EFFECT OF POLYMER ADDITION ON
THE THERMAL STABILITY AND THERMAL EXPANSION OF CEMENT

Pu-Woei Chen and D.D.L. Chung
Composite Materials Research Laboratory
State University of New York at Buffalo
Buffalo, NY 14260-4400

(Communicated by D.M. Roy)
(Received November 10, 1994)

ABSTRACT

Polymer addition to cement paste was found to decrease the thermal stability and thermal expansion coefficient (CTE). The addition of methylcellulose (0.4% of the cement weight) reduced the mechanical weakening onset temperature from 125 to 42°C, while decreasing the CTE near room temperature from $10 \times 10^{-6} \, ^{\circ}\text{C}^{-1}$ to nearly zero. The addition of latex (20% of the cement weight) reduced the mechanical weakening onset temperature from $125^{\circ}\text{C}$ to near room temperature, while decreasing the CTE near room temperature from $10 \times 10^{-6} \, ^{\circ}\text{C}^{-1}$ to $-4 \times 10^{-6} \, ^{\circ}\text{C}^{-1}$.

I. Introduction

Most previous work on the thermal properties of concrete relates to the thermal conductivity because of the need for energy conservation [1]. Less attention has been given to the thermal stability and thermal expansion, which are relevant to concrete structures in hot climates. Thermal expansion can cause cracking, so it necessitates the use of expansion joints in bridges and other large structures; these joints are locations of poor concrete durability (due to wear), add to the cost of the structure, and decrease the comfort of riding in cars travelling on the bridge. Thermal stability is usually not a problem because mechanical weakening starts to occur beyond $100^{\circ}\text{C}$ (boiling point of water), which is not encountered by most concrete structures, even in hot climates. Therefore, little work had been reported on the thermal stability of concrete. However, as shown in this paper, the temperature at which weakening starts is much decreased by the addition of a polymer to the concrete, so that the thermal stability can be of practical concern to concretes containing polymers. Although this thermal stability degradation is a negative effect, it is accompanied by a decrease of the thermal expansion coefficient, as shown in this work. As a result, a very low thermal expansion coefficient can be attained in the temperature range below the weakening onset temperature. In other words, within a limited temperature range, concretes containing polymers can have very low thermal expansion coefficients. It should be mentioned that concretes containing polymers (such as latex) are well-known for their high toughness and low permeability [2-6].

II. Experimental

The cement was Portland cement (Type I) from Lafarge Corp. (Southfield, Michigan). Two types of
polymers were used. They were (i) methylcellulose (Dow Chemical Corp., Midland, Michigan; Methocel A15-LV) in the amount of 0.4% of the cement weight and used along with a defoamer (Colloids, Inc., Marietta, Georgia; Colloids 1010) in the amount of 0.13 vol.%, and (ii) latex (a styrenebutadiene emulsion; Dow Chemical Corp., Midland, Michigan; Latex 460NA) in the amount of 20% of the cement weight and used along with an antifoam (Dow Corning 2410; an emulsion) in the amount of 0.5% of the latex weight. No aggregate (fine or coarse) was used. The slump test was performed using a 77 mm diameter and 58 mm high plastic cylinder. The slump was determined by measuring the outer surface of the horizontally displaced cement paste. The water/cement ratio was 0.32 when methylcellulose was used (slump = 150 mm) and 0.23 when latex was used (slump = 160 mm) and 0.23 when latex was used (slump = 160 mm). A water reducing agent (Rohm and Haas, TAMOL SN, 93-96% sodium salt of a condensed naphthalene sulfonic acid) in the amount of 0.5% of the cement weight was used when methylcellulose was used, but not at all when latex was used. The combined choice of water/cement ratio and water-reducing-agent/cement ratio was for the purpose of maintaining the slump in the range 150-160 mm. For the cement paste without any polymer, the water/cement ratio was 0.30, the water-reducing-agent/cement ratio was 0.5%, and the slump was 150 mm.

A Hobart mixer with a flat beater was used for mixing.

For the case of cement paste containing latex, the latex and antifoam were mixed by hand for about 1 min. Then this mixture, cement and water were mixed in the Hobart mixer for 5 min.

For the case of mortar containing methylcellulose, methylcellulose was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Then this mixture, cement, water and the water reducing agent were mixed in the Hobart mixer for 5 min.

After pouring the mix into oiled molds, a vibrator was used to decrease the amount of air bubbles.

The specimens were demolded after 1 day and then allowed to cure at room temperature in air for 7 days.

Compressive testing according to ASTM C109-80 was conducted on specimens of size 2 x 2 x 2 in (5.1 x 5.1 x 5.1 cm), using a hydraulic Materials Testing System (MTS) with a crosshead speed of 1.27 mm/min. Six specimens of each type were tested. The compressive properties of the cements pastes are shown in Table 1. Both the compressive strength and ductility (strain at fracture) are higher for the plain cement paste than the pastes containing polymers.

The change in thickness of a disc-shaped specimen (0.5 in or 1.3 cm in diameter, about 2 mm in thickness) was measured as the temperature was increased from room temperature to 120°C at a heating rate of 5°C/min. For this purpose, a Perkin-Elmer TMA7 thermal mechanical analyzer was used. The probe force was 50 mN, which corresponds to 390 Pa acting on the top face of the specimen. The sample chamber was purged with helium at a flow of 30 cc/min.

Figs. 1 and 2 show the plots of strain vs. temperature for plain cement paste and that with methylcellulose.

<table>
<thead>
<tr>
<th>Table 1 Compressive properties of cement pastes at 7 days</th>
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<td>Strength (MPa)</td>
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<td>----------------</td>
</tr>
<tr>
<td>Plain</td>
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<td>With methylcellulose</td>
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<td>With latex</td>
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Fig. 1  Strain vs. temperature during heating of plain cement paste.

respectively. The corresponding curve for the cement paste with latex has the same shape as that of the cement paste with methylcellulose. Fig. 1 shows that the plain cement paste undergoes usual thermal expansion at a rate of $10 \times 10^6/\degree C$ such that the curve is linear up to $100\degree C$, at which the slope of the curve starts to decrease; at $125\degree C$ the strain starts to decrease with increasing temperature, indicating mechanical weakening. Fig. 2 shows that the cement paste with methylcellulose has nearly zero thermal expansion coefficient up to $42\degree C$, at which the strain starts to decrease with increasing temperature. In the case of the cement paste with latex, the strain starts to decrease at room temperature (the lowest temperature in our experiment). Table 2 lists the coefficient of thermal expansion (CTE) for the various cement pastes at $30-35\degree C$ and $35-40\degree C$, as obtained from the slopes of the curves like Fig. 1 and 2. The CTE value is nearly zero up to $40\degree C$ for the cement paste with methylcellulose. It is more negative for the cement paste with latex than that with methylcellulose.

III. Discussion

The addition of methylcellulose, though in an amount of only 0.4% of the cement weight, resulted in significant changes in the thermal behavior of the cement paste. The changes are (i) the mechanical weakening onset temperature (defined here as the temperature at which the strain starts to decrease with increasing temperature while the specimen is under a constant compressive stress of 390 Pa) is decreased from 125 to $42\degree C$, and (ii) the CTE at $30-40\degree C$ is decreased from $10 \times 10^{-6}/\degree C$ to nearly zero ($-1 \times 10^{-4}$ to $-2 \times 10^{-6}/\degree C$). Thus, at temperature up to $42\degree C$, the cement paste with methylcellulose is attractive.

Fig. 2  Strain vs. temperature during heating of cement paste with methylcellulose.
Table 2  Coefficient of thermal expansion (10⁻⁶°C⁻¹) of cement pastes

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<tr>
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<th>30-35°C</th>
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<tr>
<td>Plain</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>With methylcellulose</td>
<td>-1*</td>
<td>-2*</td>
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<tr>
<td>With latex</td>
<td>-4</td>
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*Approximate due to the small absolute value.

The addition of latex in an amount of 20% of the cement weight resulted in more drastic effects than the addition of methylcellulose in the amount of 0.4% of the cement weight. The mechanical weakening onset temperature becomes near room temperature, and the CTE becomes quite negative (-4 x 10⁻⁶°C⁻¹). Thus, the latex addition is not attractive from a thermal point of view. A smaller amount of latex may result in better thermal behavior, but the typical latex amount used is high (like 20% of the cement weight, as used in this work) for the sake of high toughness and low permeability [7]. In contrast, a small amount (like 0.4% of the cement weight, as used in this work) of methylcellulose is typically used for the sake of dispersing fibers in concrete [8].

It had been reported that the CTE of concrete is increased by polymer addition due to the large CTE of the polymer compared to that of cement [9,10]. The finding of this work is opposite. The difference may be due to the difference in the method of CTE measurement. No force was applied to the specimen during CTE measurement in Ref. 10, but a compressive stress (though only 390 Pa) was applied to the specimen in the direction of strain measurement in this work.

The CTE we obtained for plain cement paste is consistent with the values (e.g., 11 x 10⁻⁶ °C⁻¹ [11]) previously reported. This implies that the measurement technique of this work is acceptable. Our technique is actually commonly used in materials research.

The adverse effect of polymer addition on the thermal stability of concrete was shown in this paper for two polymers (methylcellulose and latex) that were in vastly different proportions. Though the magnitude of the effect differs between the two cases, the effect is similar and probably applies to many other polymers as well. The severity of the effect calls for further study by mechanical testing at various temperatures. The technique used in this work determines the onset temperature of mechanical weakening, but does not provide quantitative information on the degree of weakening.

IV. Conclusion

The addition of a polymer to cement paste was found to decrease both the thermal stability and the thermal expansion of the cement paste. The extent of the effects depends on the type and amount of the polymer. The addition of methylcellulose in the amount of 0.4% of the cement weight decreased the mechanical weakening onset temperature from 125 to 42°C, while decreasing the coefficient of thermal expansion (CTE) near room temperature from 10 x 10⁻⁶°C⁻¹ to nearly zero. The addition to cement paste of latex in the amount of 20% of the cement weight decreased the mechanical weakening onset temperature to near room temperature and decreased the CTE near room temperature from 10 x 10⁻⁶ to -4 x 10⁻⁶ °C⁻¹. The methylcellulose addition thus provides concrete of low thermal expansion up to 42°C, while latex addition is not attractive thermally.
V. References


