

Original Research Paper

Effects of Curing Temperature and MMA Content on the Working Life of MMA-Modified Vinyl Ester Polymer Concrete

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Article history

Received: 7-06-2016

Revised: 21-10-2016

Accepted: 24-10-2016

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Abstract: The main purpose of this study is to identify the effects of curing temperature and methyl methacrylate (MMA) content on the working life of vinyl ester polymer concrete using MMA as a monomer, *N,N*-dimethyl-*p*-toluidine (DMP) and methyl ethyl ketone peroxide (MEKPO) as initiators and cobalt naphthenate as a promoter. The results have shown that the working life of vinyl ester polymer concrete was shortened with an increased curing temperature and a decreased MMA content. Also, it was found that the curing temperature had a greater influence on the working life of vinyl ester polymer concrete than MMA content. The working life of vinyl ester polymer concrete was found to be about 70 and 10 min longer than the setting time of vinyl ester polymeric binder at curing temperatures of -10 and 20°C, respectively. The MMA content had a much smaller effect on the curing temperature. Lastly, a linear regression equation was drawn by analyzing the correlation between setting time of the binder and working life of polymer concrete, which could be used for the prediction of the working life of vinyl ester polymer concrete based on the setting time of the vinyl ester binder.

Keywords: Vinyl Ester Polymer Concrete, Methyl Methacrylate, Curing Temperature, Setting Time, Working Life

Introduction

Polymer concrete is a sort of polymer-concrete composite material made by fully replacing the cementitious binder of conventional concrete with a polymeric binder. Due to such nature, various material properties such as strength, adhesion, water tightness, chemical resistance, freeze-thaw resistance and abrasion resistance of polymer concrete are generally improved to a great extent in comparison with ordinary Portland cement concrete (Chandra and Ohama, 1994). However, it is recognized that polymer concrete also has some limitations originated from high cost of polymer resins, large shrinkage developed during hardening process and large thermal volume changes. To resolve these issues, many studies are underway to enhance the binder characteristics and to develop shrinkage reducing agents and a new type of resins (Fowler, 1989).

Thermosetting resins including unsaturated polyester, epoxy, acrylic and vinyl ester are popularly used for manufacturing polymer concrete, whose physical and

mechanical properties are substantially different from one another depending on the type of the binder used (Haddad *et al.*, 1983; Hyun and Yeon, 2012; Ohama, 1973). A vinyl ester resin employed in this study is known to have excellent chemical and corrosion resistance coupled with outstanding heat performance, which makes the vinyl ester resin a good choice for practical applications such as in swimming pools, sewer pipes and solvent storage tanks (Cao and Lee, 2003; Cook *et al.*, 1997).

In general, the setting time of polymer concrete is significantly shorter than that of cement concrete. Owing to such short setting time, the use of polymer concrete can markedly reduce the curing time of cast-in-place components and improve the productivity of precast products-typically, formworks can be stripped within about 1 to 3 hours after placement. Accordingly, formworks can be reused for manufacturing precast products in factories, leading to labor saving in field applications (Chandra and Ohama, 1994); therefore, determination of polymer concrete's working life is an

utmost important factor for both precast and cast in place applications (Ohama, 1978) as it helps in scheduling various stages involved in construction operations such as transporting, placing, compacting and finishing of concrete (Brooks *et al.*, 2000).

This study used a vinyl ester resin modified by MMA monomer as a binder (hereinafter “MMA-modified vinyl ester polymer concrete”) so as to improve the workability and reduce the setting shrinkage. The working life of polymer concrete at ambient temperature can be widely controlled by selecting suitable initiators, promoters, hardeners and water/binder ratios, all of which are well known influencing factors. Accordingly, in this study, a focus is placed on the effects of curing temperature and MMA content on the working life of MMA-modified vinyl ester polymer concrete.

Experimental Program

Materials

Binder

This study used a bisphenolA epoxy-based vinyl ester as a resin for polymer concrete. The bisphenol A epoxy-based vinyl ester resin had a density of 1.2 (at 25°C), a viscosity of 250 mPa·s (at 20°C), a vapor density of 3.6 and a styrene content of 45 wt.%. As a monomer, the

present study employed a methyl methacrylate (MMA) monomer, which was produced by esterifying methacrylic acid with methanol. The MMA used in this study was a transparent liquid with a density of 0.942 (at 25°C), a viscosity of 0.56 mPa·s (at 20°C) and a molecular weight of 100 g/mol. As an initiator for the vinyl ester resin, a 45% *N,N*-dimethyl-*p*-toluidine (DMP)solution with 55% methyl ethyl ketone peroxide (MEKPO) was employed, whose specific gravity is 1.12 (at 25°C). To initiate the reaction between the vinyl ester resin and MMA monomer, a promotor should be added. This study used a cobalt naphthenate as a promotor as it allows polymerization even both at room and low temperatures. The cobalt naphthenate used in this study was a violet liquid with a density of 0.95 (at 25°C) and a boiling temperature of 110.6°C.

Aggregate and Filler

This study used silica sand as aggregates. Figure 1 and Table 1 show the gradation curve with the upper and lower gradation limits specified in ASTM C33 and physical properties of the silica sand used in this study, respectively. In addition, this study adopted a ground calcium carbonate powder as filler. The physical properties and chemical components of the filler are presented in Tables 2 and 3, respectively.

Table 1. Physical properties of aggregate

Size (mm)	Apparent specific gravity (-)	Bulk specific gravity (-)	Unit weight (kg/m ³)	Fineness modulus (-)	Water content (%)	Organic impurities
0.08-8	2.64	2.62	1,648	3.09	< 0.1	Nil

Table 2. Properties of ground calcium carbonate

Specific gravity	Absorption (cc/gr)	Water content (%)	pH	Mean grain size (μm)	Retained percentage of 325 mesh sieve
0.75	0.20	≤0.3	8.8	13	0.03

Table 3. Chemical component of ground calcium carbonate (unit: %)

CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	MgO	Loss on ignition
53.7	0.25	0.09	2.23	0.66	42.4

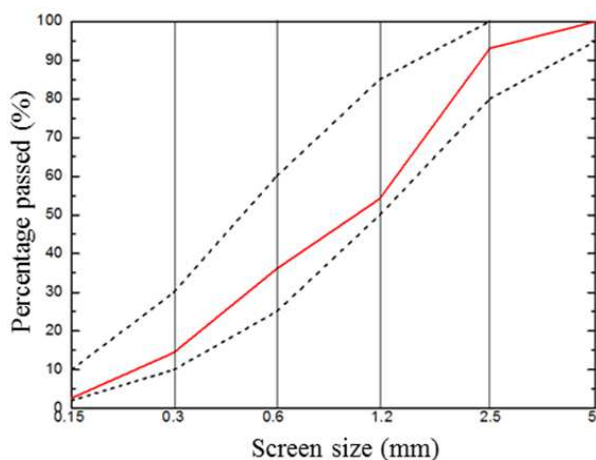


Fig. 1. Gradation curve of aggregate with upper and lower limits

Methods

Determination of Mixture Proportions

In this study, optimum mixture proportions were selected based on a series of trial tests on slump flow and strength. The mixture proportions were designed to have a maximum portion of aggregate phases with a minimum portion of polymeric binders. The binder formations and mixture proportions of the polymer concrete used are presented in Table 4.

Setting Time Measurement

This study determined the setting time of the binder based on ASTM D 2471 (*Standard test method for gel time and peak exothermic temperature of reacting thermosetting resin*), which measures the time duration right after adding an initiator into a polymeric resin until it reaches a peak exothermic temperature. For the temperature measurement over time, a data logger (Tokyo Sokki; TDS-602) with a T-type thermocouple was used.

Working Life Measurement

In this study, the finger-touching method (Ohama, 1978) as per PC-4 (*Determining methods for working life of fresh polymer concrete and mortar*) in RILEM TC 113-CPT was used to determine the polymer concrete's working life. The total time elapsed from initiator addition to caking (or gelling) was defined as the working life of polymer concrete. The caking time was estimated by the finger touching method specified in RILEM TC-CPT 1995 (*PC-4 Determining methods for working life of fresh polymer concrete and mortar*) once the fresh polymer concrete sample was placed in a plastic bag.

Results and Discussion

Setting Time of Vinyl Ester Polymeric Binder

The setting time of vinyl ester polymeric binder with different curing temperatures, MMA contents and concentrations of initiator and promoter was measured and the results are presented in Table 5. It was found that the setting time ranged from 50-315, 23-131, 21-70 and 14-45 min when the curing temperature was -10, 0, 10 and 20°C, respectively. When the concentration of MEKPO was 1.0, 1.5 and 2.0 phr, the setting time was found to be 20-315, 16-253 and 14-218 min, respectively. Also noted was that the setting time varied between 20 and 315, 17 and 195 and 14 and 92 min when the concentration of cobalt naphthenate was 1.0, 1.5 and 2.0 phr, respectively. In addition, the MMA content affected the setting time of MMA-modified vinyl ester polymer concrete; the setting time tended to vary within the range of 14-249 min, 22-285 min and 25-315 min for MMA contents of 0, 2.5 and 5.0 wt.%, respectively. Based on the results obtained, it can be

concluded that the setting time of the vinyl ester polymeric binder was shortened as the concentration of initiator and promoter and the curing temperature increased whereas the setting time was delayed with an increase in MMA content. Among these factors, the curing temperature and the concentration of cobalt naphthenate had more significant effects in reducing the setting time than the others factors, which is similar to the results of a previous study (Ohama, 1978); the concentration of initiator and promoter had a substantial effect on the reduction of polymer's gel time.

Generally, when polymer concrete is selected for cast-in-place or precast applications, a setting time of at least one hour is required to complete finishing jobs. Based on the obtained experimental data in this study, polymeric binders that can set within 1 hour even at -10°C curing temperature were achieved when the MEKPO and cobalt naphthenate concentration was 2.0 phr each. Thus, the variations in MMA-modified vinyl ester polymeric binder's setting time with different curing temperatures (-10, 0, 10 and 20°C) and MMA contents (0, 2.5 and 5.0 wt.%) were investigated while fixing the concentration of MEKPO and cobalt naphthenate at 2.0 phr. Table 6 shows the data extracted from Table 5, which was constructed to investigate the effects of curing temperature and MMA content on the setting time of vinyl ester polymeric binder (the concentrations of initiator and promoter were 2 phr each). Also, Figs. 2, 3 and 4 present the variations of the polymeric binder's setting time for different curing temperatures and MMA contents derived based on Table 6. As shown in Fig. 2, the setting time of polymeric binder was shortened with an increased curing temperature. Figure 3 demonstrates that the setting time was delayed with an increased MMA content but its effect was less significant than curing temperature. Figure 4 shows a three-dimensional plot showing the effects of these two factors on the binder's setting time. The results show that the setting time of polymeric binder becomes greater as the curing temperature decreased and the MMA content increased.

Working Life of Vinyl Ester Polymer Concrete

MMA-modified vinyl ester polymer concrete's working life was measured by fixing the concentrations of initiator and promoter at 2 phr while gradually changing the curing temperature and MMA content and the results are shown in Table 7 and Figs. 5, 6 and 7. According to the results, the working life was significantly shortened with an increased curing temperature: 120-135 min at -10°C, 39-94 min at 0°C, 24-44 min at 10°C and 20-38 min at 20°C. However, the working life was delayed but not much changed with an increased MMA content: 20-120, 30-126 and 38-135 min for the MMA contents of 0, 2.5 and 5.0 wt.%, respectively.

Table 4. Binder formation and mixture proportions of polymer concrete

Binder content (wt.%)	Binder formation			Filler (wt.%)	Aggregate (wt.%)
	VE: MMA (wt.%)	MEKPO (phr [*])	Cobalt naphthenate (phr)		
12.0	100: 0	2	2	18.00	70.00
11.5	97.5: 2.5			17.25	71.25
11.0	95.0: 5.0			16.50	72.50

*parts per hundred parts of resin

Table 5. Setting time of vinyl ester polymeric binder for different curing temperatures, MEKPO concentration, cobalt naphthenate concentration, and MMA contents (unit: min)

Curing temperature (°C)	MEKPO (phr [*])	Cobalt naphthenate (phr [*])	MMA content (wt.%)		
			0	2.5	5.0
-10	1.0	1.0	249	285	315
		1.5	139	185	195
		2.0	76	87	92
	1.5	1.0	215	235	253
		1.5	109	135	167
		2.0	69	82	89
	2.0	1.0	188	195	218
		1.5	86	89	101
		2.0	50	53	77
0	1.0	1.0	104	117	131
		1.5	53	74	84
		2.0	31	35	59
	1.5	1.0	69	80	96
		1.5	43	53	71
		2.0	29	45	57
	2.0	1.0	54	64	80
		1.5	28	47	63
		2.0	23	35	48
10	1.0	1.0	47	58	70
		1.5	33	53	59
		2.0	28	29	33
	1.5	1.0	34	43	47
		1.5	26	32	38
		2.0	19	29	33
	2.0	1.0	28	43	45
		1.5	22	32	36
		2.0	21	29	32
20	1.0	1.0	29	36	45
		1.5	26	27	39
		2.0	20	24	30
	1.5	1.0	21	29	36
		1.5	20	24	27
		2.0	16	23	26
	2.0	1.0	20	26	29
		1.5	17	24	26
		2.0	14	22	25

*parts per hundred parts of resin

Table 6. Setting time of vinyl ester polymeric binder for different MMA contents and curing temperatures when concentrations of MEKPO and cobalt naphthenate were 2 phr each (unit: min)

Curing temperature (°C)	MMA content (wt.%)		
	0	2.5	5.0
-10	50	53	77
0	23	35	48
10	21	29	32
20	14	22	25

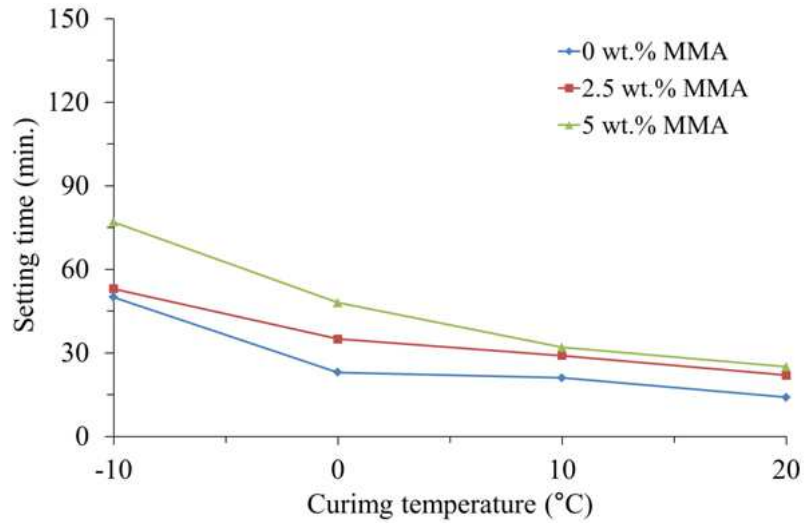


Fig. 2. Effect of curing temperature on setting time of vinyl ester polymeric binder

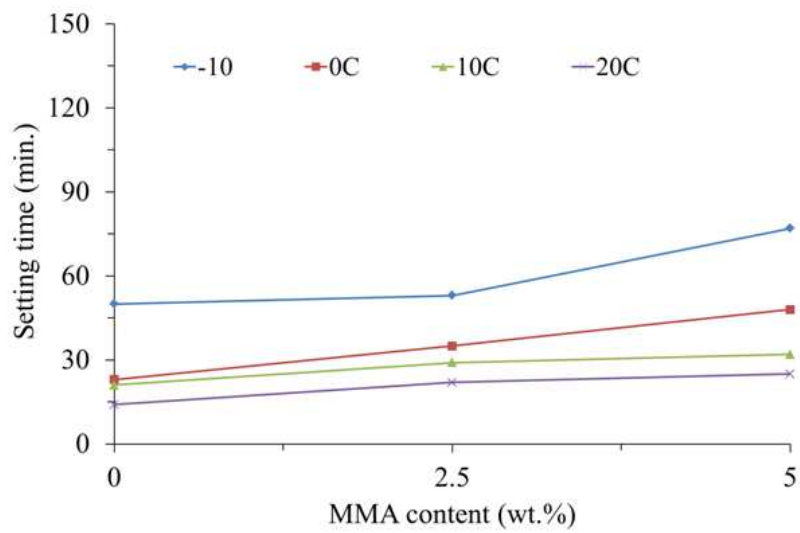


Fig. 3. Effect of MMA content on setting time of vinyl ester polymeric binder

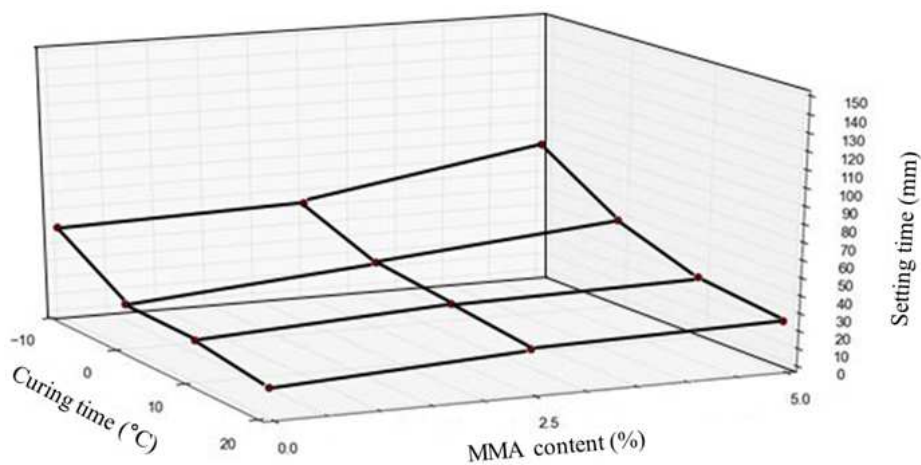


Fig. 4. Effects of MMA content and curing temperature on setting time of vinyl ester polymeric binder

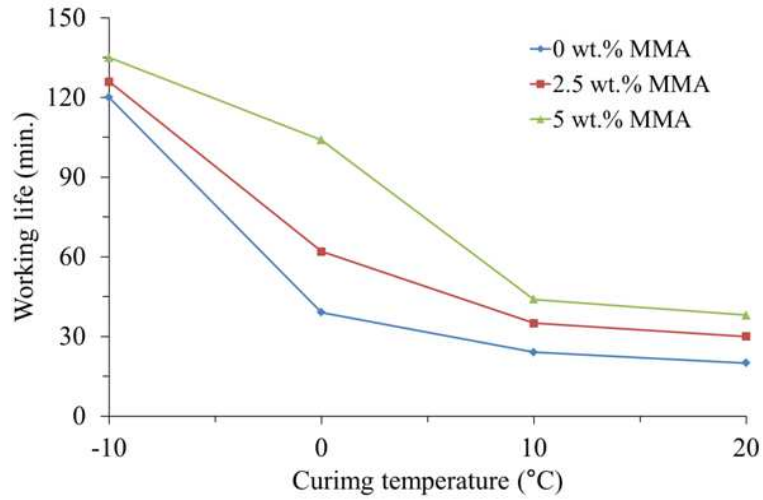


Fig. 5. Effect of curing temperature on working life of vinyl ester polymer concrete

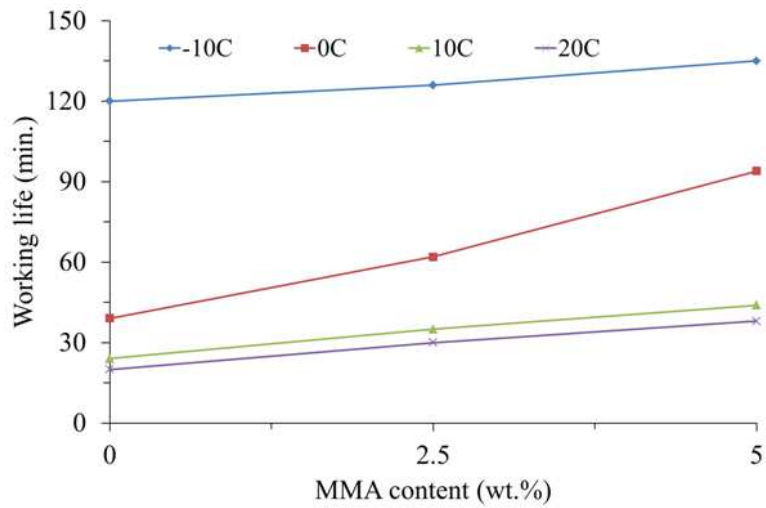


Fig. 6. Effect of MMA content on working life of vinyl ester polymer concrete

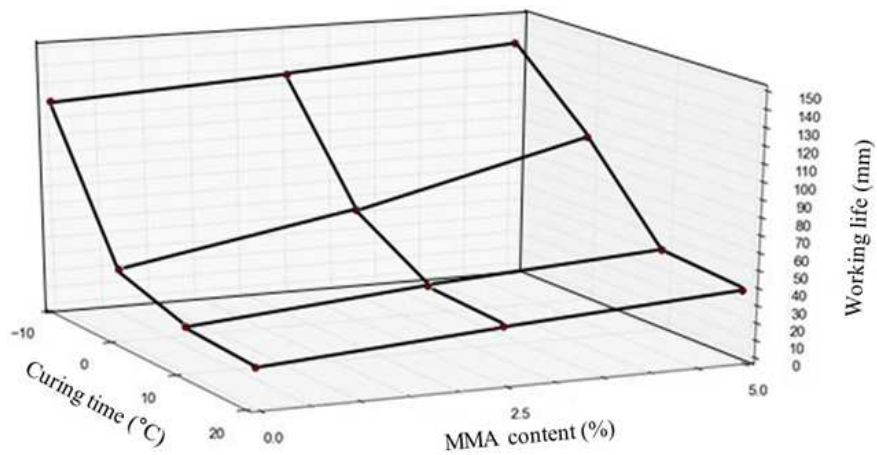


Fig. 7. Effects of MMA content and curing temperature on working life of vinyl ester polymer concrete

When comparing the measured working life of vinyl ester polymer concrete with the setting time of vinyl ester polymeric binder, the working life was delayed as much as 70 and 13 min at curing temperatures of -10 and 20°C, respectively. Also, the working life tended to increase as the MMA content increased, but the effect of MMA content was not as significant as that of curing temperature. The reason for the longer working life of polymer concrete than the setting time of polymeric binder is because the polymer concrete includes filler and aggregate up to 88–89 wt.%, which results in wider spacing among the polymer molecules than those in pure polymeric binders.

The working life of vinyl ester polymer concrete tended to be reduced as the curing temperature became higher but was delayed with an increased MMA content. Between the factors, the curing temperature had a more pronounced influence on the working life of vinyl ester polymer concrete than the MMA content. The results obtained in this paper were similar to those of previous studies in that the initial and final setting time decreased for all types of polymer concrete as the curing temperature increased (Brooks *et al.*, 2000) and the setting time of polymeric binder was largely dependent on the casting temperature (Ahn *et al.*, 2009). In addition, the results from other previous studies in relation to the working life of polymer concrete reported that the working life of unsaturated polyester polymer concrete and MMA-polymethyl methacrylate (PMMA) polymer concrete was 15-90 (Ohama, 1978) and 13-63 min (Son and Yeon, 2012), respectively, at curing temperature of 20°C. The working life of MMA-modified vinyl ester polymer concrete obtained from this study was 20-38 min, which is much shorter than the working life of polyester polymer concrete and MMA-PMMA polymer concrete, indicating that the use of

MMA-modified vinyl ester polymer concrete are beneficial in obtaining faster curing time and in turn, faster construction sequences in the field.

Correlation between Setting Time of Vinyl Ester Binder and Working Life of Vinyl Ester Polymer Concrete

Figure 8 shows the correlation between the setting time of vinyl ester resin and the working life of vinyl ester polymer concrete based on the data shown in Tables 6 and 7. A linear regression equation was derived to model their relationship as: $y = 2.254x - 16.68$, in which y is the working life of vinyl ester polymer concrete (min) and x is the setting time of vinyl ester binder (min) with a coefficient of determination R^2 of 0.901, indicating that the derived model is statistically quite confident. The results were coincided with the results of relevant previous studies (Ohama, 1978; Yeon *et al.*, 2015; Yeon and Hyun, 2012) in that the setting time of the polymeric binder is closely associated with the working life of the polymer mortar/concrete and their relationship can be modeled using a linear regression equation. Therefore, it is quite feasible that the working life of vinyl ester polymer mortar or concrete can be estimated once the setting time of vinyl ester binder is measured. Table 8 summarizes the working life of MMA-modified vinyl ester polymer concrete estimated by the predictive developed in this study. The data can be useful to determine the concentration of initiator and promoter required for achieving the working life of MMA-modified vinyl ester polymer concrete given that the curing temperature and MMA content are fixed.

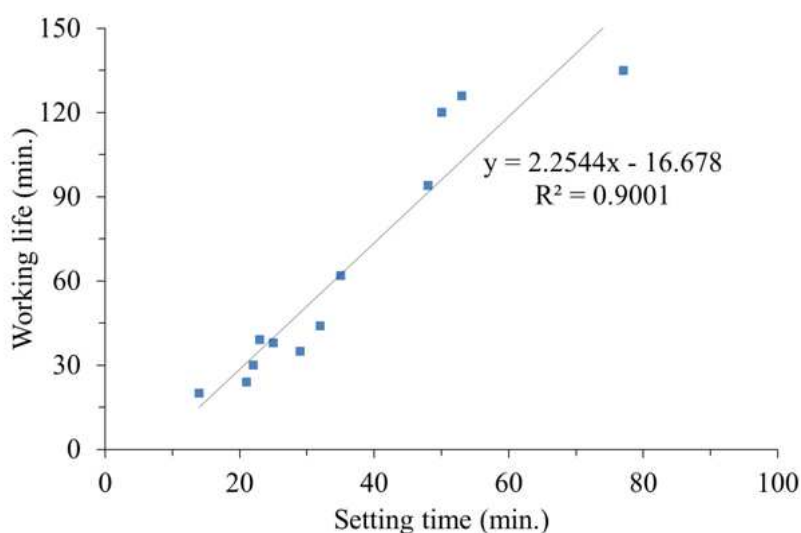


Fig. 8. Setting time of vinyl ester polymeric binder vs. working life of vinyl ester polymer concrete

Table 7. Working life of vinyl ester polymer concrete for different MMA contents and curing temperatures when concentrations of MEKPO and cobalt naphthenate were 2 phr each (unit: min)

Curing temperature (°C)	MMA content (wt.%)		
	0	2.5	5.0
-10	120	126	135
0	39	62	94
10	24	35	44
20	20	30	38

Table 8. Working life of vinyl ester polymer concrete estimated by the equation developed in this study (unit: min)

Curing temperature (°C)	MEKPO (phr*)	Cobalt naphthenate (phr*)	MMA content (wt.%)			
			0	2.5	5.0	
-10	1.0	1.0	544	625	693	
		1.5	296	400	422	
		2.0	154	179	190	
	1.5	1.0	468	513	553	
		1.5	229	287	359	
		2.0	138	168	183	
0	2.0	1.0	407	422	474	
		1.5	177	183	211	
		2.0	96	102	156	
	1.0	1.0	217	247	278	
		1.5	102	150	172	
		2.0	53	62	116	
10	1.5	1.0	138	163	199	
		1.5	80	102	143	
		2.0	48	84	111	
	2.0	1.0	105	127	163	
		1.5	46	89	125	
		2.0	35	62	91	
	20	1.0	1.0	89	114	141
			1.5	57	102	116
			2.0	46	48	57
		1.5	1.0	59	80	89
			1.5	41	55	68
			2.0	26	48	57
2.0		1.0	1.0	46	80	84
			1.5	32	55	64
			2.0	30	48	55
	1.5	1.0	48	64	84	
		1.5	41	44	71	
		2.0	28	37	50	
20	1.5	1.0	30	48	64	
		1.5	28	37	44	
		2.0	19	35	41	
	2.0	1.0	28	41	48	
		1.5	21	37	41	
		2.0	14	32	39	

*parts per hundred parts of resin

Conclusion

The purpose of this study was to investigate the effects of curing temperature and methyl methacrylate (MMA) content on working life of vinyl ester polymer concrete. The key findings of this research can be summarized as follows:

- The setting time of vinyl ester resin was reduced as the curing temperature and concentration of initiator and promoter increased, while it was delayed with an increased MMA content. Among these factors, the curing temperature and cobalt naphthenate

concentration were found to have more significant effects on the setting time reduction

- The working life of vinyl ester polymer concrete tended to decrease as the curing temperature increased, while it was delayed with an increased MMA content. Between these two factors, the curing temperature exhibited a more significant influence on the working life of vinyl ester polymer concrete
- The working life of vinyl ester polymer concrete was much longer than the setting time of polymeric binder. The difference between the working life and setting time tended to decrease with an increased curing temperature (about 70 min at -10°C and 10

min at 20°C). The MMA content had a smaller effect than the curing temperature

- A regression analysis performed between the vinyl ester resin's setting time and vinyl ester polymer concrete's working life yielded a linear equation of $y = 2.254x - 16.68$ with a coefficient of determination $R^2 = 0.901$, indicating that the obtained regression equation can be confidently used for predicting the working life of vinyl ester polymer concrete with a 11-12 wt.% binder based on the setting time of vinyl ester resin

Acknowledgements

The author would like to express their gratitude to National Research Foundation (NRF) of Korea and the research teams at Kangwon National University and Gachon University, South Korea for their support in performing this research.

Funding Information

This work was supported by National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. NRF-2013R1A1A2009).

Author's Contribution

Ki-Bong Choi: Made substantial contributions to the experimental design, results discussions and final manuscript writing.

Seung-Ho Min: Performed the testing, data collection and data analysis.

Kyu-Seok Yeon: Managed the project as a principal investigator and drafted the manuscript.

Ethics

This article is original and unpublished elsewhere. The authors declare no conflict of interest in the development of the research and publication of this article.

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