

# Mechanical Characterization and Chemical Resistances of Cured Unsaturated Polyester Resins Modified with Vinyl Ester Resins Based on Recycled Poly(ethylene terephthalate)

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**ABSTRACT:** Unsaturated polyester resin (UP) was prepared from glycolized oligomer of poly(ethylene terephthalate) (PET) waste based on diethylene glycol (DEG). New diacrylate and dimethacrylate vinyl ester resins prepared from glycolysis of PET with tetraethylene glycol were blended with UP to study the mechanical characteristics of the cured UP. The vinyl ester resins were used as crosslinking agents for unsaturated polyester resin diluted with styrene, using free-radical initiator and accelerator. The mechanical properties of the cured UP resins were evaluated. The compressive properties of the cured UP/

styrene resins in the presence of different vinyl ester concentrations were evaluated. Increasing the vinyl ester content led to a pronounced improvement in the compression strength. The chemical resistances of the cured resins were evaluated through hot water, solvents, acid, and alkali resistance measurements. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3175–3182, 2007

**Key words:** unsaturated polyesters; poly(ethylene terephthalate); vinyl ester resins; recycling; curing behaviors; mechanical characteristics

## INTRODUCTION

Recently, recycling of polymer wastes has received a great deal of attention.<sup>1</sup> Poly(ethylene terephthalate) (PET) is one of the versatile engineering plastics, which is used to manufacture films and bottles for packaging. PET waste is typically found in scrap textiles and in beverage bottles that are collected after use in many locations and recycled for use in applications not requiring contact with food. If resins such as vinyl ester resins could be made from PET waste, they could be used to produce good-quality polymeric adhesives, coatings, and polymer concrete at a competitive cost. The recycling of PET to form curable resins would also help to alleviate an environmental problem. Therefore, the recycling of PET will not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy.<sup>2</sup>

Nadkarni et al.<sup>3,4</sup> suggested the synthesis of unsaturated polyester (UP) resin from PET waste. Recent investigations<sup>5–8</sup> have shown that the production of curable resins from recycled PET is possible. Abdel-Azim et al.<sup>9</sup> investigated the compressive strength of the polymer concrete using unsaturated polyester

based on recycled PET. On the other hand, glycolized oligomers based on PET were used to produce epoxy or polyurethane resins.<sup>7,10</sup> In the previous work, vinyl ester resins from depolymerized oligomers of PET using tetraethyleneglycol (TEG) were prepared.<sup>11</sup> The first aim of the present study was to prepare unsaturated polyester and vinyl ester resins from depolymerized oligomers of PET using tetraethyleneglycol (TEG) and diethylene glycol, DEG, to produce curable resins. Second, the blending of the prepared unsaturated polyester with vinyl ester resins to influence their mechanical properties is another goal. In this respect, TEG was selected to modify the chemical structure of the vinyl ester resin and to prepare a more flexible resin. Finally, the prepared resins were evaluated in coating applications of steel.

## EXPERIMENTAL

### Materials

UP and VE resins were prepared from PET waste, collected from beverage bottles, and characterized according to previous publications.<sup>9,11</sup> The diacrylate and dimethacrylate oligomers of recycled PET/TEG were designated here as GTA and GTM, respectively. In the previous publications,<sup>9,11,12</sup> UP and VE resins have been prepared from PET waste. In this respect, VE resins were prepared from depolymerization of

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PET using tetraethyleneglycol (TEG). The produced oligomers were reacted with epichlorohydrine, EC, to produce epoxy resin. The epoxy resin was reacted with either acrylic or methacrylic acid in the presence of triphenyl phosphite to produce vinyl ester resins having acrylate or methacrylate end groups. UP was prepared from glycolyzed PET waste with DEG in the presence of  $(\text{CH}_3\text{COO})_2\text{Mn}$  as catalyst.<sup>9</sup> The preparation of unsaturated polyester is based on condensation reaction between 1.1 mol of glycolyzed oligomers with ethylene glycol and 1 mol of maleic anhydride (MA). The oligomer, GD, was reacted with ethylene glycol (EG) and maleic anhydride (MA) by fusion method. More details on method of synthesis, purification, and characterization were described in details in previous publications.<sup>9,11</sup> Methyl ethyl ketone peroxide (MEKP) and cobalt octoate (Co) were used as initiator and accelerator, respectively. MEKP was supplied as a 50% paste in dimethyl phthalate. The Co was a 10% solution in styrene. The prepared UP from recycled PET was designated as RUP. All materials were supplied from Aldrich Chemical (UK). Commercial unsaturated polyester resin (CUP) Distitron 459 LV3 from Lonza (Italy) was used. The resin is based on orthophthalic and dissolved in styrene.

### Curing of UP and VE

The curing exotherms of the unsaturated polyester UP were measured in the presence of GTA and GTM, using MEKP as initiator and Co as accelerator, as described in previous work.<sup>9</sup> The UP was dissolved in 40% (w/w) of styrene monomer and mixed with various weight percentages of GTA and GTM (0–20%). The curing exotherms were determined at temperatures ranging from 25 to 65°C. The concentrations of MEKP and CO were 2% and 0.2% (w/w) with respect to the total weight of the cured samples.<sup>9</sup>

### Chemical resistances

Hot-water resistance of the cured UP resins was evaluated using ASTM D 870-92. The acid and alkali resistances were evaluated using ASTM C581-94 procedure, and the solvent resistance was measured according to ASTM Method, D 2792-69.

### Mechanical Testing

The comparative properties of the prepared polyester were measured in the form of test specimens of standard shape. The Young's modulus in compression ( $E_Y$ ) and compressive strength ( $\sigma_{\text{max}}$ ) of UP with GTA and GTM were measured using a Shimadzu Universal Testing Machine UH-A, Series Model 2000 KN Computer – Controlled Hydraulic Servo System. The mechanical properties were measured according to ASTM

D 695-44T and were calculated as the average values from five measurements.

## RESULTS AND DISCUSSION

Using the recycled PET offers the possibility of a lower cost source for production of curable resins. The present study is intended to prepare UP and vinyl ester resins from recycled PET waste to use in coating applications. Tong et al.<sup>13</sup> found that unsaturated polyesters based on bis(2-hydroxyethyl)terephthalate, maleic anhydride, and ethylene glycol were not compatible with styrene monomer. It was found that the replacement of the ethylene glycol by another type of glycol enhances the compatibility of the products with styrene monomer. In the present study, TEG was incorporated in the vinyl ester to increase the miscibility of the synthesized resins with styrene monomers. Schulze et al.<sup>14</sup> reported on the modification of unsaturated polyesters by poly(ethylene glycol) end groups to modify its solution behavior in styrene and to modify the mechanical properties of the cured resin. It was found that the conversion of end groups of UP with poly(ethylene glycol) polar end groups improved the flexibility of the cured material. Accordingly, we presumed that the incorporation of TEG into the structure of the vinyl esters will enhance their solubility in styrene monomer. On the other hand, DEG and TEG were used to modify the chemical structure of the prepared epoxy and UP resins to modify both mechanical and chemical resistances of cured resins.

Preliminary tests have shown that 40% of the styrene was found to be the least amount of styrene, which can dissolve the polyester under investigation. The prepared polyester a was viscous liquid having dark yellow to pale brownish color diluted by a sufficient quantity of styrene monomer to give 60% solution of unsaturated polyester (UP). The hydroxyl number of the glycolyzed products, after separation of the free glycol, was used for estimating the amount of dibasic acids required for the completion of the esterification reactions. The molecular weights of the prepared UP resin were determined using end group analysis as described in the Experimental section. The acid and hydroxyl values in (mg KOH/g) and the number-average molecular weights ( $M_n$ ) derived from these values are 7.29, 26.6, and 3310, respectively.

It is also important to know the exact chemical structure and molecular weight of the commercial CUP. The average molecular weight of CUP and the styrene content were determined using <sup>1</sup>H-NMR spectroscopy.<sup>11</sup> The molecular weight of UP was determined from the integration ratio of the vinyl group in the maleic peak area to the peak area corresponding to the OH— end groups. This ratio refers to the num-

ber of repeating units ( $m$ ) or the degree of condensation polymerization between phthalic anhydride, maleic anhydride, and glycol.<sup>15</sup> The styrene content of UP was calculated from the ratio of styrene vinyl groups to that of  $-\text{HC}=\text{CH}-$  (MA) in the UP. Using this approach, the number-average molecular weight of CUP,  $M_n$ , was determined to be 6720 g/mol, and the resin was found to contain 40% styrene by weight. This procedure agrees with the data obtained by Ziaee et al.<sup>15</sup>

### Mechanical properties of cured UP and VE resins

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. It has been reported that UP composites with low styrene residue can be obtained with the use of a high level of peroxide when cured at room temperature.<sup>16,17</sup> However, a high initiator concentration may result in low molecular weight and inferior mechanical properties of the cured composites. It may also shorten the gel time, resulting in poor mold filling and fiber wetting during molding. Many studies on UP resins<sup>18,19</sup> have demonstrated that the type of initiator has a profound effect on the residual amount of UP unsaturation and styrene monomer. Some effort has been made to improve the curing agent systems for better performance at low temperature cure, i.e., high final resin conversion, long pot life, and short cycle time.<sup>20,21</sup>

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 copolymerize with crosslinking agents (i.e., styrene), forming three-dimensional networks. A postcuring step is often needed to reach high conversion for better mechanical strength, high corrosion resistance, and good thermal properties.<sup>22</sup> When the temperature rise is sufficiently high, the thermal decomposition of uncatalyzed initiators or even the self-initiation of the monomers may take place, which accelerates the curing reaction of UP resins.<sup>23</sup> 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 con-

tent in low-temperature composite manufacturing processes. In this respect, the cured rods based on PU/VE/styrene systems were subjected to postcuring at temperature 105°C for 24 h to ensure complete conversion of both styrene and vinyl ester monomer in the crosslinked networks of UP. The total conversion of monomers to crosslinked polymers was estimated using equation:

$$\text{Total conversion (\%)} = W \times 100/W_0$$

where  $W$  and  $W_0$  are the total weight of the crosslinked polymers after postcuring at 105°C and the weight of the reactants, respectively. Small molecules carrying functional groups (monomers) or preformed larger molecules carrying functional groups serve as polymer network precursors. The functionality of precursors is important because it determines the conversion or time window of processability of the reacting material (pot-life). High-functionality precursors, like primary chains in vulcanization, gel at quite low conversions. Low-functionality precursors can be blended in such a way that the gel point can be adjusted as close to 100% conversion as desired. Even more important than the precursor functionality is the type of the crosslinking reaction: step-wise or chain with fast propagation step. The crosslinking of UP/VE and styrene systems leads to nearly instantaneous curing by the formation of radicals starting both polymerization and crosslinking. A wide variety of vinyl crosslinkers has been used to form crosslinked networks. The choice of the crosslinkers is quit broad in bulk polymerization. The Flory-Stockmayer theory has been used to predict the gel network buildup of a crosslinking polymerization.<sup>24,25</sup> Many side reactions, such as interchain cyclization, decrease the efficiency of the crosslinking reactions. This can be significant at high crosslinker levels, such as used in styrene divinylbenzene copolymers where intramolecular cyclization is believed to occur. At very high levels of crosslinker 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. Okay et al.<sup>26</sup> determined that almost half of pendant double bonds in a mixture of methacrylate crosslinkers were consumed by internal cyclization reactions when the mole fraction of crosslinkers was ranged from 0.126 to 0.256 (wt %). However, Landin and Macosko<sup>27</sup> showed that the rate of intramolecular cyclization was very low at low levels of crosslinker. To understand the distribution of crosslinks 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 crosslinker, and the various double bonds that are pendant to the polymer chain after

incorporation of the crosslinker. In the present work, the reactivity of VE and styrene crosslinkers toward UP was investigated from polymerization conversion (oven recovery). In this respect, the data of total conversion (%) for crosslinking of UP in the presence and absence of crosslinkers were determined and listed in Tables I–II. In this respect, the relation between total crosslinking conversion and crosslinking temperatures for CUP in the presence of GTM was represented in Figure 1. It was found that the conversion (%) increases as the amount of VE increases and it has much pronounced effect on conversion (%). The increment of conversion (%) with increasing contents of both GTA and GTM crosslinkers suggests that the obtained networks contain either highly crosslinked copolymer or more of the linear copolymer chains are linked into the gel network. 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 crosslinking. Otherwise, VE has two double bonds, so the higher VE level makes graft polymerization and chemical crosslinking easier. Conversion data indicate that CUP has greater conversion percentage than RUP. This can be referred to the presence of more curable maleic double bonds in CUP structure than RUP, which increase probability to react with VE and styrene. It was also observed that UP/GTM has a low conversion (%) values than that determined for crosslinked copolymers with GTM. This can be attributed to the differences in the reactivity ratios of both crosslinkers with the produced polymer.<sup>28</sup> This can be explained on the basis that the reactivity of GTM toward UP promotes the reaction rate initially due to a crosslinking. It facilitated gel effect but may retard the diffusion of reactants and leave unreacted vinyl groups (trapped free monomers or pendants) within the system at the later stage. The effect of temperature and postcuring on conversion values was observed

**TABLE I**  
Conversion Values of Cured UP/GTA Having Different Composition

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

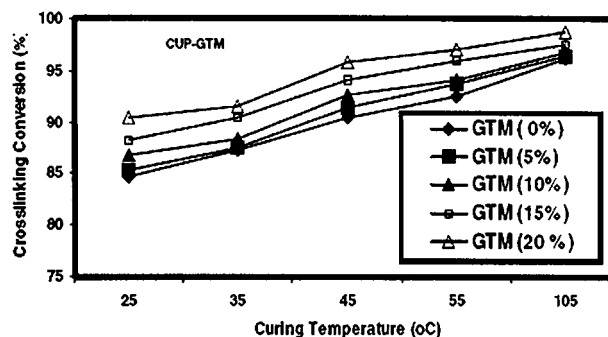
**TABLE II**  
Conversion Values of Cured UP/GTM Having Different Composition

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

from data listed in Tables I and II. It was observed that the conversion values were increased with increasing the temperature, which increases the rates of copolymerization and homopolymerization.<sup>29</sup>

#### Effect of molecular structure on the curing and mechanical properties

It is of interest to measure the mechanical properties of the cured resins to decide potential of the applications. The mechanical properties are quantified easily, since the test methods are standardized and are easily related. The derived values of the Young's modulus ( $E_Y$ ) in GPa and compression strength ( $\sigma_{max}$ ) in MPa for cured CUP and RUP are given in Tables III–VI. The values of Young's modulus,  $E_Y$ , in GPa and compressive strength,  $\sigma_u$ , in MPa were derived from the stress–strain curves for different cured resins. Data show that the  $\sigma_u$  values for CUP crosslinked with GTA and GTM are ranged between 135 and 240 MPa. The corresponding values for RUP are in the range of 106–186 MPa. The effect of the structure of the resin on its mechanical and curing behavior has been investigated. The molecular weights of the prepared polymers were determined by the end group analysis. Since methods of end group analysis count the num-



**Figure 1** Relation between crosslinking conversion and curing temperatures for cured CUP with GTM.

**TABLE III**  
**Mechanical Parameters of Cured CUP with GTA at Different Temperatures**

GTA (wt %)	Curing parameters at different temperatures							
	Compressive strength ( $\sigma_{\max}$ ) (MPa)				Young's modulus ( $E_Y$ ) (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	135	137	158	161	21	22	25	26
5	151	153	161	166	21	22	23	25
10	170	175	180	186	18	19	21	23
15	179	183	187	192	15	17	18	19
20	182	204	235	243	14	16	16	18
(GTA : styrene) (55 : 45%)	185	209	255	264	12	14	15	17

ber of molecules in a given weight of sample, they yield the number-average molecular weight for poly-disperse materials. In the present study, the resultant molecular weight of RUP is 3310 g/mol, in conjunction with the acid number of the prepared polyesters, while the molecular weight of CUP is 6720 g/mol. Accordingly, CUP exhibits a higher molecular weight and contains more terephthalate repeating units. The presence of more terephthalate repeating units between the crosslinks results in the existence of harder domains and better separation between the crosslinks in the packed crosslinked structure, and as a result, the mechanical properties are improved.<sup>29</sup>

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

riers for rotation, which enhances the flexibility of the resin. Accordingly, increasing the molecular weight of the utilized glycol or dibasic acid causes a decrease in the crosslinking density. Consequently, the mobility of the polymer segment increases, and hence an increase in flexibility is detected as manifested by a reduction in Young's modulus. The reduction in  $E_Y$  may be attributed to an increase in the length of the polymer segments. The previous argument may lead to speculation that increasing the molecular weight of the glycols decreases the crosslinking density. Consequently, the mobility of the polymer segment increases and hence an increase in flexibility is manifested by a reduction in Young's modulus.

The mechanical properties of the UP resins produced were studied in relation to the effect of the VE concentration, as well as to the effect of the oligoester diols structure used. There are different mechanical data were observed when GTA and GTM were used as crosslinkers. On the other hand, the mechanical properties are changed when CUP are replaced with RUP. It was observed that the compressive strength,  $\sigma_{\max}$  values increased with increasing of VE content from 0 to 20%. This indicates that the flexibility of resins was decreased with incorporation of VE in network structure. The increase in  $\sigma_{\max}$  on increasing the VE content can be attributed to the high content of curable double bonds, which greatly increase the crosslink density. The net effect is that the mechanical strength was significantly improved as a result of the more chemically bonded structures. The relation

**TABLE IV**  
**Mechanical Parameters of Cured CUP with GTM at Different Temperatures**

GTM (wt %)	Curing parameters at different temperatures							
	Compressive strength ( $\sigma_{\max}$ ) (MPa)				Young's modulus ( $E_Y$ ) (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	135	137	158	161	21	22	25	26
5	136	145	154	163	18	19	20	21
10	138	152	160	170	16	17	18	20
15	152	155	168	181	15	15	16	18
20	171	177	180	210	14	14	15	16
(GTM : styrene) (55 : 45%)	180	182	186	189	13	14	15	15

**TABLE V**  
**Mechanical Parameters of Cured RUP with GTA at Different Temperatures**

GTA (wt %)	Curing parameters at different temperatures							
	Compressive strength ( $\sigma_{\max}$ ) (MPa)				Young's modulus ( $E_Y$ ) (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	106	114	137	153	20	21	23	25
5	105	112	123	159	18	20	22	24
10	104	106	110	161	16	19	20	21
15	100	102	108	168	14	16	17	18
20	95	97	100	162	12	14	14	15
(GTA : styrene) (55 : 45%)	110	116	140	160	10	12	13	14

between compressive strength (MPa) and GTA and GTM concentrations for cured RUP and CUP were selected and represented in Figures 2 and 3. They show different mechanical properties when GTA was used as crosslinker for RUP. It was found that the compressive strength values were reduced with increasing concentrations of GTA. This can be explained on the basis that the reactivity of GTA with RUP is more reactive than RUP with styrene. The wide difference in reactivity between GTA and GTM during the crosslinking of the UP may be referred to the stabilization caused by the inductive effect of the methyl group present in the GTM structure. This behavior demonstrates the effect of the bulky phenyl group, afforded by styrene monomer, on the flexibility of the cured resins. It can be seen that the decrease of the amount of styrene in the network leads to decrease in the number of phenyl groups.

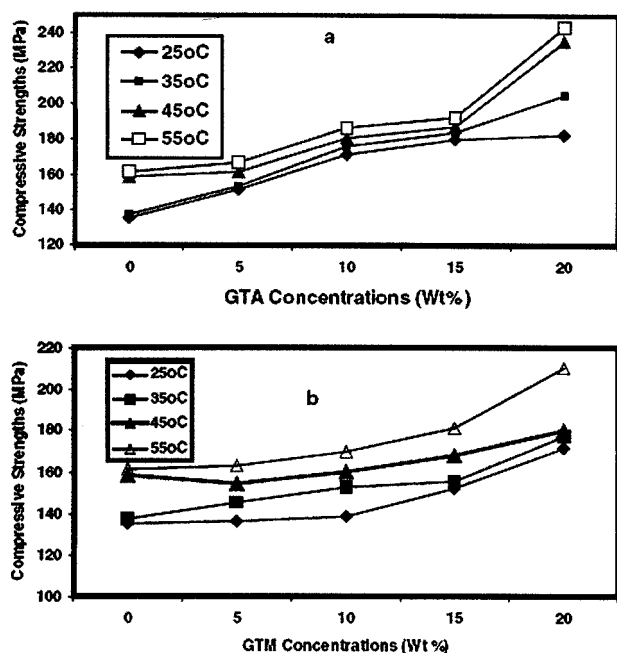
Careful inspection of data indicates that the compressive strength values of UP are reduced when GTM replaces GTA. This can be referred to the difference in the reactivity between UP, GTA, GTM, and styrene radicals. The data indicate that the rate of reaction of the UP radical with GTA is faster than that with GTM and the GTM radical reacts faster with its own monomer than does the GTA radical. Accordingly, all GTM crosslinker radicals are introduced in the crosslinked UP network before a significant number of styrene molecules can be incorporated.<sup>30</sup> So the probability that homopolymerization of styrene occurs during crosslinking is higher with GTM than

with GTA. It is well established that  $E_Y$  decreases with homopolymerization of the monomer.<sup>30</sup> This finding is in good agreement with that reported by Urban et al.<sup>31</sup> They concluded that the atactic polystyrene may form physical crosslinks when styrene content exceeds 40%. Bucknall et al.<sup>32</sup> used blends containing unsaturated polyester resin, poly(vinyl acetate), and styrene monomer in various proportions. The blends were cured by benzoyl peroxide as initiator. They reported that the peak temperature reached a maximum at 40% styrene. The Young's modulus measured by these authors was found to decrease with decreasing styrene content and increasing concentration of poly (vinyl acetate) in the blend. This speculation agrees with the data listed in Tables III–VI, which indicate that  $E_Y$  decreases on incorporation of GTM in a network of crosslinked UP. The fact that the  $\sigma_{\max}$  values were higher for crosslinked UP in the presence of GTA than GTM indicates the formation of a denser crosslinked network in the presence of GTA than with GTM crosslinkers. This can be attributed to the higher reactivity of GTA toward UP radicals. Careful inspection of data listed in Tables III–VI indicates that the resin has 55% of GTA or GTM cured with 45% of styrene monomer have higher compressive strength values. This indicates that highly cross-linked networks were obtained due to high reactivity of GTA or GTM with styrene.

The data show that the value of  $E_Y$  increased as the temperature of reaction increased. This is referred to a decrease of the molecular weight between crosslinks

**TABLE VI**  
**Mechanical Parameters of Cured RUP with GTM at Different Temperatures**

GTM (wt %)	Curing parameters at different temperatures							
	Compressive strength ( $\sigma_{\max}$ ) (MPa)				Young's modulus ( $E_Y$ ) (GPa)			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
0	106	114	137	153	20	21	23	25
5	110	116	142	155	17	18	20	23
10	118	124	152	160	15	16	18	20
15	145	159	161	180	13	15	16	17
20	152	161	173	186	12	13	13	14
(GTM : styrene) (55 : 45%)	160	169	178	190	10	11	12	13



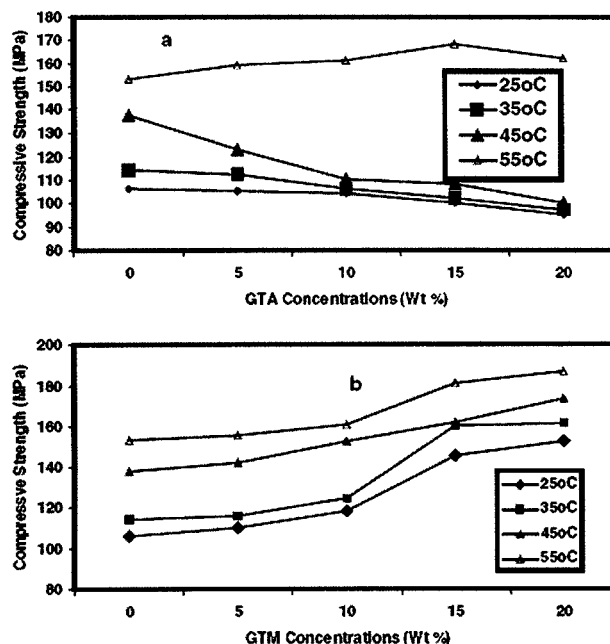
**Figure 2** Relation between Compressive strength for cured CUP with different concentrations of (a) GTA and (b) GTM crosslinkers.

with an increase in the polymerization temperature. The radical polymerization induced by thermal decomposition of an initiator, generally, as the polymerization temperature increases, the dissociation rate of initiation, propagation, and termination are enhanced.<sup>33</sup> All these factors, except the rate of termination, increase the rate of polymerization. However, a further increment in the polymerization temperature reduces the molecular weight of the polymer, due to an increase of the rate of termination and chain transfer, and increases the relative amount of the polymer chain end, which affects the mechanical properties of polymers. Accordingly, an increase in the reaction temperature forms a denser network of the cured polymers and reduces the average molecular weight between crosslinks.<sup>24</sup> Therefore, the increasing the polymerization temperature results in increase of both  $\sigma_{\max}$  and  $E_Y$  values.

### Chemical resistances of cured UP/VE systems

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 the Experimental section. Specimens were immersed in four separate environments: 5 wt % NaOH, 32 wt % HCl, 25 wt %  $H_2SO_4$ , and uncut kerosene, each at 66°C (150°F). There are two types of test methods including chemical resistance and mechanical tests

used to evaluate the durability of coatings. The present section discussed the chemical resistance test as described in experimental section. In this respect, the coated panels have been subjected to chemical environments (alkali, acid, and solvent) to study the durability of coats. The data of alkali-, acid- and solvent-resistance were determined for cured UP/VE/styrene and listed in Table VII. The sign (–) indicates failure of tests, while (+) sign indicates the coatings pass the tests. The failure of test indicates that the coating films losses their adhesion with panels and show cracking and flaking of the film. The 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. Nonpolar 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. 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.<sup>34</sup> The crosslink density can be controlled by changing the type of curing agents and the type of cured resins.<sup>35</sup> In this respect, it was found that all UP resins possess good solvent resistance with all mixing ratios with GTA or GTM. This can be attributed to increasing of crosslink density by increment of VE content, although the UP polarity is increased by increment of VE content.<sup>36</sup> The data of acid and alkali chemical resistance for cured CUP and RUP resins



**Figure 3** Relation between Compressive strength for cured RUP with different concentrations of (a) GTA and (b) GTM crosslinkers.

**TABLE VII**  
**Chemical Resistance Tests of CUP and RUP Cured with GTA and GTM at Different Mixing Ratios**

Cured network (%)	Acid resistance				Alkali resistance				Water resistance				Solvent resistance (5–20) (wt %)	Acetone test (5–20) (wt %)
	5	10	15	20	5	10	15	20	5	10	15	20		
CUP/GTA	+	+	+	+	+	+	+	+	+	+	+	+	+	+
CUP/GTM	+	+	+	+	+	+	+	+	+	+	+	+	+	+
RUP/GTA	+	+	+	+	+	+	+	+	+	+	+	+	+	+
RUP/GTM	+	+	+	+	+	+	+	+	+	+	+	+	+	+

indicates that these networks possess high resistance to alkaline and acidic aqueous solutions, although they have ester groups. The high alkaline and acidic resistance can be referred to high crosslink density of networks. This can be attributed to high crosslink density of network decreases their exposure to environment.<sup>37</sup>

This can be attributed to the decreasing of hardener content, which decreases crosslink density of network and increase the attack of ester groups of network to acidic and alkaline solutions.

### CONCLUSIONS

The compressive strength of the cured RUP resins was improved by the incorporation of GTA and GTM vinyl ester resins. The Young's modulus and compressive strength were increased when GTA vinyl ester resins were used instead GTM methacrylate end groups. It is better to use vinyl ester resins based on acrylate than those based on methacrylate resins. The data of acid and alkali chemical resistance for cured RUP and CUP resins indicates that these networks possess high resistance to alkaline and acidic aqueous solutions, although they have ester groups. The high alkaline and acidic resistance can be referred to high crosslink density of network, which decreases their exposure to environment.

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