

Gel Time and Exotherm Behaviour Studies of an Unsaturated Polyester Resin Initiated and Promoted with Dual Systems

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ABSTRACT

In this study, the various combinations of low- and high-decomposition temperature initiators and dual promoters were used to cure an unsaturated polyester resin. Methyl ethyl ketone peroxide (MEKP) and acetyl acetone peroxide (AAP) solutions were used as low-temperature initiators. Benzoyl peroxide (BPO) and t-butyl perbenzoate (TBPB) were used as medium and high-temperature decomposition initiators, respectively. Gel time and pseudo-adiabatic exotherm measurements have been used to study the curing behaviour. It is demonstrated that the low-temperature initiator decomposition does not interfere with the high-temperature initiator decomposition. It is also found that the exotherm peak and cure rate have been affected by the decomposition rate of low-temperature initiator at different ways. It is shown in this study that for cobalt naphthenate and dimethyl aniline (DMA) dual promoters systems, with the increasing of DMA concentration, namely high reactive promoter, causes the exotherm parameters sharply change. It might be due to the more reactive nature of DMA in comparison with the cobalt naphthenate reactivity. Now we can say, a judicious choice of a dual initiator or a dual promoter can avoid short time exothermic reactions, so a dual system can be much more effective than a single one.

Key Words:

dual initiator;
dual promoter;
exotherm behaviour;
gel time;
unsaturated polyester resin.

INTRODUCTION

In the processing of unsaturated polyester resins (for instance in resin transfer moulding and compression moulding processes), it has been a common industrial practice to use dual initiator systems, consisting of two initiators. One of them would be

a low-temperature initiator and the other a high-temperature one. The reason is very simple. Upon charging the mould cavity, the resin begins to cure immediately with the help of the low-temperature initiator and then completes the curing reaction

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with the help of the high-temperature initiator.

The curing reaction is a very important stage in the processing of unsaturated polyester resins for producing a composite product. In order to achieve good quality product, the curing reaction should occur in a controllable manner. It has now been recognized that [1-3] the curing of unsaturated polyester resins is a free radical chain growth cross-linking copolymerization between the reactive diluents (e.g., styrene monomer) and the polyester double bonds originating from the unsaturated dicarboxylic acid. The copolymerization is initiated by peroxides, azo and azine compounds activated by metal compounds, tertiary amines and mercaptans or by thermal activation.

A number of studies have qualitatively correlated the effect of initiator(s) [4-12] and promoter(s) [13-17], on the gel time, cure rate and exotherm behaviour of unsaturated polyester resins. There have been a few, more detailed, analyses of the effect of the concentration of initiator and promoter on cure behaviour and gel time of unsaturated polyester resins. Yang and Suspene [18] measured the gel points during curing and correlated with initiator concentration, promoter concentration and curing temperature. A correction for taking into account heat losses in a quasi-adiabatic reactor has been provided by Rojas et al. [19]. They showed that this correction would allow the determination of polymerization kinetics which are not very fast, without the use of expensive equipment. Two models based on the free radical polymerization mechanism were developed for predicting the gel time of unsaturated polyester resins cured with *t*-butyl peroxy-2-ethyl hexanoate (PDO) and 2,5-dimethyl-2,5 bis (2-ethyl-hexanoyl-peroxy) hexane (DMB)[20]. Exotherm control in

the thermal polymerization of nano-ethylene glycol dimethacrylate (NEGDM) was investigated using mixtures of two initiators with significantly different half-life temperatures by Xia and Cook [21]. The use of mixtures was found to produce two exotherm peaks and to spread the polymerization over a wider temperature range in the temperature-ramping DSC experiment. This reduced the maximum polymerization rate, thus potentially suppressing thermal over-runs and temperature gradients during non-isothermal curing. In the present paper, we investigated a series of initiators (organic peroxides and perbenzoate), promoters and their combinations (dual systems only) for the copolymerization of unsaturated polyester resin mixtures and report on studies of the curing behaviour by gel time and pseudo-adiabatic exotherm measurements.

EXPERIMENTAL

Materials

The unsaturated polyester resin used in this study was a 1, 1.15, 1.14 and 1.44 mixture of maleic anhydride, isophthalic acid, propylene glycol and diethylene glycol, respectively containing 40% by weight styrene (BUSHEPOL 751129, Bushehr Chemical Industry), with an average of 5.88 vinylene groups per unsaturated polyester molecules. The average molecular weight of the unsaturated polyester resin is 2750 g/mol and the equivalent molecular weight/(mol C = C) is 468 g/mol. The molar ratio of styrene/unsaturated polyester resin is 2.7. The unsaturated polyester resin was employed as received without removing the inhibitor. We used various amounts of methyl ethyl ketone peroxide (MEKP)

Table 1. Dual initiator systems used in the experiments.

Materials	Compositions (wt %) (initiator ratio)					
	0.00/2.00 (0)	0.25/1.75 (1/7)	0.50/1.50 (1/3)	0.75/1.25 (3/5)	1.00/1.00 (1)	1.25/0.75 (5/3)
BPO/MEKP	0.00/2.00 (0)	0.25/1.75 (1/7)	0.50/1.50 (1/3)	0.75/1.25 (3/5)	1.00/1.00 (1)	1.25/0.75 (5/3)
BPO/AAP	0.00/2.00 (0)	0.25/1.75 (1/7)	0.50/1.50 (1/3)	0.75/1.25 (3/5)	1.00/1.00 (1)	1.25/0.75 (5/3)
TBPB/MEKP	0.00/2.00 (0)	0.25/1.75 (1/7)	0.50/1.50 (1/3)	0.75/1.25 (3/5)	1.00/1.00 (1)	1.25/0.75 (5/3)
TBPB/AAP	0.00/2.00 (0)	0.25/1.75 (1/7)	0.50/1.50 (1/3)	0.75/1.25 (3/5)	1.00/1.00 (1)	1.25/0.75 (5/3)

Table 2. Dual promoter systems used in the experiments.

Materials	Compositions (wt %) (promoter ratio)				
DMA/Co ²⁺	0.0/0.1	0.1/0.1	0.2/0.1	0.3/0.1	0.4/0.1
	(0)	(1)	(2)	(3)	(4)
DMA/Co ²⁺	0.0/0.5	0.1/0.4	0.2/0.3	0.3/0.2	0.4/0.1
	(0)	(1/4)	(2/3)	(3/2)	(4)

solution containing 9.9% active oxygen and acetyl acetone peroxide (AAP) solution containing 4.1% active oxygen as low-temperature initiators supplied by Elfatochem with commercial names of Luperox K1 and Luperox K3, respectively. The chosen medium-temperature initiator was dibenzoyl peroxide (BPO) from Pamukale Co. and the high-temperature type was t-butyl perbenzoate (TBPB) with commercial name of Trigonox C from Akzo Nobel. Cobalt (II) naphthenate and dimethyl aniline (DMA) solutions (commercial grades) were used as promoters. Tables 1 and 2 give a summary of the various combinations of initiators and promoters used in the present investigation, respectively. In all formulations illustrated in Table 1, the samples contained two parts of initiator to one hundred part of the reaction mixture containing the dual initiators, promoter and unsaturated polyester resin, by weight. Table 2 also shows the samples which contained various parts of DMA solution to one hundred parts of the reaction mixture with the Co²⁺ concentration that is constant (0.1/100 parts of reaction mixture) and those that contained 0.5 parts of promoter to one hundred parts of reaction mixture, by weight.

Instrumentation and Procedures

The cure exotherm was measured according to ASTM D 2471-99. The polyester resin containing cobalt (II) promoter or its mixture with DMA were mixed with the appropriate amount of initiators at ambient temperature and the mixture rapidly mixed for 1 min. Approximately 70 g of this mixture was poured into a paper cup (4 cm diameter and 7 cm deep) at ambient temperature. The height of mixture in the paper cup was 5 cm. The time-temperature data was measured by placing a thermocouple in the centre of isolated paper cup connected to a digital thermometer.

The gel time was determined by measuring the resistance to the motion of a 3 mm diameter aluminium tube probe using a gel time meter (J. Condanhove &

Hubner). The measurements of the heat evolved during curing reaction were conducted using a PL, DSC-1500 differential scanning calorimeter with nitrogen as flushing gas. All the experiments were performed under isothermal conditions to obtain the heat flow curves.

RESULTS AND DISCUSSION

Dual Initiator Systems

Effect of BPO/MEKP and BPO/AAP Dual Initiators

Figures 1 and 2 illustrate the important role of BPO/MEKP and BPO/AAP as mixture of high- and low-temperature initiators on the curing behaviour of the unsaturated polyester resin with different compositions of dual initiators, respectively. Using these figures we determined, the time-to-peak, exotherm peak and

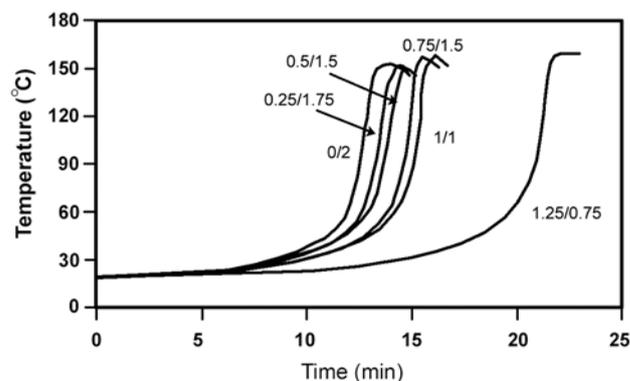


Figure 1. Measured exotherm of the unsaturated polyester resin containing 2.0 wt% dual initiator (BPO/MEKP) and 0.5 wt% cobalt naphthenate at 20°C. BPO/MEKP ratios are 0, 1/7, 1/3, 3/5, 1 and 5/3 (left to right).

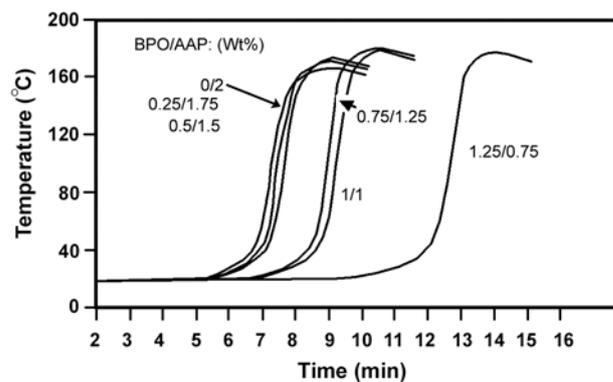


Figure 2. Measured exotherm of the unsaturated polyester resin containing 2.0 wt% dual initiator (BPO/AAP) and 0.5 wt% cobalt naphthenate at 20°C. BPO/AAP ratios are 0, 1/7, 1/3, 3/5, 1 and 5/3 (left to right).

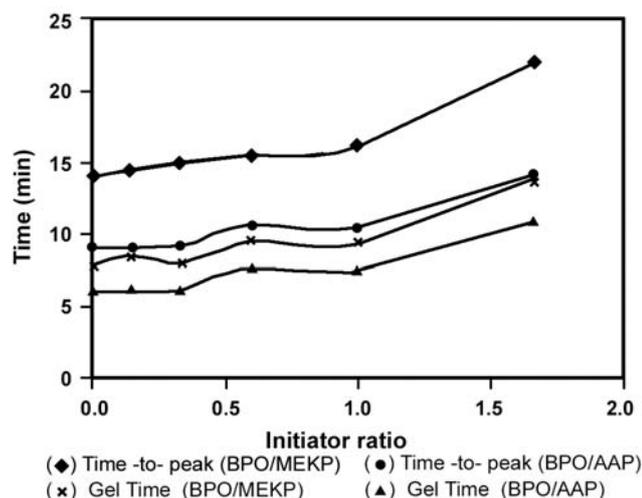


Figure 3. Dependence of gel time and time to peak on initiator ratio for an unsaturated polyester resin initiated with 2.0 wt% dual initiators and 0.5 wt% cobalt naphthenate at 20°C.

cure rate (dT/dt) of BPO/MEKP and BPO/AAP dual initiators.

We can notice the gel time and time-to-peak for BPO/MEKP and BPO/AAP mixtures in the Figure 3. It is clearly observed that the gel time and time-to-peak show the similar behaviour with respect to the initiators concentration ratio. This behaviour demonstrates that the decomposition of the low-temperature initiators (i.e., MEKP and AAP) will be completed when the reaction reaches the gel time. In other words the low-temperature initiator decomposition does not interfere with the high-temperature initiator decomposition. It is interesting to notice that the gel time and time-to-peak does not significantly change when the initiator ratios for each of mixtures are less than 1. A further increase in the initiators ratio (>1) led to decreasing of the amount of low-temperature initiators, therefore increasing the induction time and consequently the gel time. The above explanation is an evidence for rapidly increasing of the gel time and time-to-peak, as shown in Figure 3.

The results of the exotherm peak calculated using Figures 1 and 2 are presented in Figure 4. It is observed in these plots that BPO/MEKP dual initiator behaviour is quite different from BPO/AAP mixture behaviour. The maximum exotherm peak which is observed in BPO/AAP plot, but not in BPO/MEKP plot, is a result of a high decomposition rate for the low-temperature initiator. This is demonstrated by the DSC isothermal cure testing at 28°C that is illustrated in Figure 5. This

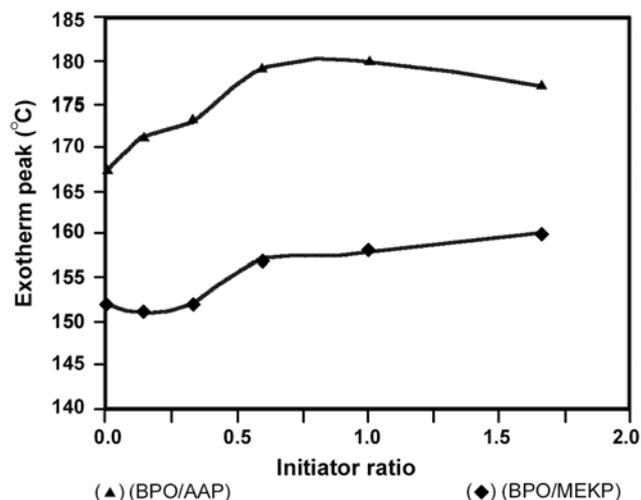


Figure 4. Exotherm peak versus initiator ratio of dual initiators added to the unsaturated polyester resin initiated with 2.0 wt% dual initiators and 0.5 wt% cobalt naphthenate solution at 20°C.

figure shows that the AAP decomposition rate is much faster than the one for MEKP. By comparing the isothermal DSC thermograms of AAP and those of MEKP, it is found that Q_{AAP} (heat of reaction for AAP) is higher than Q_{MEKP} . So we expect a higher exothermic peak for BPO/AAP mixture than the one for BPO/MEKP mixture at any initiator ratio (Figure 4).

Figure 6 gives the plots of the cure rate vs. the initiator ratio for BPO/MEKP and BPO/AAP systems. It

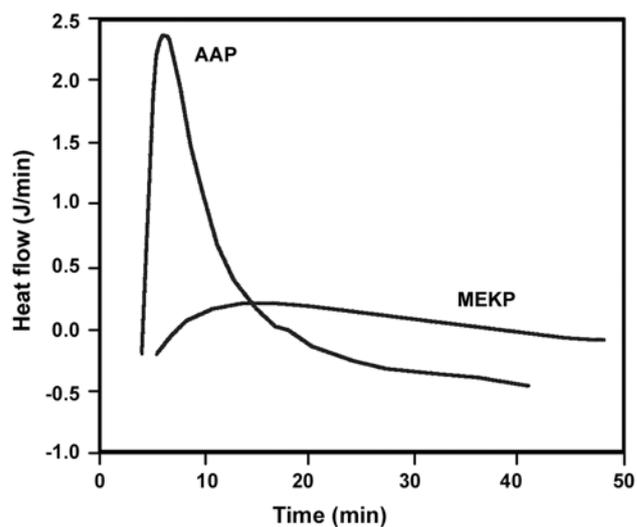


Figure 5. DSC Isothermal cure testing at 28°C for an unsaturated polyester resin containing 2.0 wt% MEKP and AAP promoted with 0.5 wt% cobalt naphthenate.

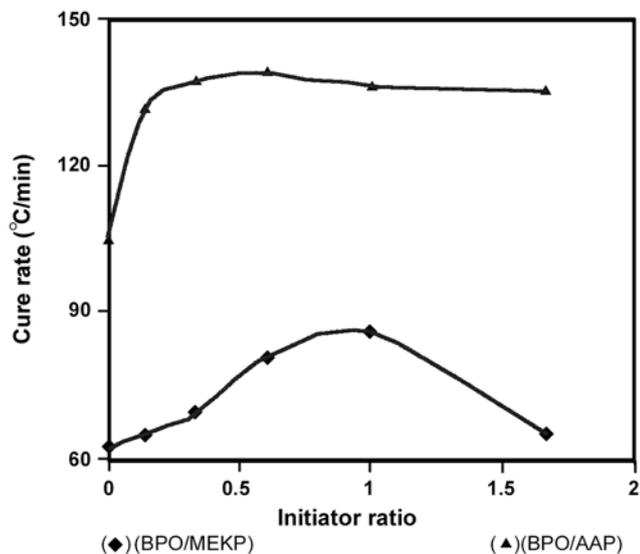


Figure 6. Variations in cure rate versus initiator ratio of dual initiators added to the unsaturated polyester resin initiated with 2.0 wt% dual initiators and 0.5 wt% cobalt naphthenate solution at 20°C.

is quite clear from this figure that there exists a maximum cure rate with BPO/MEKP system but a final limit with BPO/AAP system. The reason for this observation is a higher decomposition rate for AAP in comparison to MEKP (Figure 5).

Effect of TBPB/MEKP and TBPB/AAP Dual Initiators

The effect of TBPB/MEKP and TBPB/AAP as mixture of high- and low-temperature initiators on the curing behaviour of the unsaturated polyester resin using different compositions is illustrated in Figures 7 and 8,

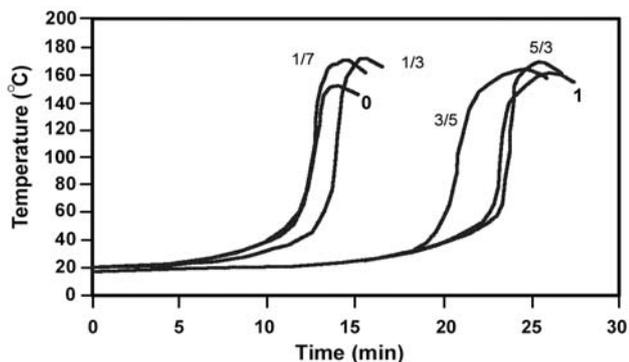


Figure 7. Measured exotherm of the unsaturated polyester resin containing 2.0 wt% dual initiator (TBPB/MEKP) and 0.5 wt% cobalt naphthenate at 20°C.

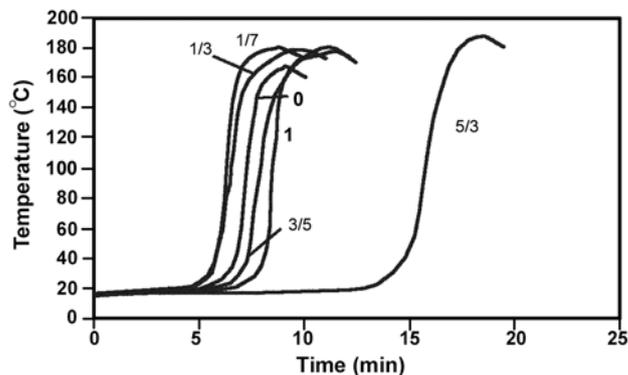


Figure 8. Measured exotherm of the unsaturated polyester resin containing 2.0 wt% dual initiator (TBPB/AAP) and 0.5 wt% cobalt naphthenate at 20°C.

respectively. The time-to-peak, exotherm peak and cure rate (dT/dt) of TBPB/MEKP and TBPB/AAP dual initiators was calculated using these figures (Figures 9-11).

By considering the plots in Figure 9 two different behaviour may be observed. For TBPB/MEKP mixture there is a plateau region (both the gel time and time-to-peak), which indicates the cure rate will be constant at initiator ratio above 0.8. By plotting the cure rate vs. initiator ratio (Figure 11), it is revealed that, there also is a plateau region above 0.8. On the other hand, the TBPB/AAP dual initiator plots show that the gel time and time-to-peak continuously increase with increasing

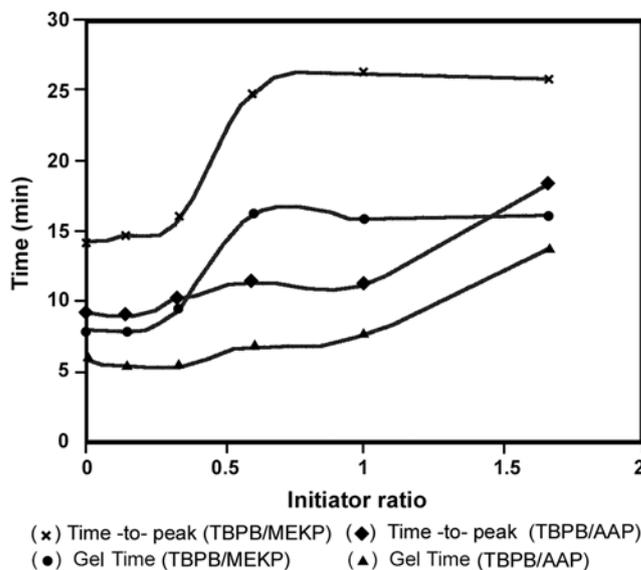


Figure 9. Dependence of gel time and time to peak on initiator ratio for unsaturated polyester resin initiated with 2.0 wt% dual initiators and 0.5 wt% cobalt naphthenate at 20°C.

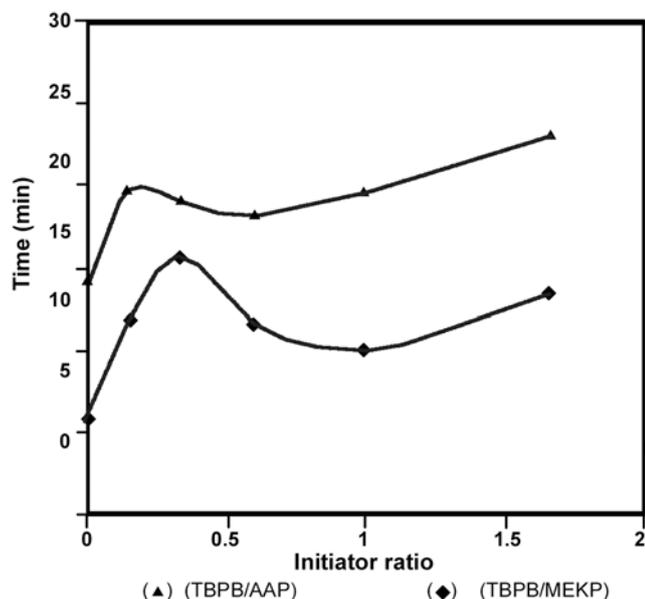


Figure 10. Exotherm peak versus initiator ratio of dual initiators added to the unsaturated polyester resin initiated with 2.0 wt% dual initiators and 0.5 wt% cobalt naphthenate solution at 20°C.

of TBPB/AAP ratio up to 13 and 18 min, respectively. It is interesting note that all plots in Figures 3 and 9 show a certain initiator ratio which the time-to-peak and gel time suddenly increase. These points are effective ratios that the high-temperature initiator (i.e., BPO or TBPB) acts as a main initiator. The longer time is needed for decomposition when the high-temperature initiator content in mixture reaches an effective concentration, therefore both the time-to-peak and gel time suddenly increase.

Figure 10 shows the maximum cure temperatures vs. initiator ratio for the cure reaction of unsaturated polyester resin initiated by TBPB/MEKP and TBPB/AAP mixed initiators. It is clearly revealed in these plots that a maximum and then a minimum occur and finally the plots rise near to or upper than the maximum temperatures. Comparing the maximum points in plots of Figure 10 with Figure 11, one can easily conclude that these maximums occur in the same initiator ratios for each one of the mixed initiator systems; i.e. 0.33 and 0.14 for TBPB/AAP and TBPB/MEKP, respectively. It is found that temperature rise due to addition of TBPB to MEKP is between 15°C to 20°C, but to AAP is lower than 10°C (Figures 4 and 10). Comparing time-temperature curve 0 (denoted in Figure 7) with correlated curve in Figure 8, one finds that

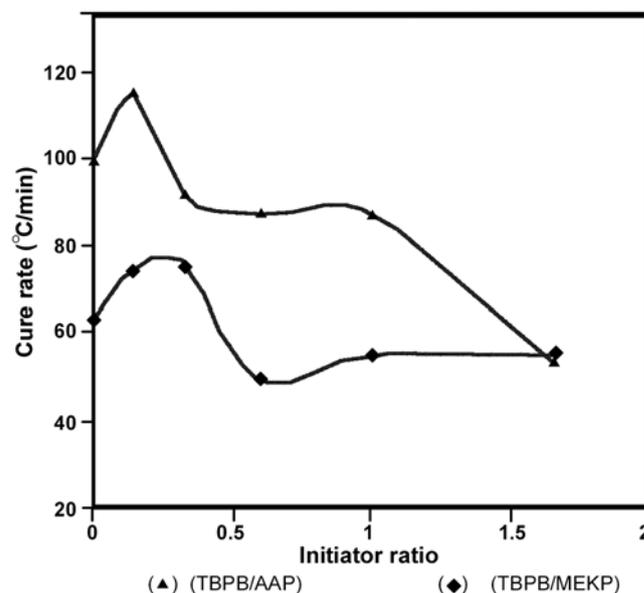


Figure 11. Variations in cure rate versus initiator ratio of dual initiators added to the unsaturated polyester resin initiated with 2.0 wt% dual initiators and 0.5 wt% cobalt naphthenate solution at 20°C.

maximum exotherm temperature with MEKP is 143°C, while with AAP is 164°C. This maximum exotherm temperature difference (i.e., 164-143 = 21°C) is a good reason for describing the higher temperature rise due to addition of TBPB to MEKP comparing with AAP.

For TBPB/MEKP dual initiators system, it is evident from Figure 11 that cure rate rises to a maximum (75.5°C/min), then falling to a minimum (49.3°C/min) and finally approaches to a limit (55.1°C/min). When the initiator ratio is higher than 0.5, the cure rate for TBPB/MEKP dual initiators is less than that for the single initiator system (i.e., for MEKP that occurring in a initiator ratio equal 0). It can be concluded that TBPB does not decompose with TBPB/MEKP ratio higher than 0.5. It can be seen that raising the initiator ratio to 0.3 (the maximum point of TBPB/MEKP plot in Figure 11) increases the cure rate, therefore TBPB takes part in decomposition reaction. Figure 9 (TBPB/MEKP) also shows that changing the gel time does not occur by ratio of 0.3, therefore the high-temperature initiator (TBPB) decomposition takes place. The cure rate plot of TBPB/AAP dual initiators is almost the same as that with TBPB/MEKP, but the former sharply drops when the initiator ratio reaches 1. When the AAP concentration in the initiators mixture is low (i.e., less than 1.0%), the heat generation due to decomposition of

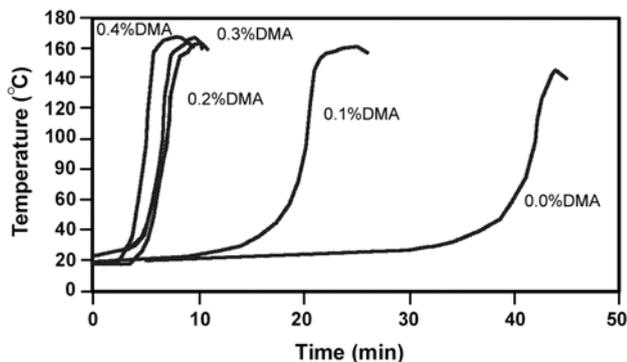


Figure 12. Measured exotherm of the unsaturated polyester resin containing 1.0 wt% MEKP, 0.1 wt% cobalt naphthenate and various amount of DMA at 20°C.

AAP will not be enough to decompose TBPB, hence the cure rate suddenly decreases. This is not true for TBPB/MEKP dual initiator because Q_{MEKP} is lower than Q_{AAP} . On the other hand, the plot of TBPB/MEKP is laid below the plot of TBPB/AAP (Figure 11) at all the points except the last point.

Dual Promoter Systems

The effect of DMA concentration on the exotherm behaviour of the unsaturated polyester resin containing 0.1 wt% cobalt naphthenate solution and 1.0 wt% MEKP solution is shown in Figure 12. It is clearly observed that the induction time rapidly decreases with increasing of DMA concentration. This is due to the reactive nature of DMA that easily attacks MEKP molecules and rapidly produces alkoxy and peroxy radicals which initiate the polymerization reactions [22].

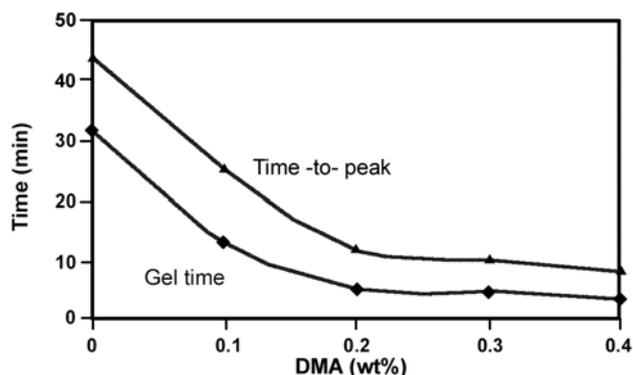


Figure 13. Dependence of gel time and time to peak on DMA concentration for unsaturated polyester resin initiated with 1.0 wt% MEKP and 0.1 wt% cobalt naphthenate at 20°C.

Figure 13 shows the gel time and time-to-peak vs. DMA concentration using data obtained from Figure 12. It is surprising to note that with the higher than 0.2 wt% DMA, the gel time and time-to-peak do not change, suggesting that they reach a limit value, because DMA is a very active promoter.

The data in Figure 14 show that increasing the DMA concentration also increases the exotherm peak (i.e., the maximum temperature in the plots of Figure 12). It should be noted that with the exception of low levels (< 0.1wt% DMA), the exotherm peak increases slowly as the DMA concentration is raised to 0.4 wt%. In general, there is an agreement between the time plots and exotherm peak ones.

Figure 15 indicates that there is a linear relationship between the DMA concentration and the cure rate of unsaturated polyester resin containing 0.1 wt% Co^{+2} and 1.0 wt% MEKP. The literature [23] shows that the rate of free radical polymerization will increase at an order of $2^{1/2}$ when it doubles the promoter concentration, due to the supposition that there is a bimolecular termination between the radicals. Our results do not support this supposition, probably because the polymerization mechanism for the dual promoter systems is different from those of the single promoter system.

The effect of varying the level of DMA/ Co^{+2} as mixture of promoters on the curing behaviour of the unsaturated polyester resin containing 0.5 wt% dual promoters and 1.0 wt% MEKP at 20°C is shown in Figure 16. At low concentration of DMA, the induction

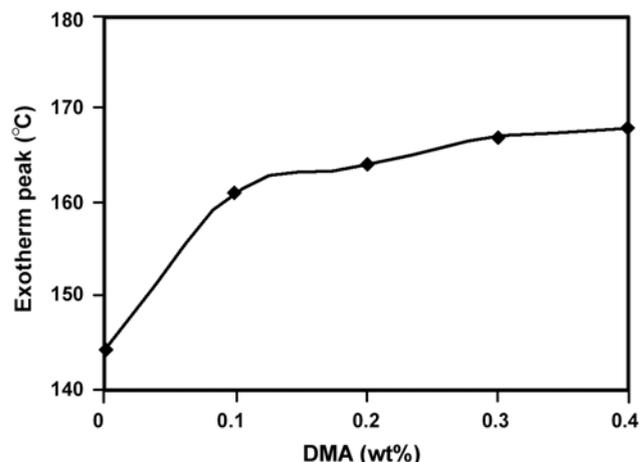


Figure 14. Exotherm peak versus DMA concentration added to the unsaturated polyester resin initiated with 1.0 wt% MEKP and 0.1 wt% cobalt naphthenate at 20°C.

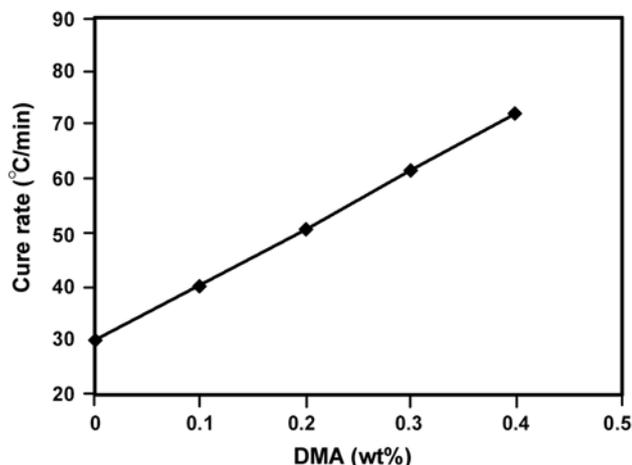


Figure 15. Variations in cure rate versus DMA concentration added to the unsaturated polyester resin initiated with 1.0 wt% MEKP and 0.1 wt% cobalt naphthenate at 20°C.

period is long and the exotherm peak is low. This suggests that the decomposition rate of the DMA is very faster than it for cobalt naphthenate. When the DMA level is increased, the induction time is progressively reduced. In Figures 17, 18 and 19 the gel and peak times, exotherm peak and cure rate of samples containing 0.5 wt% promoters mixture are plotted as a function of the promoter ratio (DMA/Co²⁺) at 20°C.

The exotherm measurements of samples containing DMA with 0.1wt% Co²⁺ and 0.5wt% DMA showed a similar trend for the gel time, time to peak and exotherm peak (compare Figures 13 and 14 with Figures 17 and 18), but the trend for their cure rate are completely different (compare Figure 15 with figure 19). Figures 17, 18 and 19 show that the exotherm

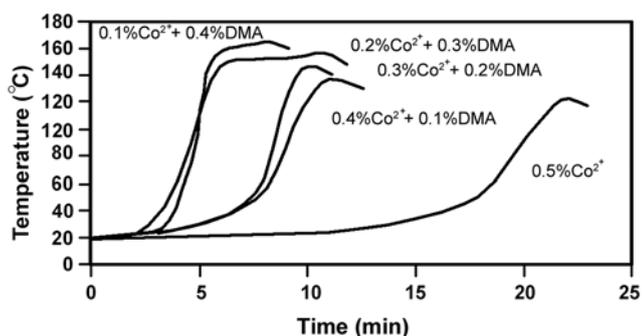


Figure 16. Measured exotherm of the unsaturated polyester resin containing 1.0 wt% MEKP and 0.5 wt% dual promoter at 20°C.

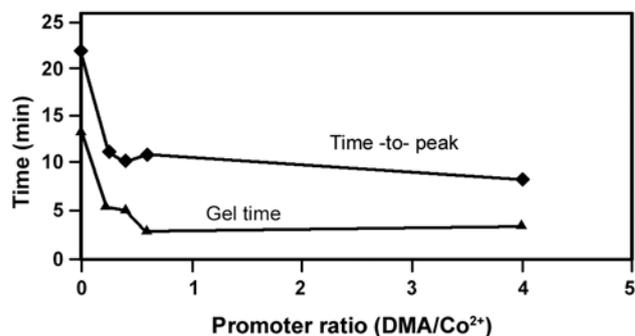


Figure 17. Dependence of gel time and time-to-peak on promoter ratio for unsaturated polyester resin initiated with 1.0 wt% MEKP and 0.5 wt% dual promoter at 20°C.

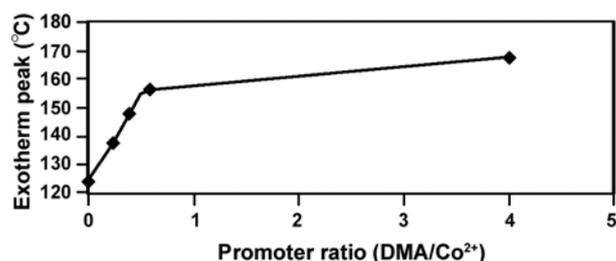


Figure 18. Exotherm peak versus promoter ratio of DMA/Co²⁺ added to the unsaturated polyester resin initiated with 1.0 wt% MEKP and 0.5 wt% dual promoter at 20°C.

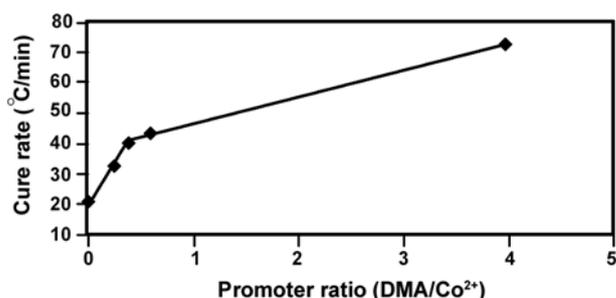


Figure 19. Variations in cure rate versus promoter ratio of DMA/Co²⁺ added to the unsaturated polyester resin initiated with 1.0 wt% MEKP and 0.5 wt% dual promoter at 20°C.

parameters are suddenly decreased or increased up to 0.75 DMA/Co²⁺ and at higher promoter ratios the exotherm parameters slowly change or remain approximately constant. A possible reason is that DMA is a very active promoter, in comparison to the cobalt naphthenate, therefore at a definite concentration the free radical formation due to DMA is completed.

CONCLUSION

The curing behaviour of an unsaturated polyester resin initiated with BPO/MEKP, BPO/AAP, TBPB/MEKP and TBPB/AAP dual initiators and cobalt naphthenate/DMA dual promoter has been studied by gel time and pseudo-adiabatic exotherm measurements. It is demonstrated that dual initiator can be much more effective than a single initiator. This is because a judicious choice of dual initiator can avoid short time exothermic reactions. Results show that the low-temperature initiator decomposition do not interfere with the high-temperature initiator decomposition. The exotherm peak plot of BPO/AAP dual initiator system has a maximum point that is a result of high decomposition rate for low-temperature initiator (AAP). Both TBPB/MEKP and TBPB/AAP systems showed a maximum point at their exotherm peak plots, so we concluded that after this maximum the cure rate is slowed down by the TBPB present in the mixture (i.e., due to the dilution of MEKP and AAP by TBPB). Existing of a maximum cure rate with BPO/MEKP system (not with BPO/AAP system) is a result of a higher decomposition rate for AAP in the comparison with MEKP. When the AAP concentration in the TBPB/AAP system is less than 1.0 wt%, the heat generation due to the decomposition of AAP will not be enough to decompose TBPB; hence the cure rate sharply decreases. This is not true for TBPB/MEKP dual initiator system because Q_{MEKP} is lower than Q_{AAP} . For dual promoter systems it is clearly observed that, with the increasing of DMA concentration, the exotherm parameters sharply change, due to the reactive nature of DMA in comparison with cobalt naphthenate.

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