Low-Temperature Curing of Polymer Methacrylate Polymer Concrete

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ABSTRACT

In recent years, polymethyl methacrylate polymer concrete (PMMA-PC) has been used extensively in the field of construction works. It is needed because it will harden within 1 hr at low temperatures. A basic investigation of the low-temperature curing characteristics of workable PMMA-PC is the focus of this paper. PMMA-PC and its binder are prepared with various binder formulations, and the working life of the binder and the peak exotherm time and compressive strength of PMMA-PC are examined under various low-temperature conditions. The working life of the binder and the peak exotherm time of PMMA-PC decrease with an increase in promoter and cross-linking agent contents and a rise in test temperature. The contents of the binder with the desired working life at low temperatures less than 0°C can be estimated by using a nomograph prepared in this investigation. The peak exotherm time of PMMA-PC can be predicted from the working life of the binder. In conclusion, the optimum binder formulations are recommended for the low-temperature applications of PMMA-PC, which hardens and develops a high compressive strength of about 500 kg/cm^2 in the range of 0°C to -20°C within approximately 1 hr.

Recently, polymethyl methacrylate polymer concrete (PMMA-PC) has been widely used for various construction works, such as the repair and restoration of concrete structures, because of its good workability and high early strength development. For its applications during winter, in cold districts, in the repair of cold stores, and so forth, the development of the high early strength is required at low temperatures, and, in many cases, the construction time is quite limited (1). This investigation was conducted to make clear the low-temperature curing characteristics of PMMA-PC.

PMMA-PC and its binder were prepared with variation of cross-linking agent and promoter contents, and the working life of the binder and the peak exotherm time and compressive strength of PMMA-PC were investigated under various low-temperature conditions in order to obtain the optimum binder formulations that give a high early strength at temperatures less than 0°C. The results of this investigation are presented in this paper.

MATERIALS

Binder System

The binder system used was methyl methacrylate (MMA) monomer, together with polymethyl methacrylate (PMMA) as a thickening agent, trimethylolpropane trimethacrylate (TMPTMA) as a cross-linking agent, 50 percent dicyclohexyl phthalate powder of benzoyl peroxide (BPO) as an initiator, and N,N-dimethyl-p-toluidine (DMT) as a promoter. The basic properties of MMA, PMMA, and TMPTMA are given in Table 1.

TABLE 1 Basic Properties of MMA, PMMA, and TMPTMA

Material for Binder	Molecular Weight	Specific Gravity (20 °C)	Viscosity (20 °C ,cP)
MMA	100.12	0.94	0.85
PMMA	ca. 250,000	1.19	——
TMPTMA	338	1.06	13.0

Filler and Aggregates

Commercially available calcium carbonate (heavy grade) was used as a filler. Hatsukari crushed andesite for coarse aggregate and Abukumagawa river sand for fine aggregate were employed. Their properties are given in Table 2. The water contents of the filler and aggregates were controlled to be less than 0.1 percent.

TABLE 2 Properties of Filler and Aggregates

Type of Filler or Aggregate	Size (mm)	Specific Gravity (20°C)	Water Content (%)	Organic Impurities
Calcium carbonate	$<2.5 \times 10^{-3}$	2.70	<0.1	Nil
Crushed andesite	10 - 20	2.51	<0.1	Nil
	5 - 20	2.51	<0.1	Nil
River sand	1.2 - 5	2.46	<0.1	Nil
	<1.2	2.46	<0.1	Nil

TESTING PROCEDURES

General Conditions for Tests

The tests, except for the viscosity of binder, were carried out at temperatures of 0°C, -10°C, and -20°C. Before the tests, all the materials were stored at the respective test temperatures. The formulations of the binder and the mix proportions of PMMA-PC are given in Tables 3 and 4.

Test of Working Life of Binder

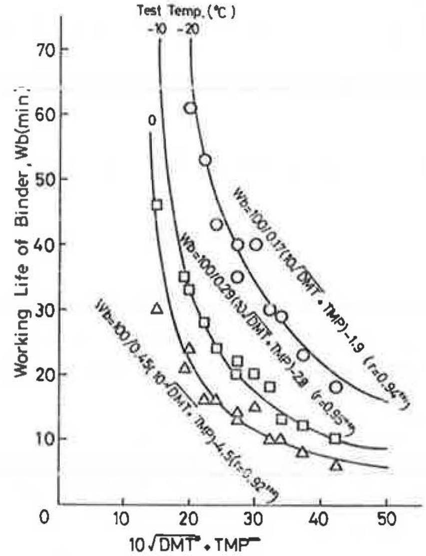
About 100 g of binder was tested for working life according to JIS K 6833 (General Testing Methods for Adhesives). The time elapsed from the addition of the initiator to the spinning of the binder was observed as the working life of the binder.

TABLE 3 Formulations of Binder

Formulation No.	Formulation by Weight			
	MMA + PMMA	TMPTMA	BPO (as solids)	DMT
1	95	5	2.0	1.0
2				2.0
3				3.0
4				5.0
5	90	10		1.0
6				2.0
7				3.0
8				5.0
9	80	20		1.0
10				2.0
11				3.0
12				5.0

TABLE 4 Mix Proportions of PMMA-PC

Materials			Weight Percent
Binder	MMA + PMMA + TMPTMA		10.00
Filler	Calcium Carbonate		10.00
Aggregate	Crushed Andesite	Size, 10-20 mm	15.02
		5-10 mm	15.02
	River Sand	Size, 1.2-5 mm	9.91
		< 1.2 mm	40.05



Note; * DMT content (%), ** TMPTMA content (%), *** Coefficient of correlation.

FIGURE 1 Effects of DMT and TMPTMA contents and test temperature on working life of binder (with BPO content 2.0%).

Test of Peak Exotherm Time of PMMA-PC

About 500 g of fresh PMMA-PC mixed according to JIS A 1181 (Method of Making Polyester Resin Concrete Specimens) was tested for peak exotherm time. The exotherm temperature was determined by chromel-alumel thermocouples embedded in PMMA-PC. The time elapsed from the addition of the initiator to the attainment of the maximum exotherm temperature of PMMA-PC was observed as the peak exotherm time of PMMA-PC.

Compressive Strength Test of PMMA-PC

In accordance with JIS A 1181, PMMA-PC was mixed, and then cylindrical specimens 7.5 x 15 cm were molded. After molding, the specimens were cured according to the following methods: (a) 1-hr, 2-hr, 4-hr, 24-hr, 3-day, and 7-day cures at casting temperatures (0°C, -10°C, and -20°C); and (b) 24-hr cure at each casting temperature plus 24-hr, -20°C cure. The specimens were tested for compressive strength in accordance with JIS A 1182 (Method of Test for Compressive Strength of Polyester Resin Concrete).

TEST RESULTS AND DISCUSSION

The effects of DMT and TMPTMA contents and test temperature on the working life of binder are shown in Figure 1. The working life of the binder tends to shorten with increasing DMT and TMPTMA contents, irrespective of the test temperature. The working life of the binder is also markedly affected by the test temperature and lengthens with a fall in the test temperature. The working life of the binder at -20°C is 2 to 3 times longer than that at 0°C. From Figure 1 it is observed that a close correlation exists between the factor ($10\sqrt{\text{DMT content}}$ + TMPTMA content) and working life of PMMA-PC regardless of the test temperature. Consequently, this empirical relationship can be expressed by

$$Wb = 100/[(0.014t + 0.44)(10\sqrt{DMT} + TMP) - (0.13t + 4.4)] \quad (1)$$

where

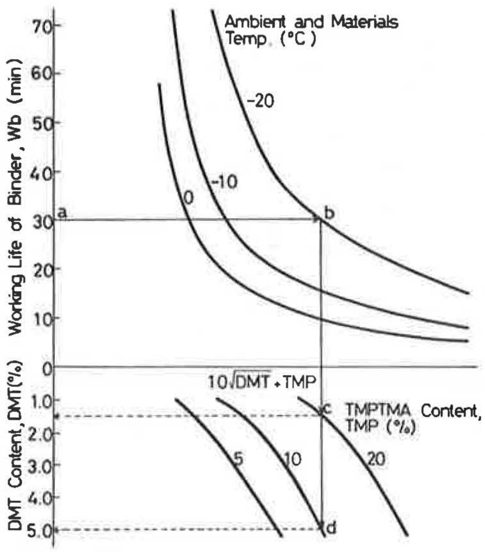
Wb = working life of the binder,
t = test temperature,
DMT = DMT content, and
TMP = TMPTMA content.

By using this relationship, a nomograph for the DMT and TMPTMA contents of the binder with the desired working life can be prepared as shown in Figure 2. The validity of this nomograph is limited in the range of the binder formulations given in Table 3. In addition, the procedure to estimate the DMT and TMPTMA contents of the binder with the desired working life at different ambient and materials temperatures less than 0°C by applying this nomograph is explained in the example that follows.

Example

It is desired to calculate the DMT and TMPTMA contents of a binder with a working life of 30 min at materials and ambient temperatures of -20°C. In Figure 2, a straight line perpendicular to the y axis is drawn from point a of Wb = 30 min, and point b on the intersection of the straight line, and the curve denoting Wb at -20°C is obtained. Then a straight line perpendicular to the x axis is drawn from point b, and the two DMT contents are estimated on the intersections, c and d, of the straight line, and the curves denoting DMT at TMP = 20 percent and 10 percent, respectively, as follows:

DMT contents (DMT) at TMPTMA contents (TMP) 20% and 10% = 1.5% and 5.0%, respectively (2)



Note: ⟶ indicates the process for estimating the desired DMT and TMPTMA contents of binder with a working life of 30 minutes.

FIGURE 2 Nomograph for DMT and TMPTMA contents of binder (with BPO content 2.0%).

If necessary, the working life of PMMA-PC can be predicted from that of its binder by using the empirical equation, Wc = 2.29Wb + 2.33 (where Wc is the working life of PMMA-PC), which was proposed by the authors' previous study (2). The effects of DMT and TMPTMA contents and test temperature on the peak exotherm time of PMMA-PC are shown in Figure 3. Like

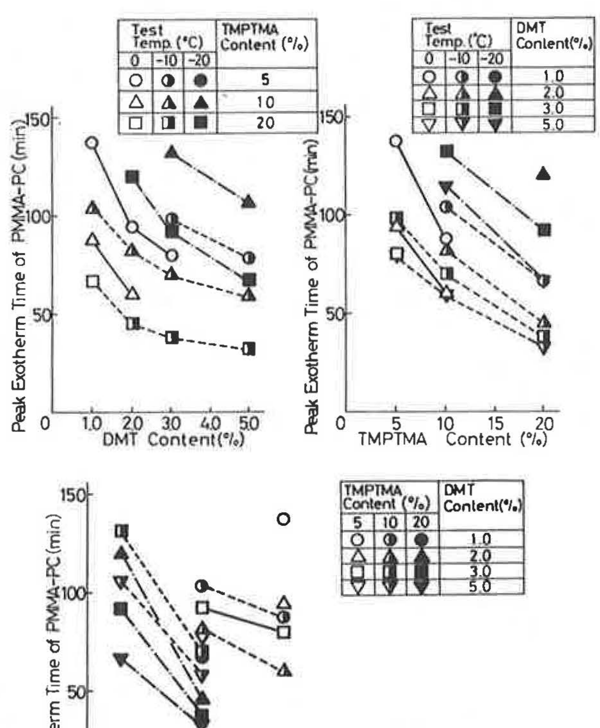


FIGURE 3 Effects of DMT and TMPTMA contents and test temperature on peak exotherm time of PMMA-PC.

the working life of the binder, the peak exotherm time of PMMA-PC decreases with increasing DMT and TMPTMA contents and rising test temperature.

It can be observed from Figure 4 that a reliable positive correlation exists between the working life of the binder and the peak exotherm time of PMMA-PC, regardless of the formulations of the binder and test temperature. This empirical relationship can be expressed by

$$Pc = 3.8\ Wb - 1.6 \quad (3)$$

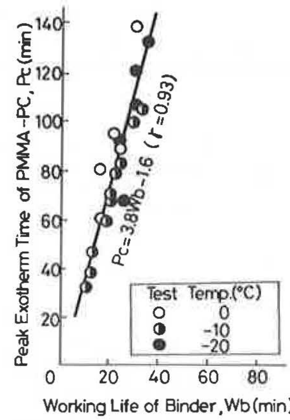


FIGURE 4 Working life of binder versus peak exotherm time of PMMA-PC.

where Pc and Wb are the peak exotherm time of PMMA-PC, and the working life of the binder, respectively. From the preceding relationship, the peak exotherm time of PMMA-PC can be predicted by determining the working life of the binder. Probably the peak exotherm time of PMMA-PC gives a measure to determine the time that is required before demolding precast products or to cure after repairing works.

Figure 5 shows the relation between the DMT content and compressive strength of PMMA-PC. An increase in the DMT content raises the compressive strength of PMMA-PC, regardless of the test temperature. PMMA-PC, when provided an additional cure at 20°C for 24 hr after curing at each casting temperature, shows a higher compressive strength than the one cured at 0°C, -10°C, or -20°C for 24 hr. This tendency is especially remarkable at a casting temperature of -20°C. The explanation for this probably is that the polymerization of unreacted monomer remaining in the binder is accelerated by rising cure temperature.

Figure 6 shows the relation between the TMPTMA content and compressive strength of PMMA-PC cast at -20°C. Irrespective of curing method, the effect of the TMPTMA content on the compressive strength of PMMA-PC is hardly recognized.

Figure 7 shows the strength development of PMMA-PC after the peak exotherm time. After the peak exotherm time, the compressive strength of PMMA-PC is elevated with additional curing time at low temperatures of 0°C and -20°C, and tends to become constant within about one day.

On the basis of the foregoing data, considering the use of the prepackaged method from a viewpoint of the simplified applications of PMMA-PC, the appropriate formulations of the binder with a good balance of performance and economy may be recommended (Table 5). By applying these formulations of the binder, PMMA-PC has a peak exotherm time of approximately 1 hr and compressive strengths of about

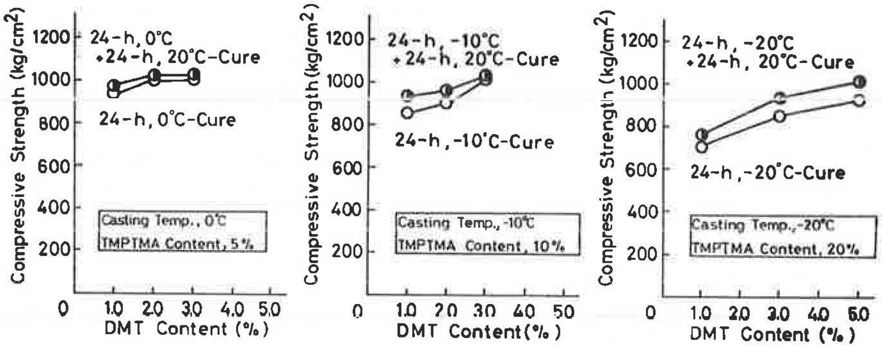


FIGURE 5 DMT content versus compressive strength of PMMA-PC.

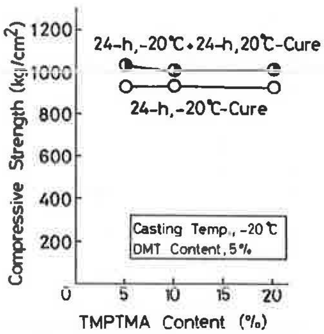


FIGURE 6 TMPTMA content versus compressive strength of PMMA-PC cast at 20°C.

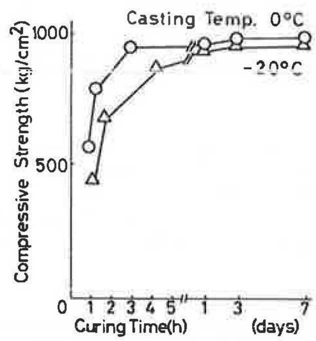


FIGURE 7 Strength development of PMMA-PC after peak exotherm.

TABLE 5 Recommendable Formulations of Binder for PMMA-PC Cast at Low Temperatures

Ambient and Materials Temperatures (°C)	Formulation by Weight			
	MMA + * PMMA	TMPTMA	BPO (as solids)	DMT
0 ~ -10	90	10	2.0	2.0~3.0
-20	80	20	2.0	5.0

Note; * MMA : PMMA = 90 : 5 (By Weight).

500 kg/cm² at the peak exotherm time, and 900 kg/cm² or higher in a 1-day cure even when the ambient and materials temperatures are in the range of 0°C to -20°C. The compressive strength of PMMA-PC cured at such low temperatures is much the same as that of a 1-day -20°C 50% R.H.-cured one.

It is evident from these test results that PMMA-PC is promising as a concrete material for construction works in cold districts because of its superior strength developed in low-temperature curing.

CONCLUSIONS

The working life of the binder and the peak exotherm time of PMMA-PC decrease with an increase in DMT and TMPTMA contents and a rise in test temperature. The relation between the working life of the binder and the DMT and TMPTMA contents can be expressed by Equation 1. By using a nomograph prepared on the basis of this equation, the DMT and TMPTMA contents can be estimated for the desired working life of the binder at different ambient and materials temperatures. The relationship between the working life of the binder and the peak exotherm time of PMMA-PC can also be expressed by Equation 2. From this relationship, the peak exotherm time can be predicted by determining the working life.

Irrespective of curing method, the compressive strength of PMMA-PC increases with a rise in DMT content, but the effect of TMPTMA content on the compressive strength is hardly recognized.

By applying the optimum formulations of the binder suggested in Table 5, PMMA-PC has a peak exotherm time of approximately 1 hr and compressive strengths of about 500 kg/cm² at the peak exotherm time and 900 kg/cm² or higher in a 1-day cure even when the ambient and materials temperatures are in the range of 0°C to -20°C. It is obvious from these results that PMMA-PC is promising as a concrete material for construction works at low temperatures.

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2. Y. Ohama and T. Kobayashi. Working Life of Polymethyl Methacrylate Concrete and Its Control. Journal of the Society of Materials Science, Japan, Vol. 32, No. 358, 1983, pp. 215-221.