JOURNAL OF MATERIALS SCIENCE 22 (1987) 2148–2152

The effect of latex on macrodefect-free cement

C. S. POON, G. W. GROVES
Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford OX1 3HP, UK

The effect of adding latex to macrodefect-free cement was studied. The porosity of the modified pastes was smaller than the normal macrodefect system but the pore size was not significantly changed. The traditional relationship between strength and flaw size in the cement system was found to be inadequate to explain the observed mechanical behaviour of the latex-modified systems. Scanning electron microscopy of the fracture surfaces of the normal and latex-modified pastes revealed that the use of different polymers resulted in different fracture paths through the cement composite. This was due to the difference in chemical nature of the polymer. The results demonstrated that the modulus (E) and fracture energy (R) terms in the traditional Griffith equation become limiting factors for strength determination in low-porosity cement systems.

1. Introduction

In the recent development of high-strength cement paste emphasis has been mainly placed on the reduction of porosity and pore size to achieve high strength. Birchall and co-workers [1, 2] demonstrated that additions of water-soluble polymers reduce the yield pressure and friction and allow cement grains to come into the most close-packed position when mixed. This mixture behaves as a plastic body and can be worked by rolling, extrusion and dough mixing. This procedure is assumed to be useful in the removal of large pores which could act as flaws under stress. The flexure strength of the resulting material is increased from 15 to 50 MPa in the case of Portland cement. Further increase in strength can be achieved in the case of aluminous cement by the removal of the remaining submicrometre pores by heat treatment and hot pressing. The resulted flexure strength is of the order of 100 to 150 MPa.

The above consideration of strength is based on Griffith's criterion of brittle failure

$$\sigma = \left(\frac{ER}{\pi c}\right)^{1/2} \qquad (1)$$

where σ = flexural strength, E = Young's modulus, R = fracture energy and c = flaw size, modulated by the effect of porosity on E on R [2] to give

$$E = E_0(1-p)^3 \qquad (2)$$

$$R = R_0\,\mathrm{e}^{-kp} \qquad (3)$$

where E_0 = Young's modulus at zero porosity, p = porosity, and R_0 = fracture energy at zero porosity. The resulting criterion for failure is

$$\sigma = \left[\frac{E_0R_0(1-p)^3\,\mathrm{e}^{-kp}}{\pi c}\right]^{1/2} \qquad (4)$$

Equation 4 demonstrates that the strength of the cement system is a function of porosity p and flaw size c. Various methods have been devised to strengthen the cementitious system by reducing the pore volume and pore size simultaneously. The new type of cement system is sometimes called macrodefect-free cement.

A similar theory on the importance of flaw size in governing strength was proposed by Alford [3] and Alford *et al.* [4]. They supported the view of Kendall *et al.* [2] that the traditional relationship between strength and total porosity, i.e.

$$\sigma = \sigma_0\,\mathrm{e}^{(-bp)} \qquad (5)$$

where σ_0 = strength at zero porosity and b = constant, is largely fortuitous and the reason for the correlation is that the methods used to reduce total porosity also decrease the critical flaw size. They also suggested that the polymer used in preparing the cement paste acts only as a rheological aid whilst by twin-roll mixing, pressing and heat treatment the porosity and pore size are reduced to their minimal values, resulting in high strength. These authors assumed that the polymers used do not contribute significantly to the strength. Sinclair and Groves [5] and Rodger *et al.* [6], however, have found that there are significant chemical interactions between polymer and cement in the macrodefect-free systems.

In the studies of the effect of pore size on the flexural strength of the macrodefect-free pastes Kendall *et al.* [2] and Alford [3] found that strength follows the Griffith criterion with relation to pore size up to a pore size of 100 μm. The strength did not rise further when the pore size was reduced far below 100 μm. It was suggested that flaws other than pores were becoming important, e.g. the large angular cement grains and cement–polymer interfaces would play the more dominant part in determining strength.

This paper presents microstructural evidence to demonstrate that not only porosity but chemical interaction between polymer and cement is also significant in affecting the strength of macrodefect-free cement.

0022–2461/87 $03.00 + .12

TABLE I Formulation and properties of macrodefect-free cement

Mix	Cement type*	Weight (g)	Polymer† (g)	Latex (g)	Water (g)	σ (MPa)	Density $(\mathrm{g\,cm^{-3}})$	Porosity (%)
1	OPC	100	4	–	16	46.5	2.12	25.7
2	OPC	100	2	15.0‡	10	32.18	2.45	12.0
3	OPC	100	4	11.75‡	14	24.42	2.00	15.0
4	OPC	100	4	15.0‡	10	24.15	1.99	14.1
5	HAC	100	7	–	12	98.56	2.45	4.0
6	HAC	100	7	10.0‡	12	44.0	2.17	3.8
7	HAC	100	7	10.0§	10	66.0	2.22	3.5

*OPC = ordinary Portland cement, HAC = high aluminous cement.

†Polyacrylamide for OPC systems and polyvinyl alcohol (PVA) for HAC systems.

‡Styrene–butadiene.

§Styrene–acrylic.

2. Experimental procedure

Macrodefect-free cements were prepared following the method described by Birchall [1] and the detailed formulation is the same as that of Sinclair and Groves [5]. Small amounts of styrene–butadiene latex (supplied by Doverstrand, Essex, UK) and styrene–acrylic latex (supplied by Vinamul, Surrey, UK) were added to selected mixes before forming the paste. The formulation is presented in Table I. The flexural strength was determined by three-point bending while the total porosity and pore size distribution were determined by methanol replacement and visual examination of back-scattered electron micrographs of polished surfaces, respectively. Fracture surfaces were examined by scanning electron microscopy (SEM) while the ion-beam thinned specimens were studied by high voltage transmission electron microscopy (HVEM).

3. Results and discussion

The results of flexural strength, density and porosity measurement are presented in Table I. It can be seen that introducing latex in the system reduced the flexural strength for both the high aluminous cement (HAC) and ordinary Portland cement (OPC) systems despite lowering the total porosity. The fact that the HAC system has a higher strength value than the OPC matrix is mainly due to the lower total porosity. The back-scattered image of the polished surfaces (Figs 1 to 4) show that in both HAC and OPC systems, the large crack-like pores have been removed. The latex systems, however, have a larger amount of continuous polymer matrix compared to the normal macrodefect-free systems. The relatively smaller and finer scale porosity found in the HAC system has been discussed by Sinclair and Groves [5]. It was thought to be due to the relatively small quantity of hydration products produced from the CA (C = CaO, A = Al_2O_3) and CA_2 grains. The OPC system, however, contains a substantial quantity of normal hydration product as revealed by HVEM studies [5].

Figs 5 and 6 show the SEM examination of the fracture surfaces of HAC–PVA and HAC–PVA–latex systems respectively. The PVA polymer in Fig. 5 formed a continuous matrix in the cement composite and fracture took place mainly through this polymer matrix. Rodger *et al.* [6] and Sinclair and Groves [5] have shown that there is chemical interaction between the polymer and cement grain and the polymer gel is rich in calcium and aluminium with a C/A ratio of approximately 1.64. The proposed mechanism of interaction is through the cross-linking of polymer by $Al(OH)_4^-$ and bonding of polymer gel to the cement grain via an aluminate-rich surface.

Fig. 6 shows that part of the fracture path in the

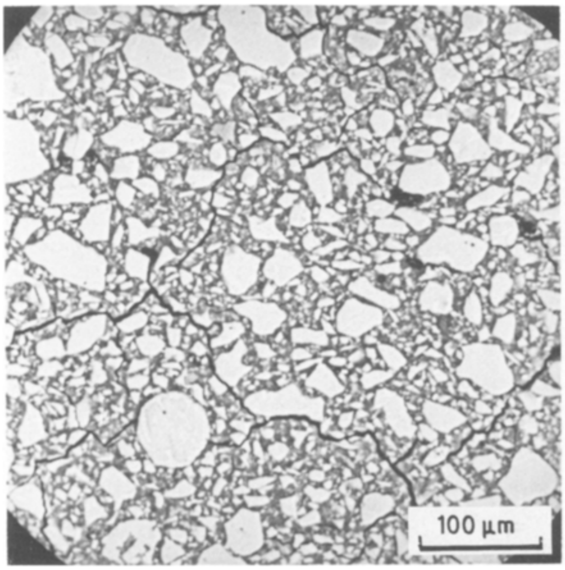

Figure 1 Back-scattered micrograph of polished OPC macrodefect-free cement.

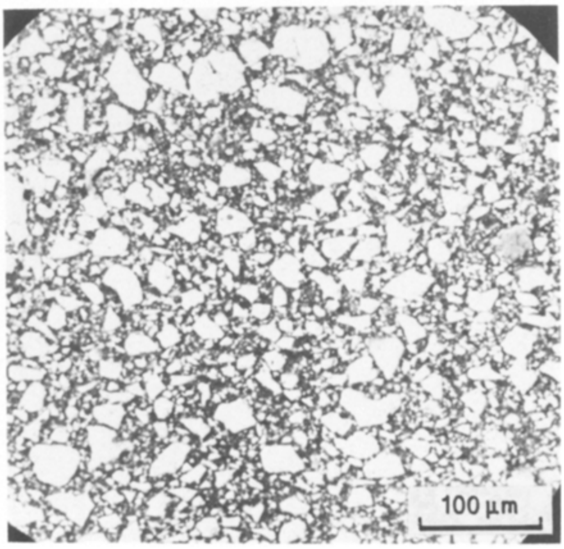

Figure 2 Back-scattered micrograph of polished OPC latex macrodefect-free cement.

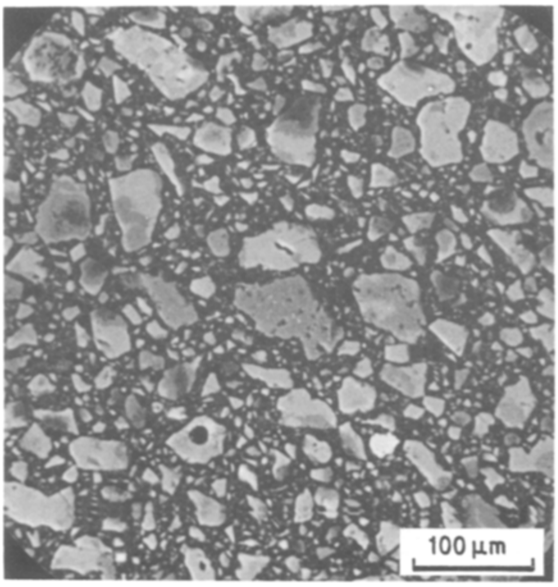

Figure 3 Back-scattered micrograph of polished HAC macrodefect-free cement

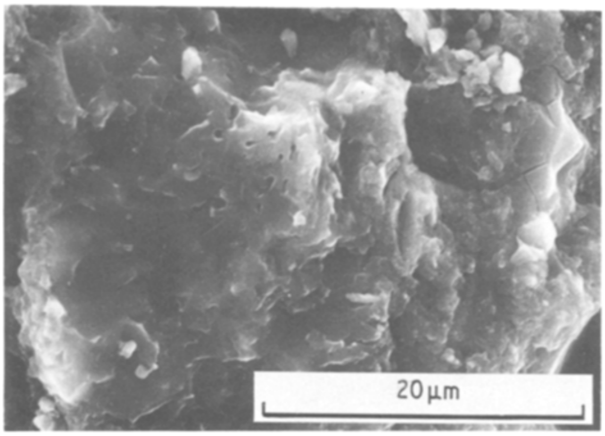

Figure 5 Fracture surface of HAC macrodefect-free cement showing fracture through polymer matrix.

HAC–PVA–latex system was through the grain–polymer/latex interface. This can be shown clearly by the appearance of individual cement grains on the fracture surface. Furthermore, the micrograph also shows that the PVA–latex polymer matrix has shrunk, probably due to dehydration, leaving a gap between the polymer gel and grain surface. This indicates that the bonding between part of the polymer matrix with the grain is poor. This resulted in lower strength of the latex-modified macrodefect-free system.

In the case of the OPC macrodefect-free cement system (Fig. 7) fracture went through some of the polymer–cement interface indicating a weakness zone located just beyond the cement grain. This may be due to poor bonding between the polymer and the OPC grain or the small-scale hydration products. Microcrystalline $Ca(OH)_2$ crystals have been detected near the grain surface by HVEM coupled with electron diffraction analysis [7]. This should act as a zone of weakness in this macrodefect-free system.

Adding latex to the system made the fracture path run through the polymer matrix (Fig. 8). This indicates that the polymer–latex gel is weak compared to the cement–polymer gel and cement–latex interfaces. This is in contrast to that of the HAC–PVA–latex system, probably due to the different chemical interactions of the latex with HAC and OPC.

In a study of the cryogenic properties of the macrodefect-free system, Smith [8] found that the strength and modulus of the latex-modified OPC system increased with decrease in temperature. Over a range of 400 K, the strength increased from approximately 25 MPa to over 100 MPa with a similar increase in the modulus (Fig. 9). The temperature at which a drastic improvement took place corresponded to the glass transition temperature of the latex polymer. This was attributed to the increase in strength of the Van der Waals forces during glass transition, and the consequent reduction in separation of adjacent molecular chains of the latex. This result supports the finding of the present study that the critical path of fracture in the latex-modified macrodefect-free system is through the latex polymer, and that improvement in

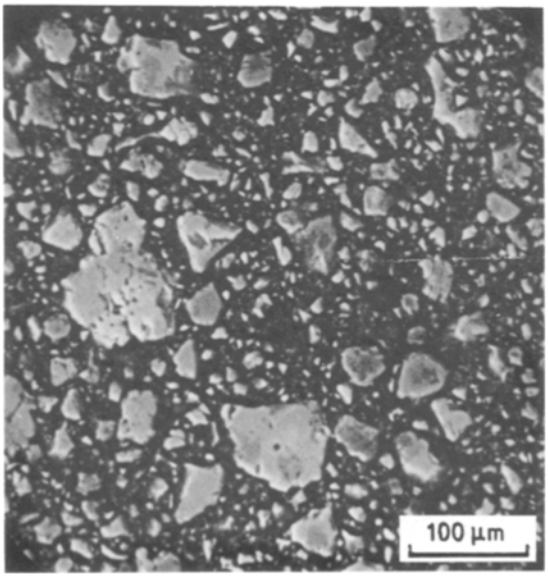

Figure 4 Back-scattered micrograph of polished HAC–latex macrodefect-free cement.

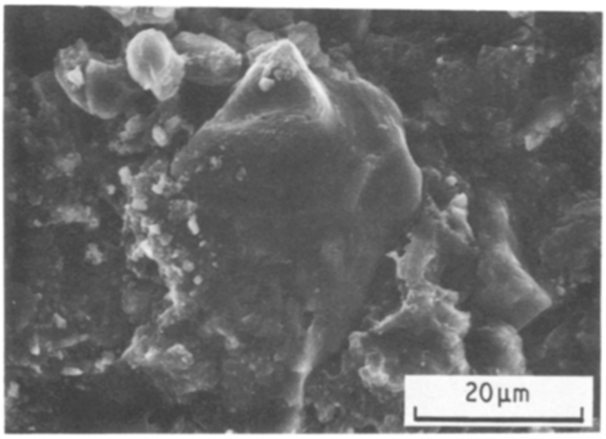

Figure 6 Fracture surface of HAC–latex macrodefect-free cement showing fracture through grain–polymer interface.

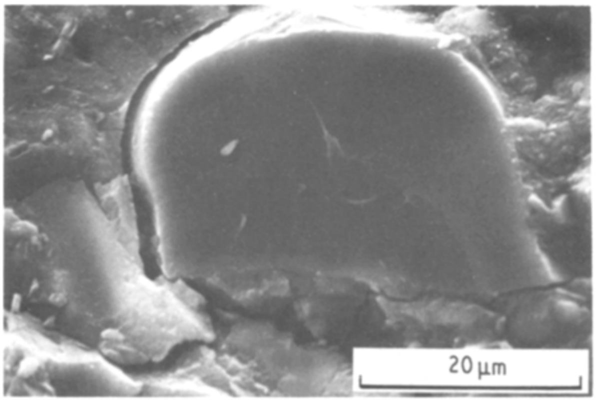

Figure 7 Fracture surface of OPC macrodefect-free cement showing fracture through grain–polymer interface.

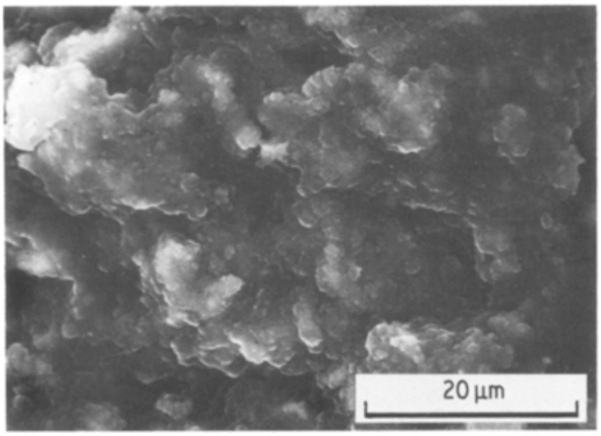

Figure 8 Fracture surface of OPC–latex macrodefect-free cement showing fracture through polymer matrix.

bonding of the latex at low temperature improves the strength of the composite.

The significance of chemical interaction can be demonstrated by using two different kinds of latex in the HAC system. Mix 7 (Table I) prepared from a styrene–acrylic latex is much stronger than Mix 6 with a styrene–butadiene latex. This may be due to the difference in chemical nature of the latexes. The styrene–butadiene latex is a polymer with few functional groups which would react in an inorganic environment. The double-bonded ethylene group is unlikely to be hydrolysed in an alkaline cementitious environment [9]. The possible effect that this latex has is therefore coalescence between cement particles as illustrated by the HVEM micrograph (Fig. 10). The figure shows that the latex acts as a thread and bridges two cement grains. The styrene–acrylic latex, however, has C=O groups in its chain which are able to react in the cementitious system and thus produce a stronger product. The non-reactive part of the chain (i.e. the styrene group) may contribute to the increased toughness of the material.

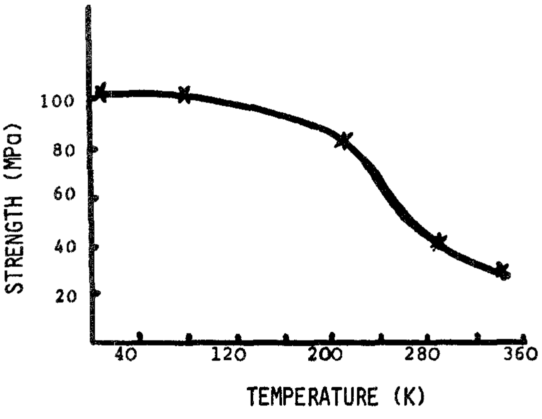

Figure 9 Strength against temperature of latex OPC paste (after Smith [8]).

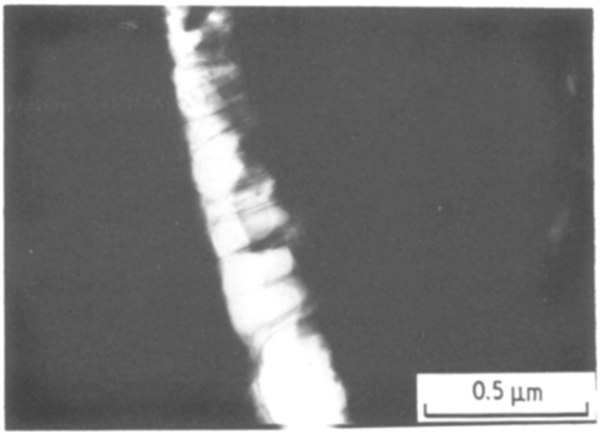

Figure 10 HVEM micrograph of latex-modified macrodefect-free cement showing threads of latex bridging two grains.

A schematic drawing of the load–deflection curve of the latex-modified macrodefect-free systems is shown in Fig. 11. The fracture energy presented in Table II is calculated from the shaded area where the load–deflection plot starts to deviate from linearity. The fact that the latex-modified pastes have a much higher fracture energy may be due to viscoelastic deformation of the latex during fracture.

4. Conclusion

The above discussion has shown that the importance of porosity and pore size in governing strength is valid to a certain extent. The fact that the latex-modified macrodefect-free system, with a lower porosity and similar if not smaller pore size, has lower strength than the normal macrodefect-free pastes showed that the terms E_0 and R_0 in Equation 4 have become the limiting factors in determining strength. These factors depend on the inherent properties of the polymer and cement and on the chemical interaction between polymer and the cementitious material. Therefore further improvement in mechanical properties of macrodefect-free cement should concentrate on

TABLE II Fracture energies of macrodefect-free cement

Mix	Fracture energy ($\mathrm{J\,m^{-2}}$)
1	–
2	264
3	161
4	535
5	–
6	532
7	1418

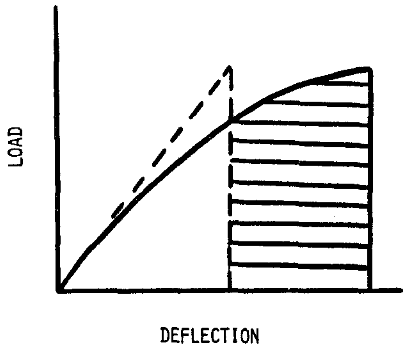

Figure 11 Schematic drawing of load–deflection curve of latex-modified pastes.

altering the composition of the matrix and achieving a fuller understanding of the chemistry of polymer–cement interaction.

Acknowledgement

The authors wish to acknowledge the financial support of the British Technology Group.

References

1. J. D. BIRCHALL, *Phil. Trans. R. Soc.* **A310** (1983) 31.
2. K. KENDALL, A. J. HOWARD and J. D. BIRCHALL, *ibid.* **A310** (1983) 139.
3. N. McN. ALFORD, *Cem. Concr. Res.* **11** (1981) 605.
4. N. McN. ALFORD, G. W. GROVES and D. D. DOUBLE, *ibid.* **12** (1982) 349.
5. W. SINCLAIR and G. W. GROVES, *J. Mater. Sci.* **20** (1985) 2846.
6. S. A. RODGER, W. SINCLAIR, G. W. GROVES, S. A. BROOK and D. D. DOUBLE, *ibid.* **20** (1985) 2853.
7. G. W. GROVES, *Cem. Concr. Res.* **11** (1981) 713.
8. A. J. SMITH, BA Part II thesis, Oxford University (1984).
9. I. L. FINAR, “Organic Chemistry”, 6th Edn, Vol. 1 (Longman, London, 1973) 108.

Received 29 July
and accepted 22 September 1986