

Tertiary Aromatic Amines As Cure Reaction Promoters For Unsaturated Polyester Resins.

II. Low Temperature Studies

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Synopsis

N,N-dimethyl-*p*-toluidine (DMPT), *N,N*-dimethyl-*m*-toluidine (DMMT), and their isomeric blends, were compared to *N,N*-dimethylaniline (DMA) as cure reaction promoters for an unsaturated polyester resin using 1% benzoyl peroxide at 15°C and 10°C. The promoters showed the following order of efficiency (by weight) as indicated by decreased gel and cure times: DMPT > DMPT/DMMT blends > DMMT > DMA. Under these conditions the optimum promoter concentration was 0.3%. At this level or higher, 80/20 and 60/40 DMPT/DMMT blends (wt/wt) performed essentially equal to DMPT but superior to DMMT and DMA. Examination of cured samples using differential scanning calorimetry showed that resins cured with DMPT or isomeric blends of DMPT and DMMT with high DMPT contents displayed higher glass transition temperatures and greater degrees of cure than samples cured using DMMT or DMA.

INTRODUCTION

Unsaturated polyester resins are cured by the free radical copolymerization of styrene, which serves as both monomer and diluent, with the unsaturated groups along the polyester chain.¹ The most commonly used initiators for this reaction are organic peroxides. To obtain reasonable rates of initiation under ambient temperature conditions it is generally necessary to add a chemical reducer, or promoter, to the resin. The most common promoters are transition metal ions, such as Co²⁺, and tertiary aromatic amines, such as *N,N*-dimethyl-*p*-toluidene (DMPT) or *N,N*-dimethylaniline (DMA).

In the course of our continuing investigations of cure reaction promoters for unsaturated polyester resins, we have shown² that for benzoyl peroxide (BP) initiation at room temperature, DMPT is 2.5 to 3 times more efficient (by weight) than the more commonly used DMA, as indicated by decreased gel and cure times. Thus, for systems where a fast cure is desired, DMPT offers the possibility for enhanced reactivity without loss of physical properties.

A recent report³ presented data comparing DMPT to DMA as the promoter in methacrylate vinyl ester resins using BP as initiator. The results showed that within the temperature range 15–32°C (60–90°F) the difference in promoter efficiency was about 4 to 1 in favor of DMPT.

The purpose of this work was to investigate the behavior of the BP/tertiary aromatic amine initiation system with unsaturated polyester resins at lower temperatures. Very often these resins must be used outdoors where temperatures cannot be easily controlled. Notable examples are polymer

TABLE I
Base Formulation for Cure Reactions

Benzoyl peroxide dispersion (50%)	2.00g
Tertiary aromatic amine	0.1-0.5g
Polyester resin	balance
Total mass	= 100g

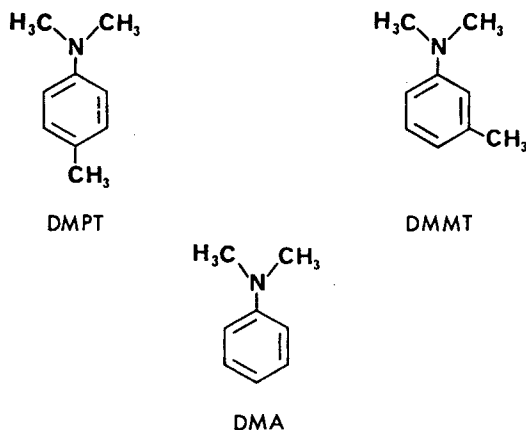


Fig. 1. Tertiary aromatic amines studied.

concrete and bolt anchoring applications. We reasoned that for reduced temperature applications where a more reactive initiation system is needed, the proven higher efficiency of DMPT should render it the promoter of choice.

DMPT, *N,N*-dimethyl-*m*-toluidene (DMMT), and their isomeric blends were compared to DMA using the basic formulation given in Table I. Structures of these tertiary aromatic amines are given in Figure 1. For simplicity, no inhibitors were added. Characteristic gel time, cure time, and hardness of each resin sample were measured. Differential scanning calorimetry (DSC) was used to estimate the degree of cure from the postcure peak exotherm and the glass transition temperature (T_g) of selected samples.

EXPERIMENTAL

Materials

DMPT and DMMT (First Chemical Corp.) and DMA (Alfa Prod.) were used as received.

BP was received as a 50% dispersion in tricresyl phosphate (Lucidol, Luperco ATC) and was used without modification.

The resin used in this study was an unpromoted, low-reactivity resin (Polylite 31-001; Reichold Chem. Co.).

PROCEDURE

All curing reactions were performed at 15°C (60°F) or 10°C (50°F) using a wide mouth mason jar (Kerr, 1/2 pint, #70610-00500) suspended in a con-

stant temperature water bath. In all cases the initiator was benzoyl peroxide (1.00 phr) and the total reacting mass was 100 g. A representative procedure was as follows: The amine promoter was weighed into a clean, dry jar to an accuracy of ± 0.001 g using a ground glass syringe for transfer. The proper quantity of resin was then weighed into the jar. The jar was placed into the constant temperature water bath and allowed to equilibrate for 30 minutes. Next, 2 ± 0.0075 g BP dispersion was weighed onto the end of a wooden tongue blade. A lab timer was activated, and the BP dispersion was mixed thoroughly into the resin by stirring for three minutes with the blade, gently to avoid air entrapment. The reacting mass was probed periodically with the blade, and the gel time was recorded as the time from introduction of the initiator to the point when the resin snapped back from the blade in a rubbery manner. Next, a thermometer wrapped in aluminum foil was inserted into the center of the gelled resin. The cure time was recorded as the time from addition of the initiator to the peak exotherm, i.e., the maximum temperature reached.

Barcol hardness of cured samples was determined 24 h after initiator injection using a Barber-Colman Impressor (model GYZJ 934-1).

DSC (Dupont 910 DSC attached to a 990 thermal analyzer) was carried out on small portions (10-20 mg) of the cured samples after about six weeks of storage at room temperature. All thermograms were produced using a programmed heating rate of $10^{\circ}\text{C}/\text{min}$ and a nitrogen atmosphere. All samples were subjected to two scans starting at room temperature and ending at an appropriate temperature well above the T_g . During the first scan, a broad exotherm occurred, representing conversion of residual unsaturation within the sample. The initial temperature, T_i , at which the postcure begins and the postcure peak exotherm, T_m , at which the maximum rate of cure takes place, were measured from the first DSC scan of the cured resin. The sample was then cooled and a second DSC thermogram was recorded to measure the glass transition temperature. First change in the slope of the thermogram was taken as the T_g . T_g values were an average of two or more measurements.

RESULTS AND DISCUSSION

In our previous report,² tests were performed using plastic-lined paper cups at 25°C . Since the heat loss from the cups was solely by convection with the surrounding air, high peak exotherms in the range $120\text{--}160^{\circ}\text{C}$ were observed. In the present studies, conducted at low temperatures, we have employed wide-mouth glass jars suspended in a thermostatted water bath. Because these vessels display a higher surface to volume ratio, and since they are suspended in water, the heat energy developed during the cure reaction is more quickly dissipated. These conditions better simulate the field applications of unsaturated polyester resins. Several experiments conducted using glass jars in the constant temperature water bath at room temperature have shown relatively reduced peak exotherms and slightly increased gel times as compared to the previous tests² conducted using paper cups.

DMPT and DMMT were compared to DMA as cure reaction promoters at 5 different concentrations (0.1% to 0.5% by weight) for the unsaturated polyester resin. The effect of promoter concentration on the gel and cure times

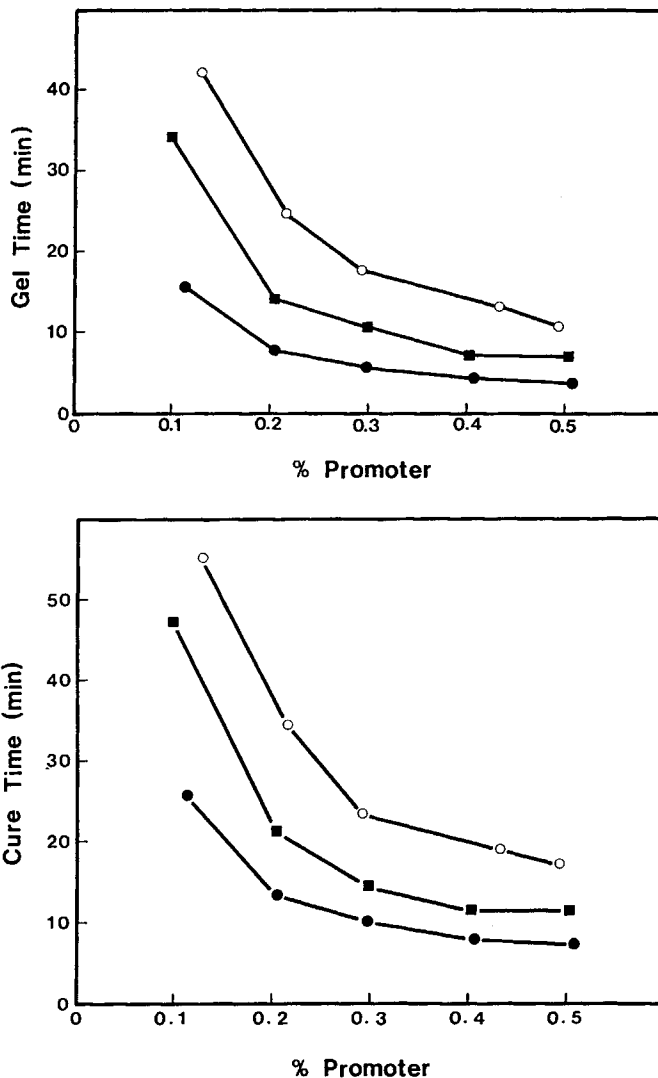


Fig. 2. (a) Gel time vs. promoter concentration for a cure reaction using 1% benzoyl peroxide at 15°C: (●) DMPT; (■) DMMT and (○) DMA. (b) Cure time vs. promoter concentration for a cure reaction using 1% benzoyl peroxide at 15°C: (●) DMPT; (■) DMMT and (○) DMA.

at 15 and 10°C is depicted in Figures 2 and 3, respectively. At 15°C (Fig. 2) DMPT produced rates of cure 2.5 to 3 times higher than DMA. The effectiveness of DMMT was also found to be higher than DMA, but less than DMPT. As shown in Figure 3, the reactivity difference was more pronounced at 10°C with 4 to 4.5-fold faster gel and cure times using DMPT versus DMA.

Blends of DMPT/DMMT in the weight ratios 80/20, 60/40, 40/60, and 20/80 were found to have reactivities intermediate between either pure isomer. As shown in Figure 4 (15°C) and Figure 5 (10°C), DMPT/DMMT blends of 80/20 and 60/40 performed essentially similar to DMPT at promoter concentrations of 0.3% and above.

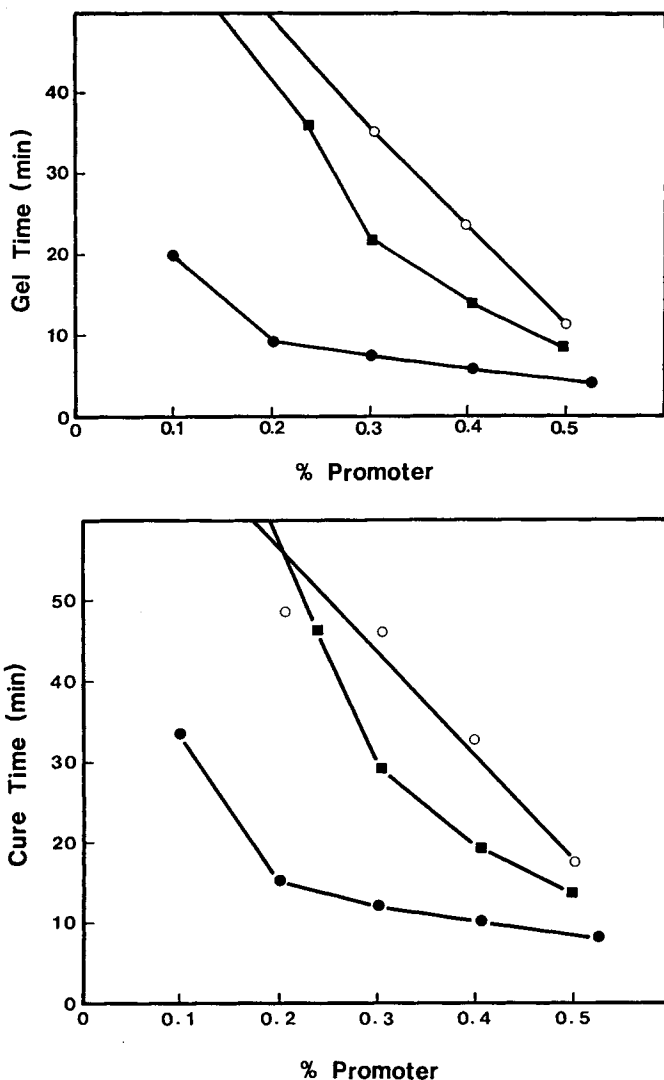


Fig. 3. (a) Gel time vs. promoter concentration for a cure reaction using 1% benzoyl peroxide at 10°C: (●) DMPT; (■) DMMT and (○) DMA. (b) Cure time vs promoter concentration for a cure reaction using 1% benzoyl peroxide at 10°C: (●) DMPT; (■) DMMT and (○) DMA.

Referring again to Figures 2–5, it may be noted that under these conditions, 0.3% promoter seems to be the optimum concentration as there is no significant increase in the rate of cure above this concentration. This fact is further confirmed by the hardness values and DSC analysis of cured samples; hardness and T_g 's of cured samples go through a maximum at about 0.3% promoter for most samples. In identical systems at room temperature, the optimum promoter concentration is slightly less, i.e., in the range 0.1–0.2%.

The greater reactivity of DMPT and high DMPT isomer blends over DMA at low temperatures can be best appreciated from a plot of gel time/cure time vs. cure temperature, as shown in Figure 6 for DMPT, DMA, and 80/20

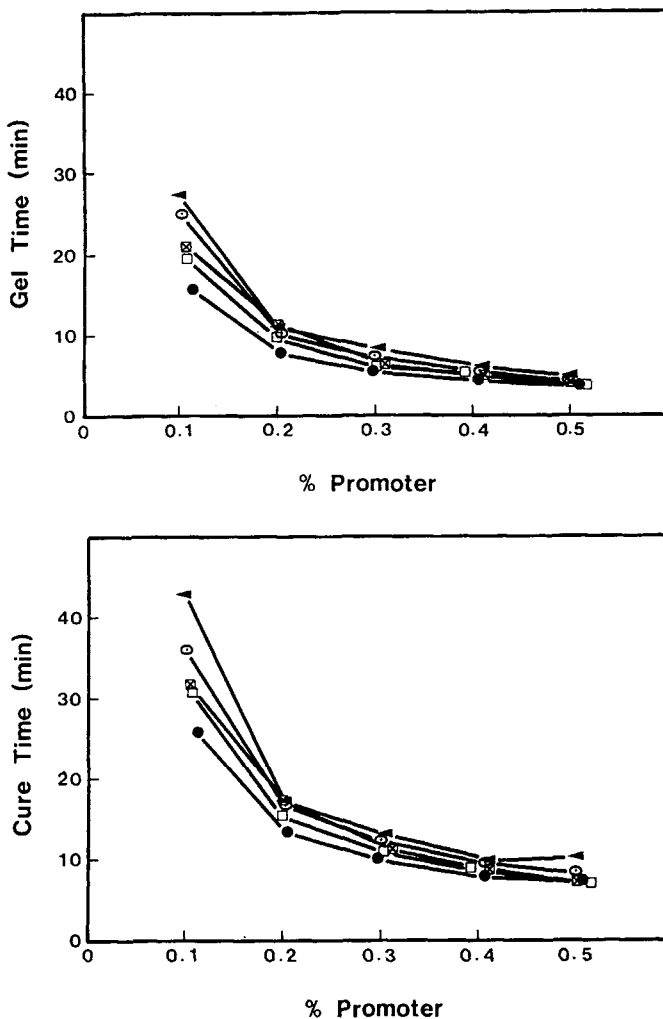


Fig. 4. (a) Gel time vs. promoter blend concentration for a cure reaction using 1% benzoyl peroxide at 15°C: (●) DMPT; (□) DMPT/DMMT 80/20; (⊠) DMPT/DMMT 60/40; (○) DMPT/DMMT 40/60 and (▲) DMPT/DMMT 20/80. (b) Cure time vs. promoter blend concentration for a cure reaction using 1% benzoyl peroxide at 15°C: (●) DMPT; (□) DMPT/DMMT 80/20; (⊠) DMPT/DMMT 60/40; (○) DMPT/DMMT 40/60 and (▲) DMPT/DMMT 20/80.

DMPT/DMMT. It can be seen that the promotion efficiency of DMA decreases precipitously as the temperature is lowered below room temperature. In fact, the reaction of DMA promoted systems at 10°C was so slow that a distinct gel time could not be discerned, in other words, the samples did not undergo a sudden, homogeneous gelation. In contrast, the efficiency of DMPT and 80/20 DMPT/DMMT is reduced only marginally as the temperature is lowered.

All of the preceding observations are consistent with the reported mechanism of promotion of BP by tertiary aromatic amines, as shown in Figure 7. Tertiary aromatic amines attack BP to form an N-benzoyloxydimethylanilinium ion (I) which then decomposes to give a radical cation of the

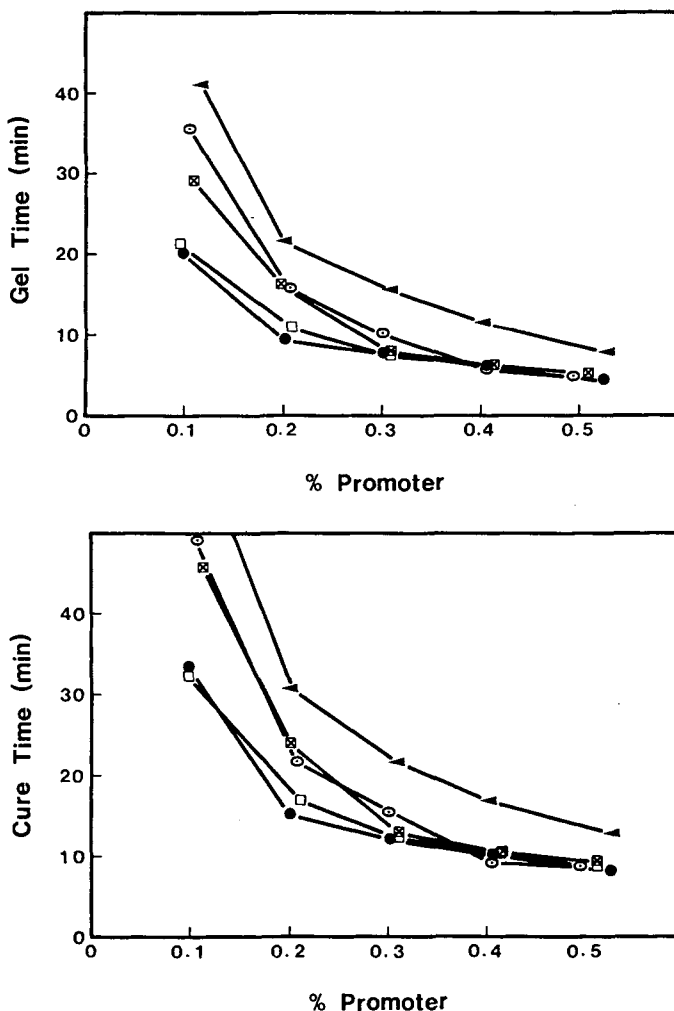


Fig. 5. (a) Gel time vs promoter blend concentration for a cure reaction using 1% benzoyl peroxide at 10°C: (●) DMPT; (□) DMPT/DMMT 80/20; (⊠) DMPT/DMMT 60/40; (○) DMPT/DMMT 40/60 and (▲) DMPT/DMMT 20/80. (b) Cure time vs. promoter blend concentration for a cure reaction using 1% benzoyl peroxide at 10°C: (●) DMPT; (□) DMPT/DMMT 80/20; (⊠) DMPT/DMMT 60/40; (○) DMPT/DMMT 40/60 and (▲) DMPT/DMMT 20/80.

tertiary amine (II) and a benzyloxy radical (III) which initiates the cure reaction.⁴ The presence of electron releasing substituents on the aniline ring, such as the methyl found in DMPT or DMMT, facilitates the nucleophilic attack of nitrogen on peroxide oxygen, resulting in faster initiation and shorter gel and cure times. This is apparently the reason for the higher efficiency of DMPT and DMMT over the conventional DMA. As expected, the effect is more pronounced when the electron releasing group is *para* rather than *meta* to the amine group. Hence, one observes heightened reactivity with the *para* isomer. Interestingly, as we reported in an earlier paper,² the *ortho* isomer (*N,N*-dimethyl-*o*-toluidene) is a very sluggish promoter. This effect is obviously due to steric hinderance of the amine.

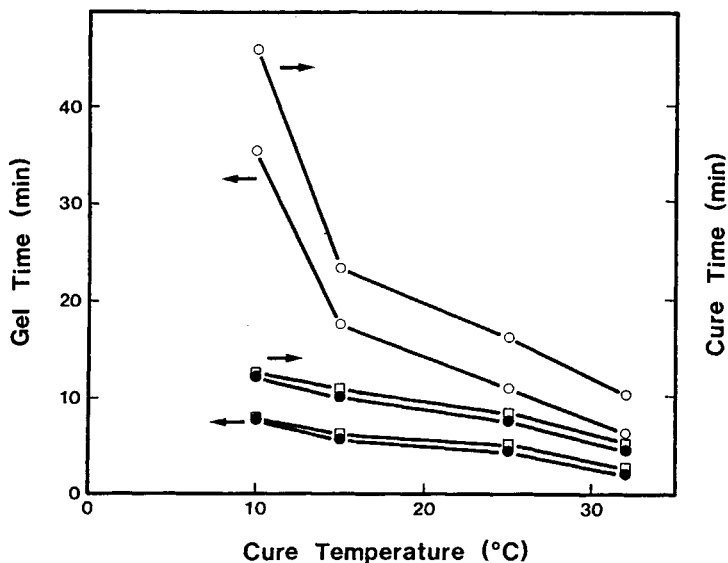


Fig. 6. Gel time/cure time vs. cure temperature for a cure reaction using 1% benzoyl peroxide and 0.3% promoter: (●) DMPT; (□) DMPT/DMMT 80/20 and (○) DMA.

Peak exotherms and Barcol hardness values of samples cured with different promoter concentrations are listed in Tables II and III for cure temperatures 15°C and 10°C, respectively. Peak exotherms in the range 80–105°C were observed at both cure temperatures. The highest peak exotherms, i.e., values above 100°C, were obtained using DMPT and DMPT/DMMT blends at either 0.2 or 0.3% concentration. In a low temperature initiator system higher peak exotherms are desirable as an aid toward complete curing of thick sections. In contrast, high peak exotherms may cause cracking and warping in high temperature initiator systems.⁵

Barcol hardness values were in the range 20–39 and 20–30 for 15°C and 10°C cure temperatures, respectively. In most cases, Barcol hardness values increased with promoter concentration up to around 0.3%. Further increase in promoter concentration did not show a particular trend in hardness. We have reported Barcol hardness values since they are widely used in the thermoset

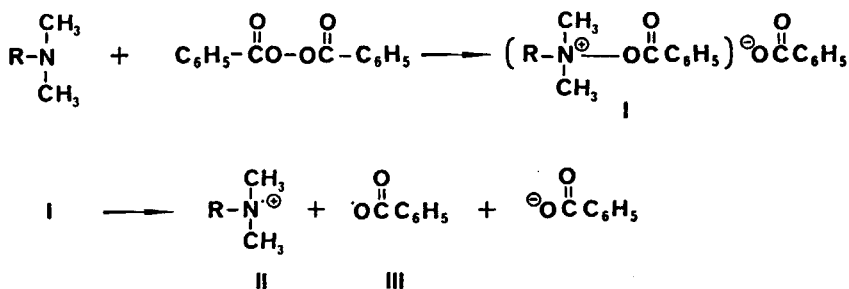


Fig. 7. Mechanism of free radical generation in the benzoyl peroxide/tertiary aromatic amine system.

TABLE II
Peak Exotherm and Barcol Hardness Values
for Samples Cured at 15°C

Promoter	Concentration (%)	Peak exotherm (°C)	Barcol hardness
DMPT	0.1	91	29
	0.2	93	39
	0.3	88	37
	0.4	86	29
	0.5	81	19
DMPT/DMMT 80/20	0.1	93	30
	0.2	99	33
	0.3	98	32
	0.4	93	33
	0.5	88	28
DMPT/DMMT 60/40	0.1	91	22
	0.2	99	25
	0.3	100	30
	0.4	87	33
	0.5	86	33
DMPT/DMMT 40/60	0.1	99	28
	0.2	99	30
	0.3	96	27
	0.4	92	35
	0.5	95	30
DMPT/DMMT 20/80	0.1	81	24
	0.2	97	31
	0.3	101	30
	0.4	88	30
	0.5	90	25
DMMT	0.1	94	19
	0.2	94	32
	0.3	91	32
	0.4	95	34
	0.5	86	34
DMA	0.1	92	25
	0.2	84	35
	0.3	84	36
	0.4	86	29
	0.5	88	37

industry. However the observed spread in the data prevents its use as a measure of cross-link density.

DSC was used on cured samples to estimate the degree of cure. With other factors held constant, the higher the glass transition temperature of a thermoset polymer, the greater the extent of cure, i.e., the higher the cross-link density. The T_g values measured for samples cured with different DMPT concentrations have again confirmed that about 0.3% promoter is the optimum concentration for curing the polyester resin under investigation. Hence, in all other promoter systems 0.3% concentration was taken as representative, and the T_g 's were measured for comparison. DSC thermograms of a representative system (0.3% DMPT/DMMT, 60/40) are shown in Figure 8. Curve A is typical of the first DSC scan taken of a sample after curing. It shows a

TABLE III
Peak Exotherm and Barcol Hardness Values
for Samples Cured at 10°C

Promoter	Concentration (%)	Peak exotherm (°C)	Barcol hardness
DMPT	0.1	86	23
	0.2	101	27
	0.3	85	24
	0.4	86	30
	0.5	83	24
DMPT/DMMT 80/20	0.1	89	22
	0.2	95	28
	0.3	89	25
	0.4	91	21
	0.5	84	23
DMPT/DMMT 60/40	0.1	80	23
	0.2	104	26
	0.3	83	—
	0.4	81	27
	0.5	85	28
DMPT/DMMT 40/60	0.1	90	26
	0.2	96	27
	0.3	105	30
	0.4	81	23
	0.5	90	27
DMPT/DMMT 20/80	0.1	89	26
	0.2	83	24
	0.3	97	24
	0.4	91	26
	0.5	90	24
DMMT	0.1	97	28
	0.2	94	26
	0.3	95	25
	0.4	96	24
	0.5	86	27
DMA	0.1	—	13
	0.2	97	25
	0.3	97	23
	0.4	90	26
	0.5	93	26

broad exotherm which represents a postcure of the sample at elevated temperature. The starting temperature of the postcure reaction is denoted as T_i , and the temperature at which the maximum rate of reaction occurs as T_m (postcure peak exotherm). Mass,⁵ in a study of the optimization of processing conditions for unsaturated polyester resins, has concluded that T_m will shift to higher temperatures as a function of the degree of cure obtained in the original curing reaction. Thus, the more complete the original curing reaction, the smaller the total postcure exotherm and the higher the T_m . T_i , T_m , and T_g for samples cured at 15°C are presented in Table IV for comparison of various promoter systems. It is interesting to note that the T_m 's are shifted toward higher temperatures in the samples promoted with DMPT and DMPT/DMMT blends when compared to DMA promoted samples; it can be

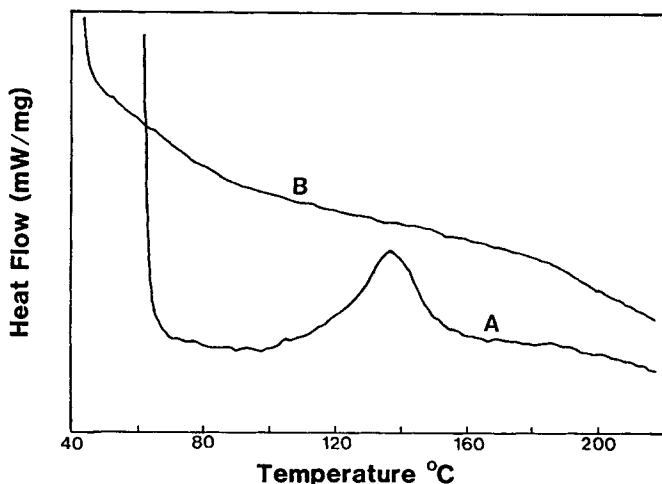


Fig. 8. Postcure DSC thermograms of polyester resins cured at 15°C using 1% benzoyl peroxide and 0.3% DMPT/DMMT 60/40 blend at 15°C: A-first scan and B-second scan.

TABLE IV
Postcure DSC Analysis of Polyester Resins Cured at 15°C

Promoter	Concentration (%)	T_i (°C)	T_m (°C)	T_g (°C)
DMPT	0.1	111	126	160
DMPT	0.3	124	147	168
DMPT	0.5	120	136	162
DMPT/DMMT 80/20	0.3	106	139	165
DMPT/DMMT 60/40	0.3	103	139	165
DMPT/DMMT 40/60	0.3	100	140	163
DMPT/DMMT 20/80	0.3	100	138	162
DMMT	0.3	103	137	163
DMA	0.3	104	137	158

seen from Table IV that the T_m 's decrease in the order DMPT > DMPT/DMMT blends > DMMT = DMA.

When the sample was allowed to cool and a second DSC scan was performed (Fig. 8, Curve B) an exotherm was not observed and the T_g could be measured in the conventional manner. As listed in Table IV, T_g 's were highest for samples cured using DMPT or high DMPT isomer blends.

CONCLUSIONS

In the temperature range studied, using BP initiation, the various promoters showed the following order of efficiency in curing an unsaturated polyester resin: DMPT > DMPT/DMMT blends > DMMT > DMA. As the cure temperature is lowered to around 10°C, DMPT and 80/20 DMPT/DMMT

continue to provide reasonable cure rates while the effectiveness of DMA decreases dramatically.

Under the conditions studied, the optimum promoter concentration was about 0.3%. At this concentration and above, DMPT/DMMT blends of 80/20 and 60/40 displayed reactivities essentially equal to DMPT but greater than DMMT and DMA. Since a mixture of isomers should be cheaper to produce than a pure compound, the cost effectiveness of these blends is probably the highest of all the promoters studied.

Glass transition temperatures and postcure peak exotherms obtained from DSC analysis show that DMPT or high-DMPT blends produce higher degrees of cure compared to DMMT or DMA. In a future paper, quantitative thermal data, obtained from DSC analysis of the various promoter systems, will be presented.

This work was supported by a grant from First Chemical Corporation, Pascagoula, Mississippi.

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Received January 16, 1986

Accepted March 4, 1986