

Original Research Paper

Setting Shrinkage Characteristics of Methyl Methacrylate-Modified Vinyl Ester Polymer Concrete

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Abstract: This study evaluated the setting shrinkage characteristics of Methyl Methacrylate (MMA)-modified vinyl ester polymer concrete with different curing ages, MMA contents and curing temperatures. Results have shown that most of the setting shrinkage developed within 24 h after curing initiation. It was also found that an increase in MMA content led to an almost linear decrease in setting shrinkage, indicating that adding an MMA monomer was an effective measure to reduce the setting shrinkage of MMA-modified vinyl ester polymer concrete. A higher curing temperature tended to result in greater setting shrinkage, indicating that low-temperature curing is beneficial for reducing the setting shrinkage. The magnitude of setting shrinkage observed in vinyl ester polymer concrete was much greater than the drying shrinkage typically observed in ordinary Portland cement concrete but was smaller than the setting shrinkage of polymer concrete incorporating other types of binder.

Keywords: Polymer Concrete, MMA-Modified Vinyl Ester, Setting Shrinkage, MMA, Curing Temperature

Introduction

Polymer concrete is a particular type of concrete composed of inorganic aggregate and filler and organic polymeric binder. Polymer concrete is extensively used not only for repair of concrete roads and bridges but also manufacturing precast products such as manholes, sewage pipes and building walls due to its high strength, short setting time and excellent impact resistance, water resistance, corrosion resistance, freeze-thaw resistance and adhesiveness (Fowler, 1989). However, polymer concrete is relatively expensive and exhibits large deformations during setting and temperature changes. To resolve these issues, various studies including modification of binder characteristics and development of shrinkage-reducing agents and/or new resins have been actively conducted (Omata *et al.*, 1995).

Unsaturated polyester resin, epoxy resin and acrylic resin are polymeric binders mainly used in polymer concrete, whose physical and mechanical properties significantly vary depending on the type of binder used. Among them, one of the most commonly used is unsaturated polyester resin due to its advantages in low price, easy-to-control setting time and high strength. In

this study, vinyl ester resin was used for polymer concrete production not only has it good workability as in unsaturated polyester resin but also excellent physical and chemical properties as in epoxy resin. Also, it has superior heat performance and corrosion resistance and thus is widely used for new industrial applications such as coatings, printed circuit boards, metal foil laminates, building materials, automotive parts and fiber reinforced composites (Patel *et al.*, 1990). Vinyl ester used in this study was modified using an Methyl Methacrylate (MMA) monomer (hereinafter “MMA-modified vinyl ester polymer concrete”). An MMA monomer has a low viscosity and thus is effective in controlling the viscosity of resin and reducing setting shrinkage, along with benefits in excellent chemical and corrosion resistance and high adhesiveness. It is anticipated that such advantages of vinyl ester resin and MMA monomer can lower binder’s viscosity and, in turn, improve the physical and mechanical properties polymer concrete.

This study intended to examine the setting shrinkage characteristics of MMA-modified vinyl ester polymer concrete for different curing ages, MMA contents and curing temperatures since the setting shrinkage is an important element related to the adhesion property with

substrate concrete when used as a repair material and the volume stability when used in precast products (Morgan, 1996; Ohama *et al.*, 1987; Chandra and Ohama, 1994).

Materials and Methods

Materials

Vinyl Ester Resin

A vinyl ester resin was produced by the esterification of polyfunctional epoxy resin with unsaturated monocarboxylic acid (usually methacrylic or acrylic acid) in the presence of polymerization inhibitor, followed by the addition of polymerization diluent (usually styrene) (White and Hensen, 1991). The vinyl ester resin used in this study was a bisphenol A epoxy-based vinyl ester resin and its properties are shown in Table 1.

MMA Monomer

Methyl Methacrylate (MMA) is a colorless liquid, which was made by producing methacrylic acid through oxidization of C4 raffinate-extracted isobutylene at a gaseous state and then esterifying the methacrylic acid with methanol. Generally, MMA tends to have high stability, along with excellent transparency, climate resistance and colorability. Table 2 shows the properties of MMA used in this study.

Initiator

A DMP solution with 55% Methyl Ethyl Ketone Peroxide (MEKPO) was used as an initiator for a vinyl ester resin. The properties of the initiator are shown in Table 3.

Promotor

Vinyl ester resin and MMA do not react with each other at a copolymerization state when only an

initiator was added. Accordingly, to accommodate a quick reaction, a promotor is essentially required. In this study, cobalt naphthenate, which enables the polymerization at both room temperature and low temperature, was used as a promotor. The properties of the promotor are presented in Table 4.

Aggregate and Filler

If aggregate for polymer concrete absorbs water, water film formed on the aggregate's surface weakens the binder-aggregate adhesion and thus lowers the strength of polymer concrete. Thus, it is necessary to dry the aggregate before mixing to keep the water content less than 0.1% (Ohama, 1973). The physical properties and of the aggregate used in this study are shown in Table 5. This study used ground calcium carbonate as a filler because it is inexpensive and easily available. Also, it has good workability since it rarely absorbs polymer binders. The physical properties and chemical component of the filler used are shown in Table 6 and 7, respectively.

Methods

Determination of Mixture Proportions

Mixture proportions of polymer concrete vary depending on the type of polymer binder, shape and particle size of aggregate and working condition. The optimum mixture proportions can be achieved when maximizing the amount of aggregate, while minimizing the amount of polymer binder, as long as a certain degree of workability and strength is ensured. In this study, the optimum mixture proportions were determined by a series of preliminary experiments. The binder formations and mixture proportions for the polymer concrete used in this study are as shown in Table 8.

Table 1. Properties of vinyl ester resin

Density (25°C)	Viscosity (20°C, mPa·s)	Vapor density	Styrene content (wt%)
1.2	250	3.6	45

Table 2. Properties of MMA monomer

Density (25°C)	Viscosity (20°C, mPa·s)	Molecular weight (g/mol)	Appearance
0.9420	0.56	100	Transparent

Table 3. Properties of MEKPO

Component	Specific gravity (25°C)	Active oxygen
MEKPO 55% DMP 45%	1.12	10.0

Table 4. Properties of cobalt naphthenate

Density (25°C)	Boiling point (°C)	Appearance
0.95	110.6	Violet liquid

Table 5. Physical properties of aggregate

Size (mm)	Apparent density	Bulk density	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 6. Properties of ground calcium carbonate

Specific gravity (gr/cc)	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 7. 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

Table 8. Binder formation and mix proportion of polymer concrete

Binder content (wt%)	Binder formation				
	VE: MMA (wt%)	MEKPO (phr [*])	Cobalt naphthenate (phr)	Filler (wt%)	Aggregate (wt%)
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

Setting Shrinkage Test

Setting shrinkage developments in MMA-modified vinyl ester polymer concrete were measured as per the method proposed by Ohama *et al.* (1987) because this method is recognized to reasonably evaluate the linear shrinkage strains in hardening materials (Jensen and Hansen, 1995). The test setup consisted of two Linear Variable Differential Transformers (LVDTs) mounted at both ends of the mold. The size of the specimen was 70×70×320 mm and the test was conducted in an environmental chamber maintaining constant temperature and humidity conditions (test temperatures of -10, 0, 10 and 20°C and relative humidity of 60±3%). Measured data were recorded using a data logger (Tokyosokki; TDS-602) with an interval of 10 min for the first 3 h and 30 min thereafter.

Results

Setting Shrinkage Developments for Different Curing Ages

Figure 1 shows the setting shrinkage developments of MMA-modified vinyl ester polymer concrete for the first 24 h of curing period; the period of setting shrinkage measurements was determined based on the results of a previous study (Ohama and Komiyama, 1979), in which the setting shrinkage of polyester resin concrete became almost constant at curing age of 24 h. Also, test results for setting shrinkage for different curing temperatures, MMA contents and curing ages are summarized in Table 9. In the table, each value is the average of two measurements. The result shows that the setting shrinkage developments with respect to the ultimate setting shrinkage measured at 24 h were 0.06 to 76.71% at a curing age of 1 h. At 3 h, the rate of the setting shrinkage developments increased up to 74.9 to 95.7%. This finding indicates that, except for the temperature level of -10°C, over 90% of the ultimate setting

shrinkage occurred within the first 3 h after curing initiation. At a curing age of 6 h, 92.65 to 98.26% of the ultimate setting shrinkage took place and the rate of setting shrinkage increase reached a nearly negligible level. The setting shrinkage measured was 0.02 to 30.33×10⁻⁴ at 1 h, 25.87 to 37.85×10⁻⁴ at 3 h and 34.53 to 39.54×10⁻⁴ at 24 h after curing initiation.

Setting Shrinkage Developments for Different MMA Contents

Figure 2 plots the effect of MMA content on the setting shrinkage development of MMA-modified vinyl ester polymer concrete. The result shows that an increase in MMA content led to an almost linear decrease in setting shrinkage regardless of the curing temperature. The measured setting shrinkage was found to be 35.85 to 39.54×10⁻⁴ with 0 wt.% MMA, 34.94 to 38.68×10⁻⁴ with 2.5 wt.% MMA and 34.53 to 37.66×10⁻⁴ with 5 wt.% MMA, indicating that the greater MMA content resulted in a reduction in setting shrinkage. The average setting shrinkage reduction rate with respect to the reference value (i.e., setting shrinkage with 0 wt.% MMA) was found to be 2.3% when 2.5 wt.% MMA was added and 4.3% when 5 wt.% MMA was added. From the results, it can be concluded that the addition of MMA monomer was quite effective in reducing the setting shrinkage of MMA-modified vinyl ester polymer concrete.

Setting Shrinkage Developments for Different Curing Temperatures

Figure 3 illustrates the effect of curing temperature on the setting shrinkage of MMA-modified vinyl ester polymer concrete. The result revealed that an increase in curing temperature led to an almost linear increase in setting shrinkage. The measured setting shrinkage was 34.53 to 35.85×10⁻⁴ at -10°C, 34.69 to 37.05×10⁻⁴ at 0°C, 35.90 to 38.59×10⁻⁴ at 10°C and 37.66 to 39.54×10⁻⁴ at 20°C, which implies that the higher curing temperature resulted in greater setting shrinkage.

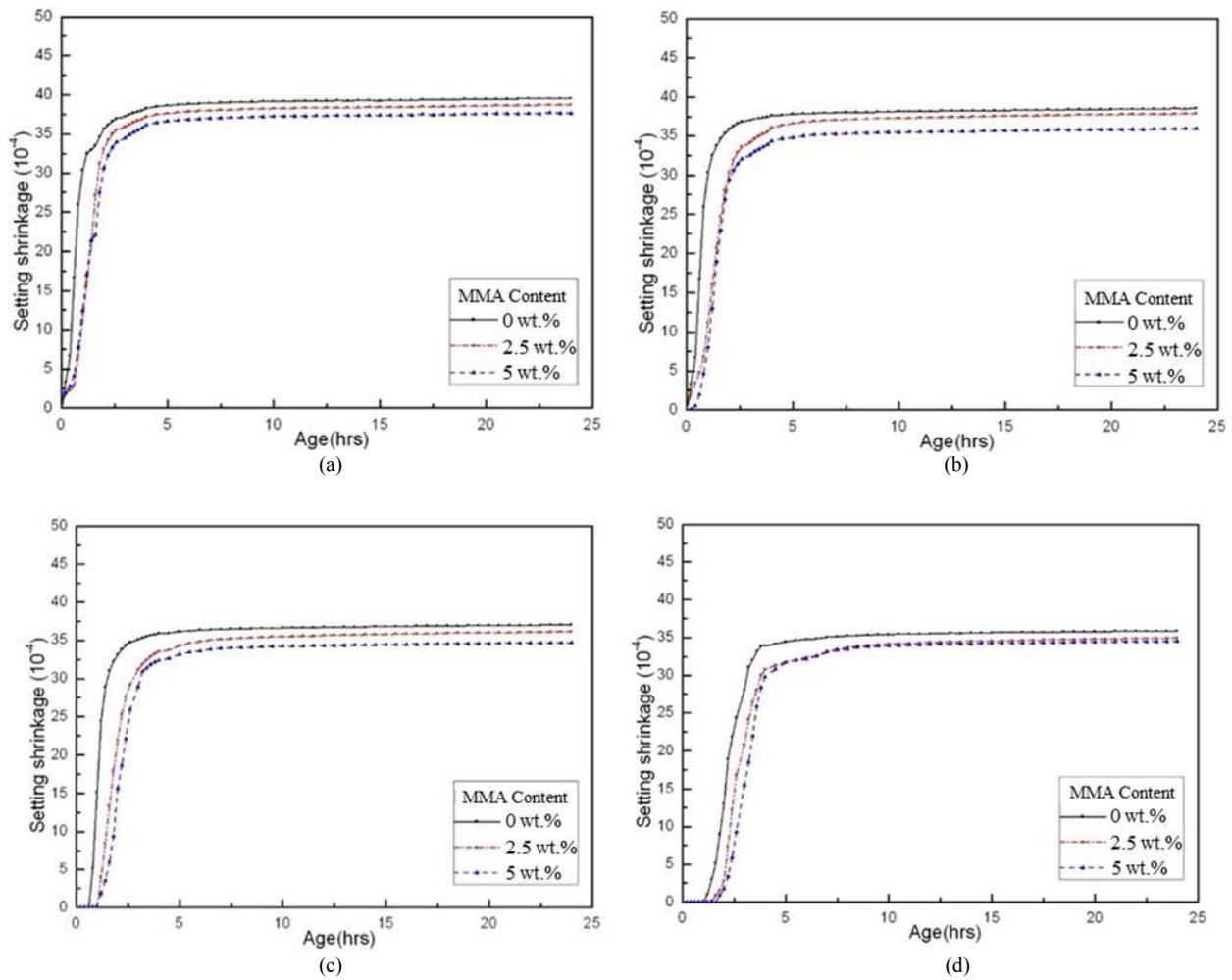


Fig. 1. Effect of curing temperature on setting shrinkage developments (a) 20°C (b) 10°C, (c) 0°C, (d) -10°C

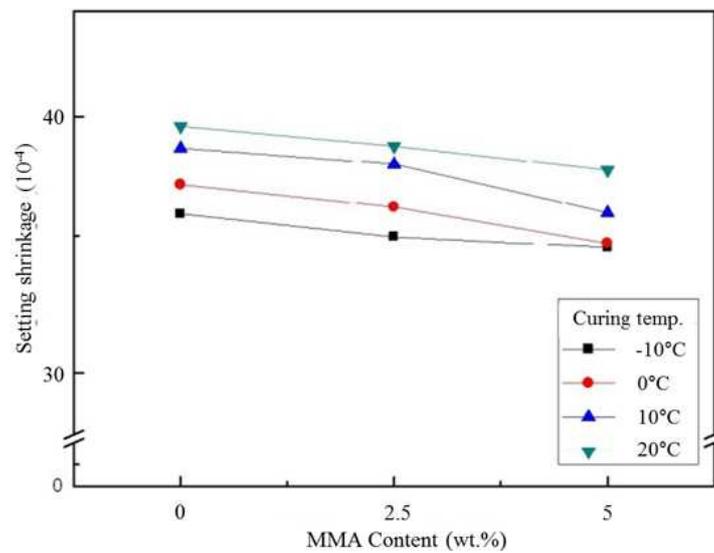


Fig. 2. MMA content vs. setting shrinkage at age of 24 h

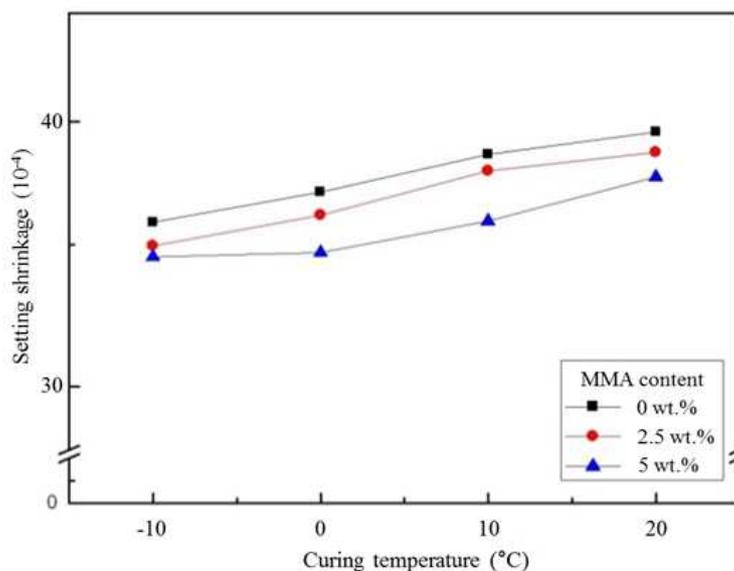


Fig. 3. Curing temperature vs. setting shrinkage at age of 24 h

Table 9. Test results of setting shrinkage

Curing temperature (°C)	MMA content (wt%)	Setting shrinkage (×10 ⁻⁴)				
		1 h	3 h	6 h	12 h	24 h
-10	0.0	0.07 (0.20 [*])	33.15 (92.47)	34.78 (97.02)	35.52 (99.01)	35.85 (100%)
	2.5	0.04 (0.11)	28.02 (80.19)	32.37 (92.65)	34.36 (98.34)	34.94 (100%)
	5.0	0.02 (0.06)	25.87 (74.92)	32.18 (93.19)	34.11 (98.78)	34.53 (100%)
0	0.0	15.19 (41.00)	35.65 (96.22)	36.35 (98.11)	36.72 (99.11)	37.05 (100%)
	2.5	0.15 (0.42)	32.86 (90.95)	34.83 (96.40)	35.65 (98.67)	36.13 (100%)
	5.0	0.04 (0.12)	31.83 (91.76)	33.59 (96.83)	34.29 (98.85)	34.69 (100%)
10	0.0	24.16 (62.61)	37.38 (96.86)	37.92 (98.26)	38.25 (99.12)	38.59 (100%)
	2.5	11.31 (29.84)	35.25 (93.01)	36.85 (97.23)	37.43 (98.76)	37.90 (100%)
	5.0	4.00 (11.14)	33.56 (93.48)	35.13 (97.86)	35.55 (99.03)	35.90 (100%)
20	0.0	30.33 (76.71)	37.85 (95.73)	38.83 (98.20)	39.25 (99.27)	39.54 (100%)
	2.5	11.21 (28.98)	36.71 (94.91)	37.87 (97.91)	38.30 (99.02)	38.68 (100%)
	5.0	12.42 (32.98)	35.50 (94.26)	36.88 (97.93)	37.34 (99.15)	37.66 (100%)

*Percentage of setting shrinkage development with respect to 24-hr ultimate setting shrinkage

The average setting shrinkage increase rate was 1.9% between -10 and 0°C, 3.7% between 0 and 10°C and 3.9% between 10 and 20°C. This finding indicates that (1) the setting shrinkage increase rate increased as the curing temperature increased and (2) low-temperature curing is beneficial for minimizing the setting shrinkage of MMA-modified vinyl ester polymer concrete.

Discussion of the Results

There have been a number of research studies on the setting shrinkage of polymer concrete. Chandra and Ohama (1994) stated that the large setting shrinkage of polymer concrete is a problematic issue to be considered in the practical applications because the setting shrinkage typically reaches about five to ten times the drying shrinkage of Portland cement concrete,

i.e., 50 to 60×10⁻⁴. Ohama *et al.* (1987) stated that Polymethyl Methacrylate (PMMA) concrete had a large setting shrinkage of about 60×10⁻⁴ and developed a method to reduce the setting shrinkage to nearly zero in the temperature range of -20 to 20°C using a shrinkage-reducing agent. Yeon and Yeon (2012) found that the setting shrinkage of UP-MMA polymer concrete ranged from 29.2 to 82.6×10⁻⁴, which was affected by UP-MMA ratio, shrinkage-reducing agent content and curing temperature. Ohama and Komiyama (1979) discovered that the setting shrinkage of polyester resin concrete with a compressive strength of 70 to 80 MPa was 40 to 50×10⁻⁴. Also, they reported that the setting shrinkage can be reduced to an almost negligible level by incorporating a shrinkage-reducing agent. Also, Yeon *et al.* (2014) observed that the setting shrinkage

of acrylic polymer concrete fell between 29.6 and 39.6×10^{-4} and the magnitude increased as the MAA content increased because an increase in MAA content promotes the setting reactions.

In addition, many research efforts have been made to identify the drying shrinkage behavior of conventional Portland cement concrete. Neville (1996) described that there are various factors affecting the drying shrinkage of ordinary cement concrete. This study reported that the typical drying shrinkage after six months were 2 to 12×10^{-4} . Ngab *et al.* (1981) reported that high strength concrete with 60-day compressive strength of 62 to 63 MPa experienced drying shrinkage of 3.4 to 4.3×10^{-4} . Huo *et al.* (2001) stated that high-performance concrete with compressive strength of 51 to 99 MPa had the maximum drying shrinkage of 3.0 to 4.0×10^{-4} .

The MMA-modified vinyl ester polymer concrete investigated in this study showed the compressive strength of 64 to 70 MPa and the setting shrinkage of 34.53 to 39.54×10^{-4} at curing age of 24 h. When compared with the previous studies, the setting shrinkage monitored in this study was much greater than the drying shrinkage of ordinary cement concrete but was less than the setting shrinkage of polymer concrete using binders other than vinyl ester resin. Rather, the setting shrinkage observed in this study was quite similar to that of acrylic polymer concrete (29.6 to 39.6×10^{-4}), which is quite beneficial for ensuring volume stability and reducing cracking risk at early ages.

In this study, only setting shrinkage strain of MMA-modified vinyl ester polymer concrete was evaluated based on a laboratory test. Using the setting shrinkage data, along with materials' constitutive relationship, restraint condition and viscoelastic properties, stresses due to setting shrinkage could be achieved. The analysis of setting shrinkage stress requires further research.

Conclusion

Based on the experimental results obtained in this study, the following conclusions can be made:

- Results revealed that the setting shrinkage developments with respect to the ultimate setting shrinkage monitored at 24 h were 92.65 to 98.26% at 6 h, indicating that most of the setting shrinkage in Methyl Methacrylate (MMA)-modified vinyl ester polymer concrete occurred within the first 6 h after curing initiation
- An increase in MMA content led to an almost linear decrease in setting shrinkage, regardless of the curing temperature. With addition of 5 wt% MMA, approximately a 4.3% decrease in setting shrinkage was observed. This finding implies that the addition of MMA monomer is an effective measure to reduce

the setting shrinkage of MMA-modified vinyl ester polymer concrete

- As the curing temperature increased, the setting shrinkage increased almost linearly. This result indicates that low-temperature curing is effective for minimizing the setting shrinkage of MMA-modified vinyl ester polymer concrete
- When compared with the results of former studies, the setting shrinkage obtained in this study was much greater than the typical drying shrinkage of Portland cement concrete. However, it was less than the setting shrinkage of polymer concrete incorporating other binder types, which is beneficial for minimizing early-age cracking risk

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Author's Contributions

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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