAUP4	400	12.8	11	6
APAUP5	400	2.3	2	8
APAUP6	400	7.1	6	7
MPAUP1	300	18.3	15.8	5
MPAUP2	300	13	11	6
MPAUP3	300	18.3	15.8	5
MPAUP4	300	18.3	15.8	5
MPAUP5	300	7.1	6	7
MPAUP6	300	13	11	6

*ASTM Method, D1654-92

Table (3.47): Salt Spray Resistance of Cured UP Styrene and 10(w%) of AVEMPR Resins.

Sample no.	Exposure TIME (h)	Disbonded area		ASTM RATING*
		cm^2	%	
APAUP1	650	7.1	6	7
APAUP2	650	2.33	2	8
APAUP3	650	2.33	2	8
APAUP4	650	2.3	2	8
APAUP5	650	1.2	1	9
APAUP6	650	2.3	2	8
MPAUP1	650	12.9	11	6
MPAUP2	650	7.1	6	7
MPAUP3	650	7.1	6	7
MPAUP4	650	13	11	6
MPAUP5	650	2.3	2	8
MPAUP6	650	7.1	6	7

*ASTM Method, D1654-92

Table (3.48): Salt Spray Resistance of Cured UP Styrene and 10(w%) of MAVEMPR Resins.

Sample no.	Exposure TIME (h)	Disbonded area		ASTM RATING*
		cm^2	%	
APAUP1	500	13	11	6
APAUP2	500	7.1	6	7
APAUP3	500	7.1	6	7
APAUP4	500	7.1	6	7
APAUP5	500	2.3	2	8
APAUP6	500	2.3	2	8
MPAUP1	500	12.9	11	6
MPAUP2	500	13	11	6
MPAUP3	500	12.9	11	6
MPAUP4	500	13	11	6
MPAUP5	500	2.3	2	8
MPAUP6	500	7.1	6	7

*ASTM Method, D1654-92

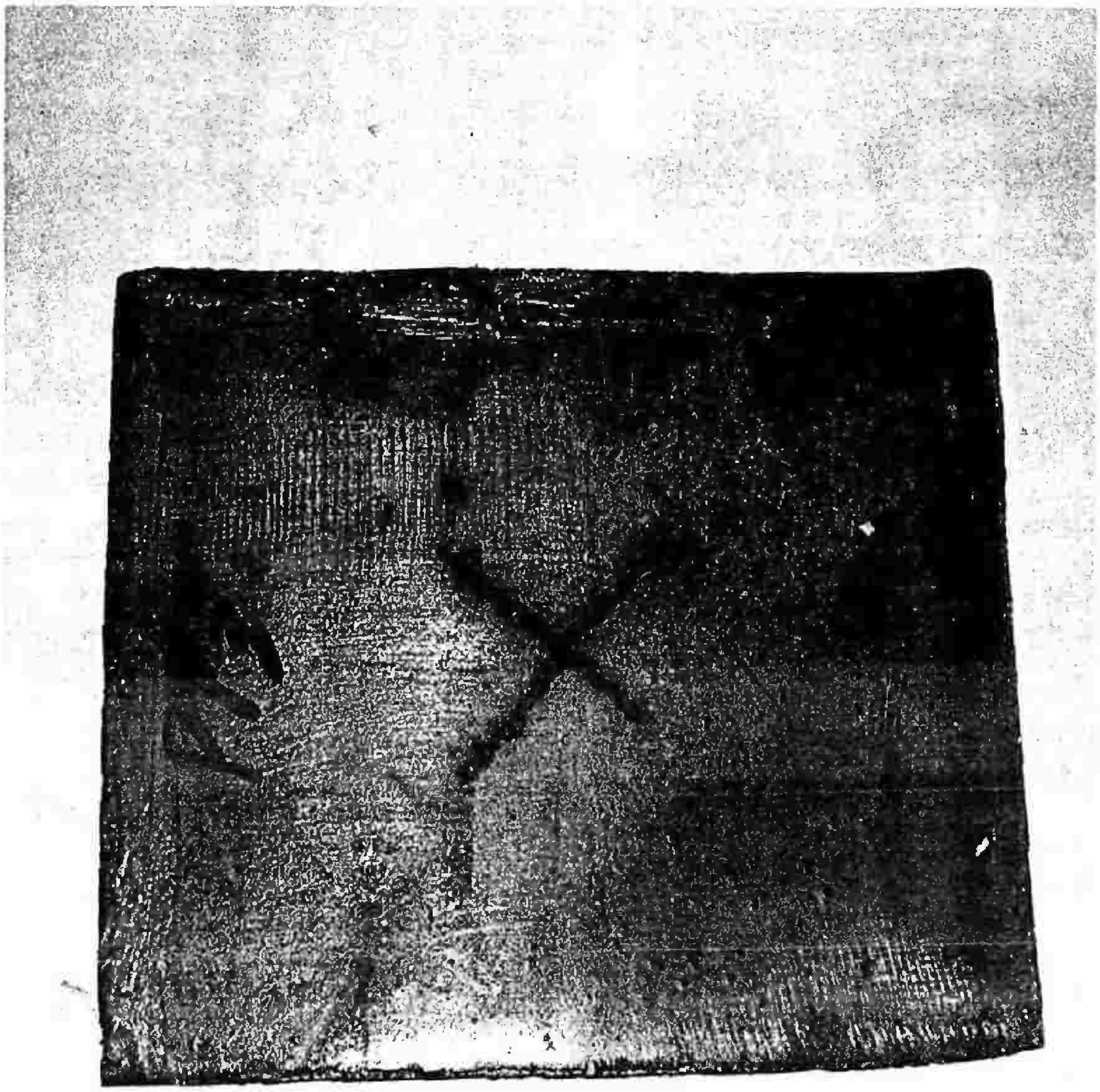


Figure (3.31): Salt Spray resistance of MPAUP4 coatings.

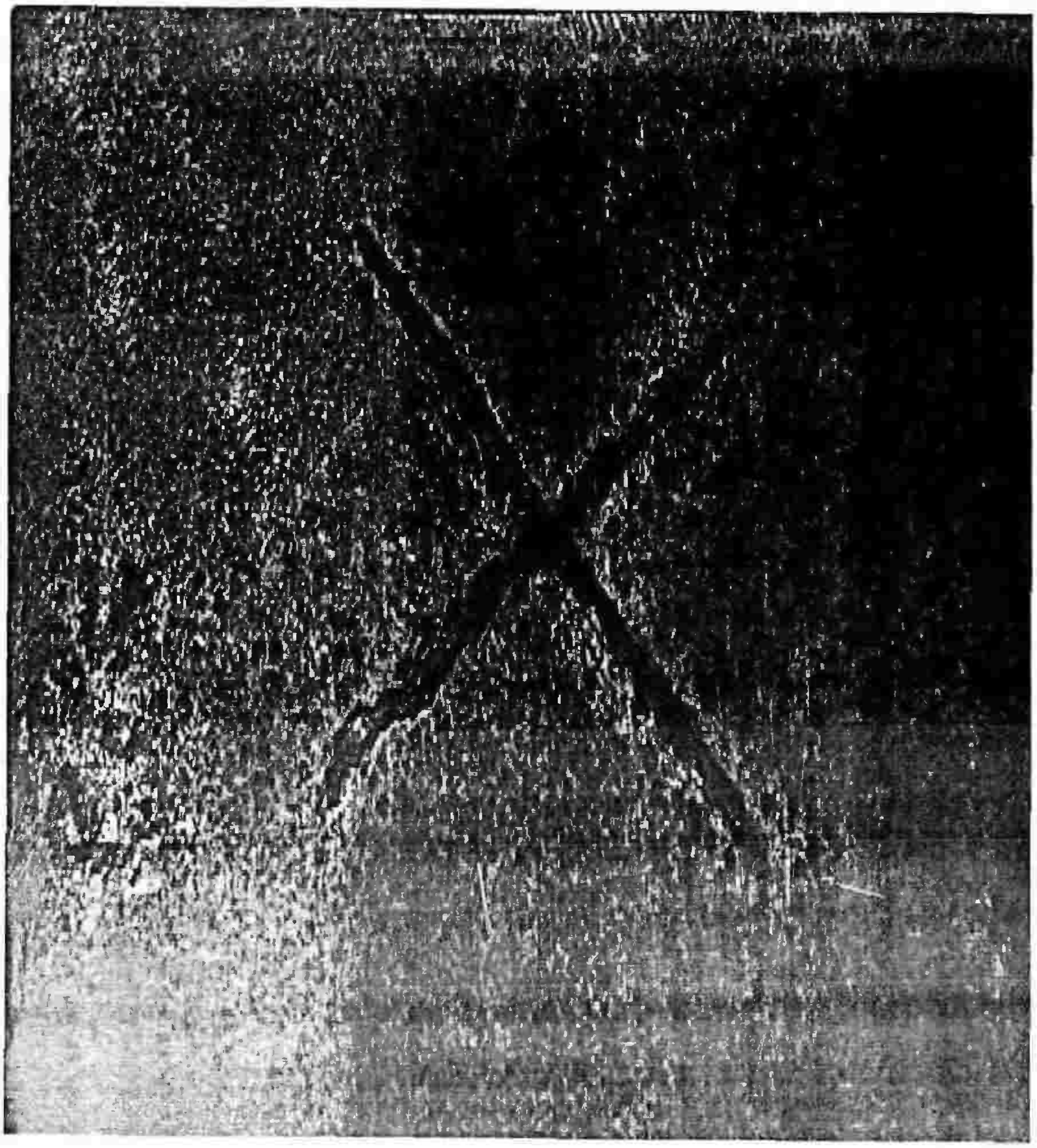


Figure (3.32): Salt Spray resistance of APAUP5 coatings.

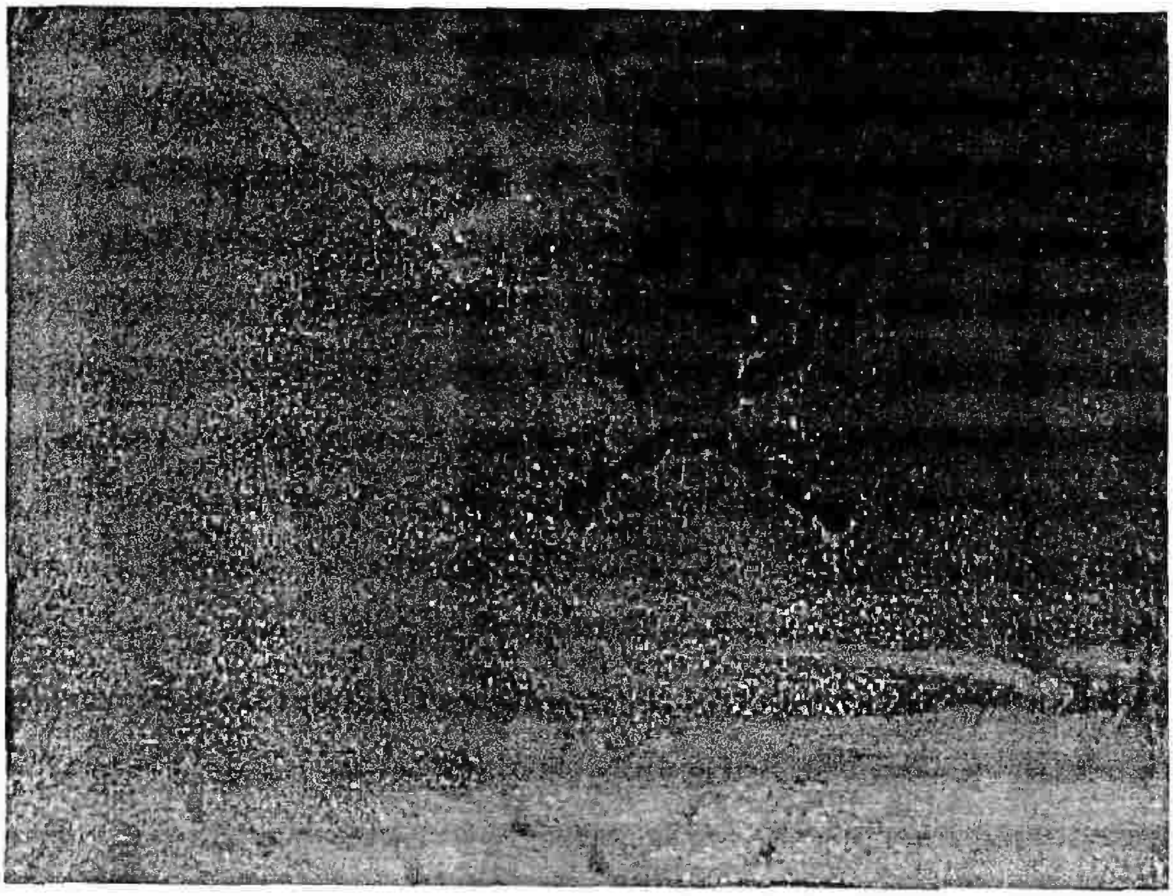


Figure (3.33): Salt Spray resistance of APAUP5+10 % AVEMPR coatings.

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 UP systems, it was observed that increasing of MA content of UP increases the adhesion of coat with steel. This can be referred to the formation of highly crosslinked network which prevents the penetration of salt solution from coat to steel [237]. The results of salt spray resistances agree with the data reported for acid and alkali resistance. Accordingly, the same discussion can be included in this section. The results of salt spray results indicate that the UP coatings pass 500 h without adhesion failure can be used in petroleum pipeline, tanker and marine coatings. Furthermore, cured UP resins have excellent alkali, acid and solvent resistance and provide a dense hard coating with good adhesion 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.