

Military Technical College
Kobry Elkobbah,
Cairo, Egypt



8th International Conference
on Aerospace Sciences &
Aviation Technology

1
2
3

CONVERTING POLY(ETHYLENE TEREPHTHALATE) WASTE TO CURABLE RESINS

Abdel-Azim A. Abdel-Azim* and Guda S.R.†

4

ABSTRACT

Different glycolyzed oligomers were prepared by depolymerization of poly(ethylene terephthalate), PET, waste in presence of manganese acetate catalyst. Diethylene glycol (DG), triethylene glycol (TG), propylene glycol (PG) and mixtures of DG/TG and DG/PG (50/50 wt%) were used for glycolysis. The weight ratio of PET to the glycol system was 1 : 0.65. The hydroxyl value of the glycolyzed products before and after removing the free glycol were determined. The amount of free glycol in each case was analyzed. These glycolyzed products were reacted with maleic anhydride (MA) to prepare a series of unsaturated polyesters (UP) having different molecular weights. These polyesters were dissolved in styrene monomer and their curing behavior was investigated and compared with the curing behavior of UP made from virgin materials. The effect of accelerator and initiator concentrations on the curing characteristics of the recycled resins was studied. The mechanical properties and the hardness of the cured resins were measured and correlated to their molecular structure. The synthesized UP are intended to be used for repairing and maintaining the damaged runways and workshops of military airports.

KEYWORD

Unsaturated polyester, propylene glycol, diethylene glycol, triethylene glycol, poly(ethylene terephthalate), styrene, curing, glycolysis, recycling,

5

* To whom all correspondence should be addressed

* Egyptian Petroleum Research Institute,

† Military Technical College, Kobry El-Kobba, Cairo, Egypt

INTRODUCTION

Fiber-reinforced plastics (FRP) form a versatile class of material that are increasingly replacing conventional structural materials such as metals, wood and concrete in engineering applications. The matrix materials of FRP are usually thermosetting resins. Among the thermosetting resins, unsaturated polyester (UP) and epoxies are the most commonly used. Besides their low cost, the UP resins can be tailor-made to meet specific requirements by proper choice of their chemical building blocks. The UP resins are made by the reaction of aliphatic diols with saturated and unsaturated diacids. The most commonly used diols are ethylene glycol, propylene glycol (PG), neopentyl glycol and diethylene glycol (DG). The use of PG offers better hydrolytic resistance relative to ethylene glycol, since the ester linkages are shielded by the pendant methyl groups. A further improvement in hydrolytic resistance is achieved by using neopentyl glycol because of the presence of two pendant methyl groups in its structure that enhances the steric protection for the ester linkage. The incorporation of DG is used to impart flexibility to the cured resin. The aromatic saturated diacids, used as monomers in UP, impart rigidity, whereas the aliphatic diacids are used to give flexibility. The unsaturated acid monomers used are maleic anhydride and fumaric acid. It is thus possible to achieve a wide range of properties by proper selection of the monomers used for synthesis of UP resins.

Investigations done recently have shown that the production of unsaturated polyester resins based on recycled Poly(ethylene terephthalate) (PET), is possible [1-3]. The PET wastes are typically found in scrap textile and beverage bottles that are collected after use in many locations and recycled in applications not requiring contact with food. If resins made with recycled PET can be used to produce good-quality polymer concrete (PC) at a potentially lower cost, their use will be important to the success of the PC industry. The main advantage of recycling PET into PC is that the PET materials do not have to be purified, or the colored material separated, to the extent that other recycling applications might require.

This article reports the results of synthesis and characterization of unsaturated polyester resins prepared by glycolysis of PET waste.

EXPERIMENTAL

Synthesis of Unsaturated Polyester (UP) Resins

The PET waste (beverage bottles) was depolymerized using five different glycol systems, diethylene glycol (DG), triethylene glycol (TG), propylene glycol (PG), a mixture of DG/TG and a mixture of DG/PG (50/50 wt%) in presence of manganese acetate as a trans-esterification catalyst. The concentration of the catalyst was 0.5 % (by weight) based on the weight of the PET while the weight

INTRODUCTION

Fiber-reinforced plastics (FRP) form a versatile class of material that are increasingly replacing conventional structural materials such as metals, wood and concrete in engineering applications. The matrix materials of FRP are usually thermosetting resins. Among the thermosetting resins, unsaturated polyester (UP) and epoxies are the most commonly used. Besides their low cost, the UP resins can be tailor-made to meet specific requirements by proper choice of their chemical building blocks. The UP resins are made by the reaction of aliphatic diols with saturated and unsaturated diacids. The most commonly used diols are ethylene glycol, propylene glycol (PG), neopentyl glycol and diethylene glycol (DG). The use of PG offers better hydrolytic resistance relative to ethylene glycol, since the ester linkages are shielded by the pendant methyl groups. A further improvement in hydrolytic resistance is achieved by using neopentyl glycol because of the presence of two pendant methyl groups in its structure that enhances the steric protection for the ester linkage. The incorporation of DG is used to impart flexibility to the cured resin. The aromatic saturated diacids, used as monomers in UP, impart rigidity, whereas the aliphatic diacids are used to give flexibility. The unsaturated acid monomers used are maleic anhydride and fumaric acid. It is thus possible to achieve a wide range of properties by proper selection of the monomers used for synthesis of UP resins.

Investigations done recently have shown that the production of unsaturated polyester resins based on recycled Poly(ethylene terephthalate) (PET), is possible [1-3]. The PET wastes are typically found in scrap textile and beverage bottles that are collected after use in many locations and recycled in applications not requiring contact with food. If resins made with recycled PET can be used to produce good-quality polymer concrete (PC) at a potentially lower cost, their use will be important to the success of the PC industry. The main advantage of recycling PET into PC is that the PET materials do not have to be purified, or the colored material separated, to the extent that other recycling applications might require.

This article reports the results of synthesis and characterization of unsaturated polyester resins prepared by glycolysis of PET waste.

EXPERIMENTAL

Synthesis of Unsaturated Polyester (UP) Resins

The PET waste (beverage bottles) was depolymerized using five different glycol systems, diethylene glycol (DG), triethylene glycol (TG), propylene glycol (PG), a mixture of DG/TG and a mixture of DG/PG (50/50 wt%) in presence of manganese acetate as a trans-esterification catalyst. The concentration of the catalyst was 0.5 % (by weight) based on the weight of the PET while the weight

of the glycol mixture used for glycolysis was 65% of the weight of PET. The reaction was carried out at temperature about 200°C under reflux for 4 hr in nitrogen atmosphere, and at 210°-230°C for 3 hr. The temperature of the reaction system was then allowed to drop to 100°C and maintained at this temperature for 1 hr. The temperature of the reaction mixture was allowed to drop to room temperature. The glycolized products were then analyzed for hydroxyl value and the amount of free glycols. The hydroxyl values were determined by the conventional acetic anhydride / pyridine method [4]. In order to determine the amount of the free glycol, a weighed quantity of the glycolized product was extracted with water and filtered. The aqueous filtrate containing free glycol and some water - soluble oligomers was concentrated by evaporation of water. The water-soluble oligomers were separated by precipitation from the free glycol by cooling the filtrate. The precipitated water-soluble oligomers were filtered and added to the residue remaining after the first filtration and weighed together. The difference between the initial and the final weights represents the amount of free glycol removed by water extraction.

The UP resins were prepared by reacting the glycolized products with maleic anhydride at a value of the hydroxyl to carboxyl ratio of 1.1 / 1. The hydroxyl number of the glycolized product before removing the free glycol was used to determine the amount of maleic anhydride. The reactions were carried out in an esterification reactor in which the reactants were heated from room temperature to 180°C in nitrogen atmosphere in about 1.5 hr. Then the temperature was held at 180°C for 4 hr and finally raised to 200°C and maintained until the acid value reached about 30 mg KOH/g. The acid value was monitored throughout the course of the reaction. The acid value was determined by titrating the solution of the weighed quantity of resin in acetone, with about 0.2N standard alcoholic KOH solution using phenolphthalein indicator. The water of the reaction was removed throughout the course of the reaction. At the end of the reaction the temperature of the entire contents of the reactor was allowed to drop to 100°C, then diluted with the desired amount of styrene containing hydroquinone as an inhibitor.

Determination of Peak Exotherm

The curing exotherms of unsaturated polyesters, using methyl ethyl keton peroxide (MEKP) as an initiator and cobalt octoate (CO) as an accelerator, were measured with a Digitron digital differential thermometer, type K, model 3202 with a resolution of 0.1° C, as described in our previous work [5,6].

Mechanical Properties

The compressive stress-strain diagrams and the hardness (shore D) were measured using a Zwick mechanical testing machine and a Zwick hardness tester (3102) according to ASTM method E9 and D2240, respectively as described in our previous work [7,8]. A constant loading rate of 44500 N / min

was applied on cylinders of 25-mm diameter and 50-mm for testing the compressive stress-strain diagrams. A flat plates of 5 mm thickness was used for measuring the hardness.

RESULTS AND DISCUSSION

Preparation and Characterization of the Glycolyzed Products

Five glycolyzed products, coded G-1 - G-5, were obtained by reacting PET, respectively with DG, TG, PG and mixtures of DG/TG and DG/PG having 0.5 weight fractions of DG. The weight ratio of glycol mixture to PET waste was kept constant (0.65 : 1) in all depolymerization reactions of PET with different glycols. The DG and TG were utilized among the glycol-systems to impart flexibility to the final cured resins. Tong et al. [9] found that the unsaturated polyester based on bis(2-hydroxyethyl)terephthalate, maleic anhydride and ethylene glycol was not compatible with styrene monomer. These authors found that it is necessary to substitute part of ethylene glycol with propylene glycol to enhance the compatibility of the product with the styrene monomer. Accordingly, in the present study, the PG was combined with DG to increase the miscibility of the synthesized resin with styrene monomer. We presumed that the incorporation of the hydroxypropylene in the glycolyzed products increases the lipophylicity of the polymers based on these glycolyzed products and consequently, enhances their solubility in styrene monomer.

The free glycol in each of these glycolyzed products was measured according to the procedure described before. The resultant data for the glycolyzed products are tabulated in Table (1) in conjunction with the hydroxyl number before and after removing the free glycol. The measured values of free glycols indicate that only about 2-4% of the glycols are used up in the transesterification. This finding runs in harmony with that found in a previous publication [10]. With respect to the hydroxyl numbers after removing the free glycol, it is obvious that there is a decrease from 348 mg KOH/g to below 300 mg KOH/g, when PG is replaced with another higher glycol. This reduction in the hydroxyl number reveals that PG is more effective in depolymerizing PET waste than other higher glycols. The hydroxyl numbers after removing the free glycols indicate that the extent of depolymerization is considerable and the glycolyzed products are, mainly, terminated with hydroxyl groups. Based on the obtained values of the hydroxyl number after removing the free glycol and the ¹H n.m.r. study carried out by Tong et al. [9], the following monomer, dimer and trimer compounds are exist:





In these formulae R may be:



Synthesis of UP Resins

The oligomers G-1 to G-5 were reacted with MA to produce the UP resins, coded UP-1 - UP-5, respectively. The hydroxyl number of the glycolized product before separation of the free glycol was used for estimating the amount of MA. The results of the characterization of the prepared unsaturated polyester resins are given in Table (2). In this table the measured values of acid and hydroxyl numbers are listed in column 3 and 4, respectively. These values were used for determining the number average molecular weight for each of the synthesized unsaturated polyester. Molecular weight determination through end-group analysis requires the polymer to contain a known number of determinable groups per molecule. The long-chain nature of polymers limits such groups to the end groups. Thus, the method is usually referred to as end-group analysis [4]. 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 weights, as the fraction of end groups becomes too small to be measured with precision. Although published procedure [4] often indicate that loss of precision occurs at molecular weights above 25,000, there is no doubt that the adoption of more sensitive techniques, such as gas chromatography or mass spectrometry to estimate the reaction products, can raise this limit by at least a factor of 10. Similar considerations apply to the use of infrared spectroscopy to measure end groups.

End group analysis in condensation polymers usually involves chemical methods of analysis for functional groups. Carboxyl groups in polyesters [11] are usually titrated directly with bases in alcoholic solvents and hydroxyl groups are usually determined by reacting them with a titratable reagent [12]. The chemical method used in determining the molecular weight of the polyesters prepared in the present investigation is described in detail in reference [4]. In all cases, unsaturated polyesters of number average molecular weight ranging between 1790 and 2430 were obtained. This range of molecular weights is slightly higher than that obtained by Vaidya and Nadkarni [13] who prepared three polyesters having molecular weights ranging between 1045 and 1325. At first glance, the data quoted in Table (2) show that the molecular weight decreases with increasing the PG content in the glycolized products. This may attributed to the

decrease in the molecular weight of the average molecular weight of the glycolized product that reacted with maleic anhydride in order to synthesize the unsaturated polyester resin. The highest molecular weight, $M_n = 2430$, was obtained for UP-1 for which the DG was used as a unique glycol for depolymerizing the PET waste. We believe that the accuracy of the determined values is good enough since the highest molecular weight is less than 25,000 as previously established [4]. When 1,5-pentanediol was used in conjunction with maleic anhydride, for synthesis of unsaturated polyester, Larez et al. [14] obtained an unsaturated polyester with higher molecular weight, $M_n = 3307$, as compared with that obtained with lower glycols [15,16].

Curing exotherms of UP Resins

The curing exotherms of the prepared formulae diluted with styrene were obtained by plotting the curing temperature as a function of time. Since the amount of heat evolved upon curing depends on the sample size, it was desirable to consider this parameter. For this reason it was very important to use glass bottles of the same volume in all measurements to achieve the repeatability of the measurements and affording legitimate comparative study. The temperature / time plots of curing process for the synthesized UP resins dissolved in styrene monomer (60% resin / 40% styrene) cured by 2.0 wt% initiator in presence of 0.02 wt% activator are illustrated in Fig. (1). The maximum heat evolved, T_{max} upon curing and the times required for complete curing, t_{max} obtained from these plots are included in Table (3).

The following section concerns with the possibility of modifying the curing behavior of the prepared resins by changing the amounts of the styrene solvent, initiator (MEKP) and accelerator (CO).

Effect of cobalt octoate (CO) and methyl ethyl keton peroxide (MEKP) concentrations on curing behavior

The effect of the CO and MEKP concentration on the curing parameters of 60% solution of UP-3 dissolved in styrene monomer is shown in Table (4).

Referring to the above discussed results, it is clear that the curing behavior can be manipulated as per requirement by varying the amount of the styrene solvent as well as the quantity of the initiator and accelerator. It is clear from the data that the maximum reaction temperature, T_{max} , attained and measured during the course of curing, increases with an increasing concentration of the accelerator. This behavior may be explained by the capability of the accelerator to decompose the initiator molecules into free radicals. These free radicals initiate the exothermic copolymerization reaction. The temperature of the reaction mixture rises only when the number of initiator free radicals is sufficient to make the rate of heat generation, due to copolymerization, larger than the heat dissipation. Consequently, the heat accumulation augments the reaction rate and

the polymer molecular weight rises steadily throughout the reaction. In the final stage of curing the viscosity of the reaction mixture increases due to the increasing polymer molecular weight [17-19] and the length of the crosslinks. This increase in viscosity causes a decrease in the rate of polymerization because of the retardation of diffusion. The mobility of unsaturated units that have not yet reacted is reduced not only by the increasing viscosity of the resin but also, and primarily, by the incorporation of these units into the three dimensional network, thus, the diffusion of unsaturated acid units towards the growing radical chains is inhibited to a greater extent than the diffusion of remaining free styrene molecules towards these radicals. The reaction of the unsaturated acid units is therefore expected to drop rapidly, and the curing proceeds primarily through the reaction of styrene units; hence the temperature continues to increase at a slower rate. At T_{max} the rate of heat dissipation starts to become larger than the heat generation and the temperature decreases slowly. As the copolymerization is almost completed, the temperature decreases rapidly due to the normal cooling of a hot body in the absence of heat generation. This behavior was found to run in harmony with the explanation given by Banno [20]. A similar explanation suggested by Bratychak et al. [21] stated that a satisfactory cure was achieved by degradation of peroxy groups, of peroxy urea- formaldehyde oligomers, to form oligoradicals capable of initiating polymerization through the UP double bonds.

The variations of the maximum reaction temperature, T_{max} , and the time required to reach it, t_{max} , with the CO concentration show that the maximum value of T_{max} is attained when about 0.02 wt% CO is used. The addition of more accelerator raises T_{max} very slightly.

The same behavior is obtained for the curing time t_{max} , with a minimum obtained with 0.02 wt% CO. Consequently, the addition of more CO does not cause an appreciable decrease in t_{max} . The behavior shown in column 4 - Table (4) can be explained according to the view that, as the content of accelerator increases, the decomposition rate of the initiator to free radicals increases, leading to an increasing rate of copolymerization. Consequently, the rate of heat accumulation increases, giving a shorter curing time t_{max} and a higher T_{max} .

For the purpose of studying the effect of MEKP concentration on the curing exotherm, different concentrations of MEKP were utilized in conjunction with a constant CO concentration of 0.02 wt%. The curing exotherms of various MEKP concentrations were measured (not produced here for brevity). The derived values of T_{max} and t_{max} are tabulated in Table (3). A considerable reduction in t_{max} , from 49.1 min. to 19.8 min. ($\approx 60\%$), is obtained by increasing the initiator (MEKP) concentration from 0.25 wt% to 3.01 wt%. It is to be noted that the increase of the initiator concentration from 2.0 wt% to 3.01 wt% only decreases t_{max} by 1.2 min. ($\approx 5.7\%$). A sharp increase in T_{max} with increasing MEKP concentration up to 2.00 wt% is obvious, a further increase in the MEKP concentration leads to a slight increase in T_{max} .

Effect of Styrene Content on Curing Time

To study the influence of the styrene content on the curing time of the prepared unsaturated polyesters, six different resin solutions in styrene monomers for each resin were prepared. The weight percentage of styrene in these solutions was ranging between 30% and 40%. The measured curing times are illustrated in Table (5). It can be seen that, in all cases, the curing time slightly reduces with increasing the styrene content. This may be attributed to the reduction of the viscosity of the resin solution and hence this facilitates the diffusion of styrene molecules towards the unreacted double bonds embedded in the three-dimensional network.

Abdel-Azim et al. Published an article [8], in which a series of UP resins based on phthalic anhydride, maleic anhydride and different glycol mixtures was prepared. The structure of formula No. 5 in this series is almost similar to the structure of UP resins prepared in the present study. The UP chains in the former formula contain *o*-phthalate group instead of the ethylene terephthalate group existing in the present formulae. The characteristics of formula 5 are shown in last row in Table (4). Comparing the curing characteristics of these two types of formulae reveals that the existence of terephthalate group increases the curing reaction time by about 30% - 50% and reduces the heat evolved during cure by about 4%-14%. This may be attributed to the increase of the distance between the curable double bonds. This increase of the distance is afforded by the extra -CH₂-CH₂- moiety existing in the recycled formulae as well as the position of the two ester groups in terephthalate moiety. It can be seen also that T_{max} decreases with decreasing the average molecular weight of the glycol system used for the preparation of the glycolized products and hence an increase in t_{max} is obtained. This finding afford a great body of evidence that the structure of the UP chains affecting the amount of heat liberated while curing as well as the curing time.

Mechanical Properties of Cured UP Resins

To a great extent, physical properties are the credentials that qualify the application of polyester resins. The mechanical properties are quantified easily, since the test methods are standardized and are easily related. As a sample is loaded, a force (stress) versus strain curve is recorded. The derived values of Young's modulus in GPa and σ_u in MPa are tabulated in Table (6). The data show that the UP-3 and UP-5 are rigid cured polyesters. These are the only polyesters comprise PG in their molecular chains. It can be seen that the Young's modulus (E) decreases from 0.83 GPa to 0.73 GPa with replacing half of the quantity of PG by DG. It is obvious that the UP resins based on the glycolized products derived from PET waste using DG and/or TG are flexible resins. The flexibility of these resins is confirmed since the value of Young's modulus is completely vanish. From the above mentioned results one can conclude that increasing the molecular weight of the glycol used for depolymerizing PET waste,

leads to an abridgment in Young's modulus of the final product. This persuades the speculation that the introduction of a tenuous network of primary chemical-bond crosslinks to the chains having long repeating units does not completely restrict the local freedom of motion of these chains. Accordingly, as the length of the polymer segment increases, many conformations can be held and the flexibility increases.

The dependence of the hardness of the cured resins with their segment length can be easily noticed from the data listed in Table (6). In this respect, it can be seen that as the segment length increases, the hardness of the cured resin decreases. On the other hand, the values of the hardness for the rigid resins (UP-3 & UP-5) are higher than that of flexible ones.

CONCLUSIONS

- The DG-, TG- and PG-based glycolized products of PET waste can be further converted into unsaturated polyesters that are compatible with styrene monomer.
- The exotherm temperatures and curing time of PET-based resins can be manipulated per processing requirements by varying the type of glycol used for depolymerizing the PET waste.
- The quantities of the accelerator and initiator have a great influence on the extent of heat evolved during the curing process as well as on the time required for complete curing.
- The recommended resin : styrene ratio is 60 : 40 to attain the faster curing time.

REFERENCES

1. Abdel-Azim A. Abdel-Azim, *Polymer Eng. & Sci.*, 36(24), (1996).
2. Abdel-Azim A. Abdel-Azim, *Polymer Journal (Japan)*, 29(1) 21 (1997).
3. Rebeiz K.S. and Fowler D.W., *Polym.-Plast. Tech. Eng.*, 30(8), 809 (1991).
4. Sorenson W.R. and Campbell T.W., "Preparative Method of Polymer Chemistry" Interscience, New York, p.155 (1968).
5. Abdel-Azim A.A., Attia I.A. and Nasr E.S., *Polym-Plast. Technol. Eng.*, 34(1), 79 (1995).
6. Abdel-Azim A.A., Mahmoud B.H. and Farhat M.S., *Polym. Advanc. Technol.*, 5: 269 (1994).
7. Nasr E.S. and Abdel-Azim A.A., *Polym. advanc. Technol.*, 3, 407 (1992).
8. Abdel-Azim A.A., Nasr E.S. and Farhat M.S., *Polym. J.*, 26(4), 423 (1993).
9. Tong S.N., Chen D.S., Chen C.C. and Chung L.Z., *Polymer*, 24, 469 (1983).

10. Abdel-Azim A.A. and Attia I.A., Polym. Advanc. Technol., 6, 688 (1995).
11. Pohl H.A., Anal. Chem., 26, 1614 (1954).
12. Conix A., Makromol. Chem., 26, 226 (1958).
13. Vaidya U.R. and Nadkarni V.M., J. Appl. Polym. Sci., 34, 235 (1987).
14. Larez V., Cristobal J. and Gilberto A., Polym. Bull., 26, 313 (1991).
15. Larez V., Cristobal J., Mendoza P. and Gilberto A., Polym. Bull., 22, 513 (1989).
16. Larez V., Cristobal J., Mendoza P. and Gilberto A., Polym. Bull., 23, 577 (1990).
17. Abdel-Azim A.A. and Moustafa S.S., Polym. Commun., 29, 85 (1988).
18. Abdel-Azim A.A., Moustafa S.S., El-Dessouky M.M., Abdel-Rehim F. and Hassan S.A., Polym., 27, 1406 (1986).
19. Abdel-Azim A.A. and Faramawy S., Egypt. J. Petrol., 1, 41 (1992).
20. Banno S., Kyoka Purasuchikkusu, 35(11), 100 (1984).
21. Bratychak M.N., Bychkov N.A., Puckin V.A. and Kushnir L.V., Lakokras. Mat. Ikh. Primer, 2, 8 (1985).

Table 1. Characterization of glycolized PET waste

Oligomer	Glycol system	free glycol, %	-OH value(1)	-OH value(2)
G-1	DG	62.7	804	295
G-2	TG	62.5	694	250
G-3	PG	61.0	974	348
G-4	DG/TG	62.3	635	233
G-5	DG/PG	62.1	900	324

-OH value(1) = hydroxyl value before free glycol removal

-OH value(2) = hydroxyl value after free glycol removal

Amount of glycol mixture = 65% of the weight of PET waste.

Table 2. Characterization of the Up resins obtained from the PET waste

Polyester	glycolized product used	carboxyl value (mg KOH/g)	hydroxyl value (mg KOH/g)	molecular weight <Mn>
UP-1	G1	17.90	28.27	2430
UP-2	G2	19.06	31.25	2230
UP-3	G-3	27.35	35.33	1790
UP-4	G-4	18.70	34.15	2123
UP-5	G-5	22.35	33.19	2020

Table 3. Curing behavior of UP resins specimens based on recycled glycolized products.

Parameter	Polyester				
	UP-1	UP-2	UP-3	UP-4	UP-5
t _{max} (min.)	23.9	27.3	21.0	25.2	21.5
T _{max} (° C)	39.3	36.2	42.0	37.8	41.7

Table 4. Effect of initiator concentration and activator concentration on curing behavior of UP-3 resin.

No.	Concentration (wt%)		t _{max} (min.)	T _{max} (° C)
	MEKP	CO x 100		
1	2.0	0.30	35.1	35.1
2	2.0	0.51	30.5	36.2
3	2.0	0.82	27.2	38.1
4	2.0	1.31	24.6	39.7
5	2.0	2.00	21.0	42.0
6	2.0	3.00	20.6	42.5
7	2.0	3.80	20.1	42.9
8	0.25	2.00	49.1	35.0
9	0.50	2.00	37.4	36.3
10	1.01	2.00	32.7	38.1
11	1.52	2.00	26.8	39.2
12	2.00	2.00	21.0	42.0
13	3.01	2.00	19.8	44.7
5 ⁺	2.00	2.00	16.0	43.7

+ data for formula No. 5 published in reference [8]

Table 5. Effect of styrene content on curing characteristics of the prepared UP resins.

Weight % of styrene	t _{max} (min.)				
	UP-1	UP-2	UP-3	UP-4	UP-5
30	25.4	29.4	23.6	27.9	24.2
32	24.9	28.9	23.0	27.3	23.6
34	24.6	28.5	22.6	26.8	23.0
36	24.3	28.2	21.9	26.2	22.5
38	24.2	27.8	21.5	25.7	21.9
40	23.9	27.3	21.0	25.2	21.5

Table 6. Mechanical characteristics of the cured UP resins.

polyester	Mechanical properties		Hardness
	σ_u (MPa)	E (GPa)	shore D
UP-1	183.0	----	80.5
UP-2	114.0	----	78.3
UP-3	130.5	0.83	87.3
UP-4	134.5	----	79.1
UP-5	160.3	0.73	85.2

Curing condition : resin / initiator / accelerator = 100 / 2 / 0.2 (parts by weight)

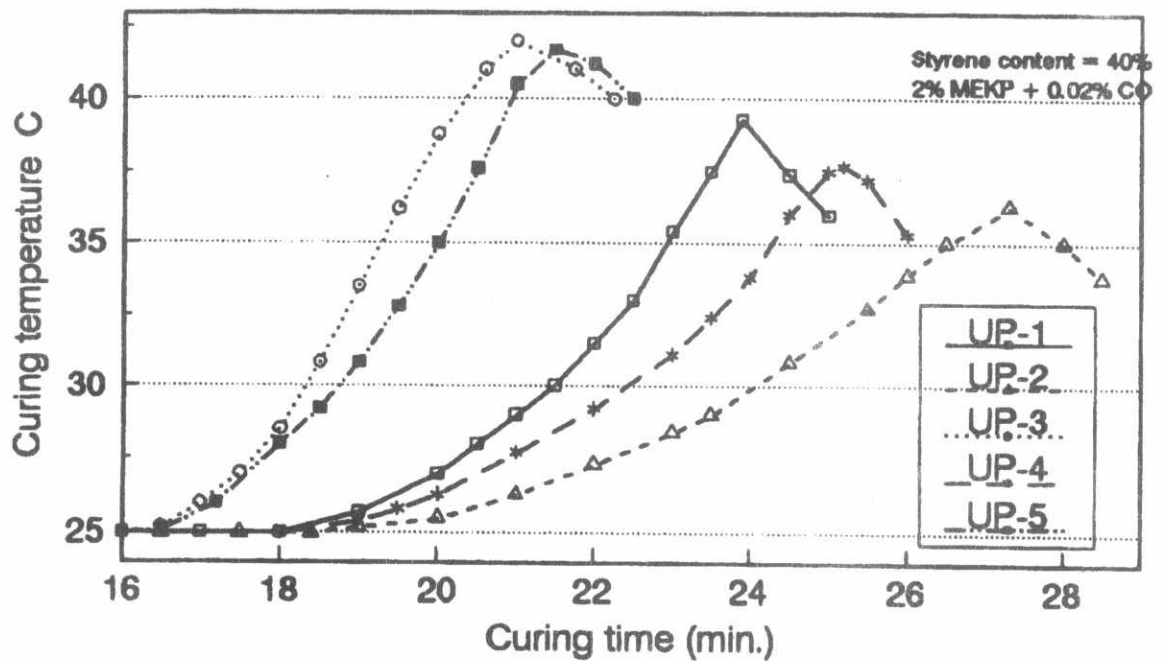


Fig. (1) Curing exotherms of UP-1 - UP-5 resins