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REVERSIBLE DECREASE OF THE FLEXURAL DYNAMIC MODULUS OF CEMENT PASTES UPON HEATING

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ABSTRACT

The flexural storage modulus was found to decrease gradually and reversibly with increasing temperature from 30 to 150°C for cement pastes. Among the admixtures used (latex, methylcellulose and silica fume), silica fume (15% by weight of cement) gave the highest flexural storage modulus at all temperatures (30-150°C), but also the greatest fractional decrease in modulus upon heating. Methylcellulose (0.4% by weight of cement) gave higher modulus than latex (20-30% by weight of cement). The modulus increased with increasing latex/cement ratio. Cement paste without admixture gave the lowest modulus. *© 1997 Elsevier Science Ltd*

Introduction

Due to the high temperatures encountered by concrete structures in hot regions, in addition to the heat associated with a fire, the effect of heating on the properties of concrete is of interest. The degradation upon heating can be in the form of weight loss (due to spalling and moisture loss) (1-4), porosity increase (2) and decreases in strength and modulus (2-11). The fractional loss in weight is larger when silica fume is present (1,2). The temperature for the onset of mechanical weakening is decreased when a polymer (latex or methylcellulose) is present (12).

Measurement of a property as a function of temperature for a given specimen is preferred to the measurement of different specimens for different temperatures, in order to obtain accurate determination of the temperature dependence. This is because different specimens of the same type can be a little different. As strength measurements are destructive to the specimens, they cannot be carried out as a function of temperature for a given specimen. For example, Ref. 2 reported the compressive and tensile strengths of different specimens that had been heated to different temperatures (100-600°C) and then cooled to room temperature. On the other hand, measurement of the dynamic modulus (8,11) is non-destructive. Furthermore, the dynamic modulus is a fundamental mechanical property that relates to the elastic stiffness. Therefore, this paper focuses on the effect of heating on the dynamic modulus, particularly the flexural dynamic modulus, since flexural properties are technologically useful for civil infrastructure systems.

TABLE 1

Amounts of Water and Water Reducing Agent (WR) for Each Mix

	Water/cement ratio	WR/cement ratio
Plain	0.45	0
+ L	0.23	0
+ M	0.32	1%
+ SF	0.35	3%
+ M + SF	0.35	3%

Note: L = latex; M = methylcellulose; SF = silica fume

Ref. 8 and 11 reported that the dynamic modulus decreased with increasing temperature. We have previously reported the flexural dynamic (storage) modulus of cement pastes at 30, 60, 90, 120 and 150°C (13). This paper provides a more detailed study of the effect of temperature and addresses the reversibility of the effect. In contrast to Ref. 5-9, we found that the modulus decreased reversibly with increasing temperature from 30 to 150°C.

Experimental Methods

Dynamic mechanical testing (ASTM D4065-94) at controlled frequencies (0.20, 1.00 and 2.00 Hz) and temperatures (25-150°C) were conducted under flexure using a Perkin-Elmer Corp. Model DMA 7E dynamic mechanical analyzer. Measurement of the storage modulus was made as a function of temperature at a constant frequency of 1.0 Hz. The heating rate was 2°C/min, which was selected to prevent any artificial damping peaks which may be caused by higher heating rates. The specimens were in the form of beams (24 × 8 × 3 mm) under three-point bending, such that the span was 20 mm. The loads used were all large enough so that the amplitude of the specimen deflection was always over the minimum value of 5 μm required by the equipment for accurate results. The loads were set so that each different type of specimen was always tested at its appropriate stress level. Six specimens of each type were tested.

Cement paste made from Portland cement (Type I) from Lafarge Corp. (Southfield, MI) was used for the cementitious material. The admixtures used include (i) latex, a styrene butadiene polymer (Dow Chemical Co., Midland, MI, 460NA) with the polymer particles making up about 48% of the dispersion and with styrene and butadiene in the weight ratio 66:34, such that the latex (20%, 25% or 30% by weight of cement) was used along with an antifoam (Dow Corning Corp., Midland, MI, #2410, 0.5% by weight of latex), (ii) methylcellulose (Dow Chemical Corp., A15-LV, 0.4% by weight of cement), which was used along with a defoamer (Colloids Inc., Marietta, GA, Colloids 1010, 0.13 vol.%), and (iii) silica fume (Elkem Materials Inc., Pittsburgh, PA, EMS 965, 15% by weight of cement). The water reducing agent was a sodium salt of a condensed naphthalenesulfonic acid (TAMOL SN, Rohm and Haas Company, Philadelphia, PA) used in amounts as shown in Table 1 for the various mixes. Table 1 also shows the water/cement ratio for each mix. The amounts in Table 1 were chosen in order to maintain the slump at around 170 mm. No aggregate (whether fine or coarse) was used.

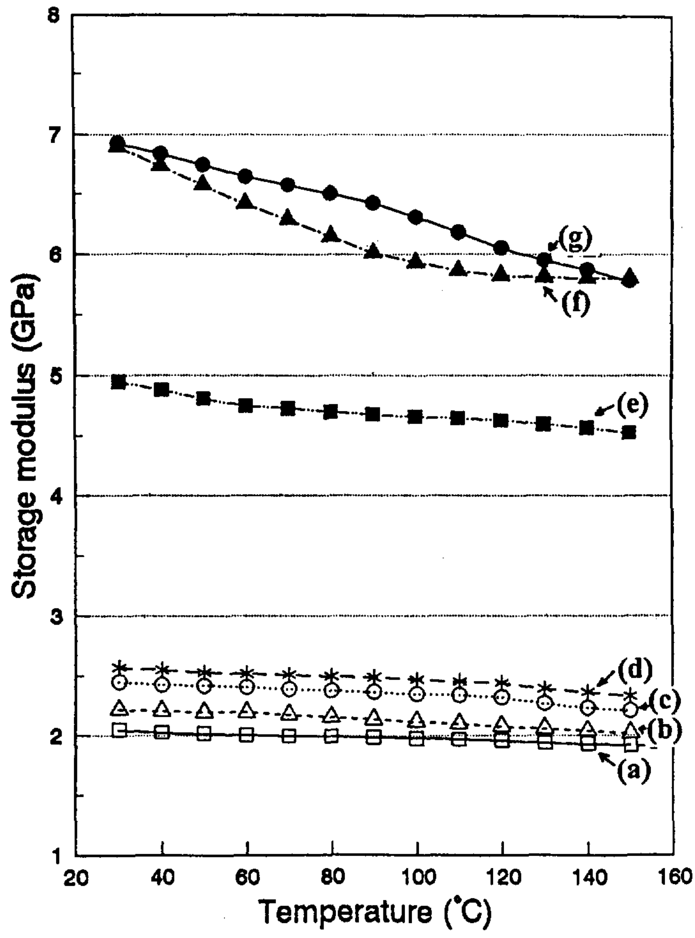

FIG. 1.

Variation of the flexural storage modulus with temperature during heating for (a) plain cement paste, (b) cement paste with latex (20% by weight of cement), (c) cement paste with latex (25% by weight of cement), (d) cement paste with latex (30% by weight of cement), (e) cement paste with methylcellulose, (f) cement paste with methylcellulose and silica fume, and (g) cement paste with silica fume.

A Hobart mixer with a flat beater was used for mixing. For the case of cement pastes containing latex, the latex and antifoam were first 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 pastes 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 and water were mixed in the Hobart mixer for 5 min. After pouring the mix into oiled molds, an external 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 (relative humidity = 30%) for 28 days. Mechanical testing was performed at 28 days.

Results and Discussion

Fig. 1 gives the storage modulus (±0.02 GPa) as a function of temperature for seven cement pastes. The addition of latex, methylcellulose or silica fume increased the storage modulus. The highest storage modulus value was attained by silica fume at all temperatures studied. Methylcellulose was less effective than silica fume, but more effective than latex for enhancing the storage modulus, even though methylcellulose was used in a much smaller quantity than latex. The greater the latex/cement ratio, the higher the modulus. This means that polymer addition is not as effective as silica fume addition for enhancing the modulus, but the type of

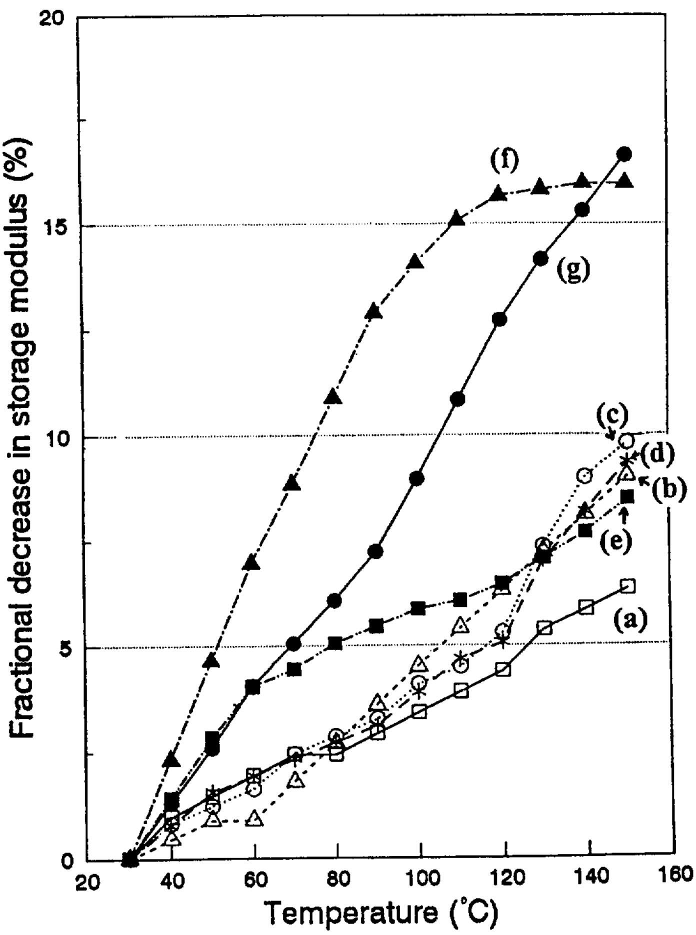

FIG. 2.

Fractional decrease in flexural storage modulus as a function of temperature during heating for (a) plain cement paste, (b) cement paste with latex (2% by weight of cement), (c) cement paste with latex (25% by weight of cement), (d) cement paste with latex (30% by weight of cement), (e) cement paste with methylcellulose, (f) cement paste with methylcellulose and silica fume, and (g) cement paste with silica fume.

polymer is more important than the quantity of polymer in affecting the modulus. The greater effectiveness of methylcellulose than latex is probably related to the liquid form of methylcellulose and the solid particle dispersion form of latex, and the consequent superior dispersion of methylcellulose than latex in the cement paste. The storage modulus decreased with increasing temperature for all seven pastes. Fig. 2 shows the fractional decrease in storage modulus as a function of temperature for the seven pastes. The addition of silica fume or methylcellulose increased this fraction relative to the value for plain cement paste at all temperatures studied. The addition of latex increased this fraction relative to the value for plain cement paste only at 80°C or above. The greatest value of this fraction was attained by the addition of methylcellulose + silica fume. This fraction was higher for silica fume addition than any of the polymer additions.

Although silica fume addition gave a high storage modulus, it also gave a large fractional decrease of the storage modulus upon heating. Although plain cement had a low storage modulus, it had a small fractional decrease of the modulus upon heating.

The effect of heating on the storage modulus (Fig. 1) was reversible, as observed upon cooling at 2°C/min immediately after the heating. However, thermogravimetric analysis (TGA) using Perkin-Elmer TGA7 during heating at 10°C/min and subsequent cooling at 10°C/min showed that all cement pastes exhibited totally irreversible weight loss (presumably due to moisture loss), primarily from 70 to 100°C during heating. Figs. 3 and 4 show the storage modulus and relative weight respectively, during both heating and subsequent cooling, for the case of cement paste with silica fume. After heating to 350°C at a heating rate of 10°C/min, the fractional loss in weight was 9.0%, 7.5% and 2.8% for plain cement paste, cement paste with silica fume and cement paste with latex respectively. Although silica fume cement paste gave a smaller fractional loss in weight than plain cement paste, it gave a larger fractional decrease in modulus than plain cement paste. In spite of the irreversible weight loss (Fig. 4), the decrease in storage modulus upon heating was reversible (Fig. 3). This means that the moisture loss had negligible effect on the modulus. It also means that the decrease in modulus upon heating was not due to moisture loss, but was probably due to the softening of the solid network itself. This

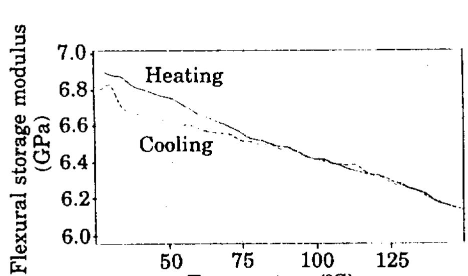

FIG. 3.

Variation of the flexural storage modulus (1 Hz) with temperature during heating (solid curve) and cooling (dashed curve) for cement paste with silica fume. the static stress was 1.84 MPa; the dynamic stress was 0.703 MPa; the flexural strength (ASTM C348-80) was 2.75 MPa.

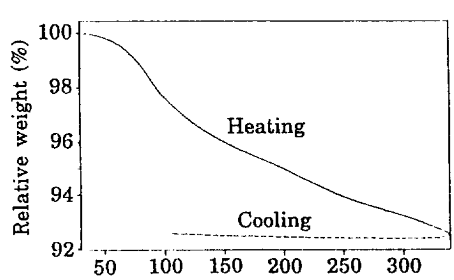

FIG. 4.

Variation of the relative weight with temperature during heating (solid curve) and cooling (dashed curve) for cement paste with silica fume. The initial sample weight was 63.966 mg.

interpretation is consistent with the fact that the modulus decreased gradually with increasing temperature from 30 to 150°C, whereas the weight loss occurred abruptly at 70-100°C. It is also consistent with the observation that the sealing had no significant effect on the modulus at various temperatures from 50 to 240°C [10]. The reversible modulus decrease is in contrast to the irreversible modulus decrease reported by previous workers [5-9]. The apparent discrepancy is partly due to the difference in measurement method. The ASTM D4065-94 method used in this work had not been used in previous work. Furthermore, most previous work addressed the static modulus rather than the dynamic modulus, and most previous work addressed the effect of heating rather than the effects of both heating and cooling.

Conclusion

The flexural storage modulus was found to decrease gradually with increasing temperature from 30 to 150°C for cement pastes, such that the effect was reversible, in contrast to the irreversibility of the weight loss upon heating. Among the admixtures used (latex, methylcellulose and silica fume), silica fume gave the highest flexural storage modulus at all temperatures (30-150°C), but also the greatest fractional decrease in modulus upon heating. Methylcellulose (0.4% by weight of cement) gave higher modulus than latex (20-30% by weight of cement). The modulus increased with increasing latex/cement ratio. Plain cement paste (without any admixture) gave the lowest modulus.

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