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The mechanical properties and tensile failure mechanism of a high strength polymer modified Portland cement

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The mechanical properties of one of the new high strength polymer modified hydraulic cements have been investigated. An important parameter for the material is the amount of polymer present, and the properties are found to be dependent upon the degree of drying. For example, in the wet state, polymer content has little effect upon ultimate flexural strength, but does cause nonlinearity in the stress–strain behaviour. Although increasing polymer content causes a reduction in the initial tangent modulus, it is shown that retardation of hydration may account for this. In the dry state, increasing polymer content leads to increasing flexural strength, fracture toughness and failure strain, but leaves initial elastic modulus relatively unchanged. It is concluded that removal of pores is not the principal strengthening mechanism since strength increases are consequent upon water removal from the microstructure in the presence of the polymer. A fibrillar pull-out model is proposed to explain the observed behaviour of both "wet" and "dry" material and ordinary Portland cement paste, which shows good correlation with experimental results. The principal effect of the polymer is to act as an adhesive at the interface between interacting CSH fibrils.

1. Introduction

This paper reports studies of the mechanical properties of one of the new polymer modified cements [1]. It has been suggested that pore size is the overriding factor in determining the tensile and flexural strength of such hydraulic cements [1] and this appears to conflict [2] with earlier work on the fracture mechanics of hardened cement paste (HCP).

From an investigation of de-aired HCP, it was concluded that the removal of air voids in the range 0.1 to 1 mm does not account for the large improvements in strength gained by the polymer modified cement [3]. Preliminary experiments indicated that the strength improvement occurs late in the fabrication process, when the cement is dried, suggesting that the water-soluble polymer is playing an important role in strength development as well as being a rheological aid.

This study was undertaken to examine the effects of the polymer addition on mechanical properties before and after the critical drying stage. A mechanism of failure for both HCP and polymer modified cement is proposed.

2. Experimental methods

The mix proportioning of conventional cement paste (i.e. cement and water) is normally described in terms of the water/cement ratio by weight. This is satisfactory for a two-phase system, and small quantities of admixtures, usually below 1% of the cement weight, do not grossly affect the overall mix proportions. When the additive quantity becomes more significant, and especially with a low water/cement ratio, it is necessary to consider the mixture as a three-phase system. Furthermore, when considering, for instance, the packing efficiency of the cement grains, space for hydrate growth or resultant properties such as porosity, it is more meaningful to work in terms of the volume fraction of the cement, rather than weight ratios.

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For this study, therefore, the mixes were designed using volume fractions, taking into consideration the contribution of all three mix constituents: cement, water and polymer.

The effects of the volume fraction of polymer and of curing and drying times were examined, and finally three mixes were examined for fracture mechanics parameters.

The polymer, a hydroxypropyl methyl cellulose, Celacol HPM 15000 DS, was supplied in powder form and had an as-packed moisture content of 9.5%. This amount of water is small in relation to the total mix water, and is disregarded in the mix proportioning. When added to water, the polymer particles swell and disperse, eventually forming a homogeneous gel, the volume of which is approximately that of the sum of the volumes of "dry" polymer powder and water. In the wet state, therefore, the "volume" fraction of polymer is meaningless, in that it does not signify a separate phase with definable boundaries. It is useful, however, in calculating the actual packing density of the cement grains.

Films of the polymer dried at ambient humidity have a specific gravity of 1.4 and equilibrium moisture content of 6.5% [4]. It was assumed, as a first approximation, that, unless the polymer reacted chemically with the cement, it would revert to this condition when the final hydrated polymer cement was dried at ambient humidity. A density of $1.4 \times 10^3 \text{ kg m}^{-3}$ was therefore used when calculating "volume fraction of polymer".

The total volume of each mix was then calculated assuming that all air would be excluded during processing, that volume changes during curing and drying would be small and that the volume of the mixture is approximately equal to the sum of the volumes of polymer, cement and water.

The cement is an ordinary Portland cement, specific gravity 3.17 and specific surface 366 $\text{m}^2 \text{ kg}^{-1}$, the same cement as used in the previous study of de-aired pastes [3]. No attempt was made to alter the particle size distribution of the cement.

Production of sheets of the polymer modified cement followed the method of Birchall *et al.* [5], whereby the cement and polymer gel (i.e. polymer and water) were mixed in a planetary mixer to form a crumb, which was then fed onto a callendering mill. The two steel rollers of this mill had a diameter of 150 mm and working width of 250 mm, the back and front rollers working at speeds of 25 and 32 rpm respectively. Initial nip clearance was set at 1.3 mm, and rolling was continued until the mixture had a uniform colour. The resultant sheet was then folded and re-rolled repeatedly through a 6 mm nip to produce a thicker sheet.

After trimming to 200 mm × 200 mm, each sheet was pressed between "melinex" sheets at a pressure just sufficient to begin squeezing the sheet out sideways (see Section 3, Fig. 1). Movement of the plattens was then stopped and the sheet allowed to cure under pressure for 23 to 24 h at room temperature, with the edges sealed with plastic tape to prevent moisture loss. Relaxation of the sheet led to a reduction of the load of between 10 and 20% during the first few minutes after stopping the plattens. Following removal from the press, each sheet was immersed in water, which had previously been used for curing the same cement, to complete curing for the desired period of time. This period was taken as the total time, starting at the time of mixing, during which the plate was kept deliberately wet to encourage hydration of the cement.

On completion of the curing period the plate was cut into strips, 11 to 12 mm wide × 200 mm long, on a water-cooled diamond saw. Half the strips were lightly wiped with a damp tissue and left to dry on wire racks. Unless otherwise stated, this was standardized at 7 days in the laboratory atmosphere [5, 6]. The remainder were tested immediately, under water to maintain saturation, over a span of 180 mm in three-point flexure with the plate thickness as the beam depth. The test rig was that used in the previous investigation [3].

Flexural strength was calculated from the load at failure and simple beam theory. Modulus of elasticity was similarly calculated from the slope of the load–deflection plot. The high span/depth ratio (30:1) ensured that a valid measurement of Young's modulus was made, since it had been found that lower span/depth ratios led to erroneously low values of modulus [3].

Fracture toughness tests were carried out using a simple notched bar test, as described before [3]. A range of notch/depth ratios was used, with a span of 50 mm, and beams 11 mm wide × 6 mm deep, to obtain comparative values for K_{1c}, and the work of fracture was computed

TABLE I Mix proportions

Mix number	Volume fraction (%)		Water/cement ratio	Celacol (% of dry cement weight)
	Celacol	Water		
66.7% OPC				
1	1	32.3	0.153	0.66
2	2	31.3	0.148	1.33
3	3	30.3	0.143	1.99
4	4	29.3	0.139	2.65
5	5	28.3	0.134	3.31
6	6	27.3	0.129	3.97
64% OPC				
7	2	34	0.168	1.39
8	4	32	0.158	2.76
9	6	30	0.148	4.14

from slow-bend stable fractures at a high notch/depth ratio of 0.65.

The moisture contents of some of the test materials after curing, and also following the drying period, were obtained by heating the samples to 105° C and drying until constant weight had been achieved.

From preliminary trials at moderate polymer contents, a maximum volume fraction of about 67% dry cement was found to be easily mixable on the type of rolls available. The polymer content was varied from 1 to 6% by volume and Table I gives the mix proportions used, with equivalent weight ratios also calculated for comparative purposes. Also included in Table I are the mix proportions for the lower cement content used for the more detailed investigation of ageing effects and fracture toughness.

3. Results*

3.1. Effect of polymer content

A series of mixes, numbers 1 to 6 were used to examine the effects of varying the polymer content. The early rheology was examined very briefly, and flexural tests carried out on saturated specimens after short curing periods of 28 h and 3 days, and then in a "dry" state after subsequent drying in the laboratory atmosphere for 7 days.

The minimum load required to deform "as prepared" 200 mm x 200 mm x 6 mm thick plates (66.7% v.f. OPC) was found to follow the relationship shown in Fig. 1. The curve suggests that there is a minimum amount of polymer required to lubricate the cement grains fully, occurring in this case at about 2% v.f. (1.33% by weight of cement). With less polymer, the dough, while still formable on the rolls, is stiffer.

As the polymer content is increased, and hence the water content decreased, the gel becomes considerably more viscous, changing from an almost pourable fluid at the 1% v.f. level (1:32.3 Celacol/water ratio by weight) to a soft gel at the 6% v.f. level (1:4.55 weight ratio). This has the effect of decreasing the deformability of the dough considerably, as seen in Fig. 1. It was not possible to incorporate more than the 6% v.f. of polymer at this high cement packing density, as a further increase led to overheating and crumbling on the rolls.

Fig. 2 shows the dry strengths of the series of mixes at 66.7% OPC compared with published results by Alford *et al.* [6] and Birchall *et al.* [5], recalculated in terms of volume fractions, in both cases apparently using an unclassified Portland cement and the same polymer as this study.

There is little difference between the strength results of this study and those of Alford *et al.* [6] over a limited range of cement contents and curing times. It is not clear why those of Birchall *et al.* [5] fall considerably below this curve.

The most interesting aspects of these results are that the dry strength increases with polymer content and that the degree of cure i.e. 28 h or 3 days, is of no apparent consequence. The wet flexural strengths of the same materials, i.e. before drying (Fig. 2), did not show any increase with polymer content over this time scale. The major effect of the polymer addition on the wet properties is to induce a considerable degree of nonlinearity, dependent upon polymer content,

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*Mechanical properties were measured on at least six specimens per set. Coefficients of variation were generally less than 8%; error bars in the figures represent the standard deviation.

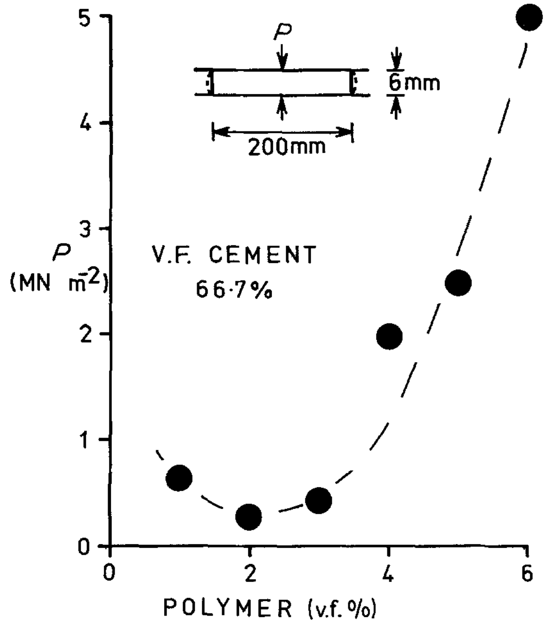

Figure 1 The pressure required to deform a 200 mm × 200 mm × 6 mm thick sheet of polymer-modified cement dough immediately after rolling.

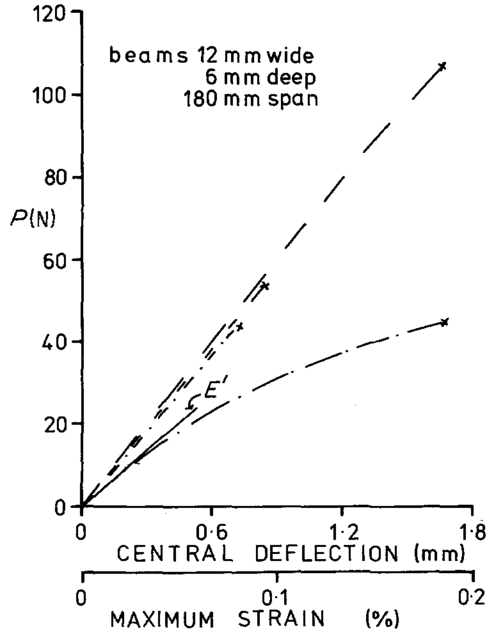

Figure 3 Load–deflection curves for a high and a low polymer content cement. The solid line marked E' is the initial tangent modulus for the wet 6% polymer content. —·— 6% polymer, wet; —·—·— 6% polymer, dry; —·—·—·— 1% polymer wet; – – – – 1% polymer, dry.

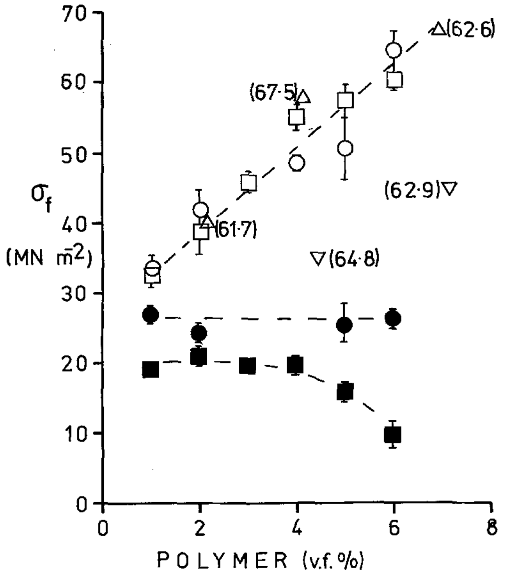

Figure 2 The effect of polymer content on the wet and dry flexural strength of a polymer modified Portland cement. Figures in brackets are percentage volume fraction of cement (this study, 66.7%). ■ wet, 28 h cure at 20° C, this study; □ dry, 28 h cure at 20° C, this study; ● wet, 3 dry cure at 20° C, this study; ○ dry, 3 day cure at 20° C, this study; △ dry, 7 dry cure at 30° C [6]; dry, 7 dry cure at 20° C [5].

into the load–deflection behaviour, as seen in Fig. 3. It should be noted that the increase on drying cannot be accounted for in terms of a porosity reduction since there was no significant change in the external volume of the specimen on drying.

The analysis of beam flexure of nonlinear materials is complex, the stresses no longer being directly proportional to the load on the beam, although strain is still proportional to radius of curvature and hence deflection. However, changes in the curvature of the load–deflection curve would be expected to reflect changes in the stress–strain behaviour. It can be seen from Fig. 3 that the high polymer content wet material does not have a clear yield point or initial elastic region, but curvature begins at very low strains indicating that the stress–strain relationship is curved, rather than being linear up to a yield point, as in the case of ideal plasticity.

In general, a concave-down stress–strain curve will result in an overestimation of the final rupture stress when calculated simply from the failure load of a flexural test, the overestimation being greater with a more sharply curved σ–ϵ

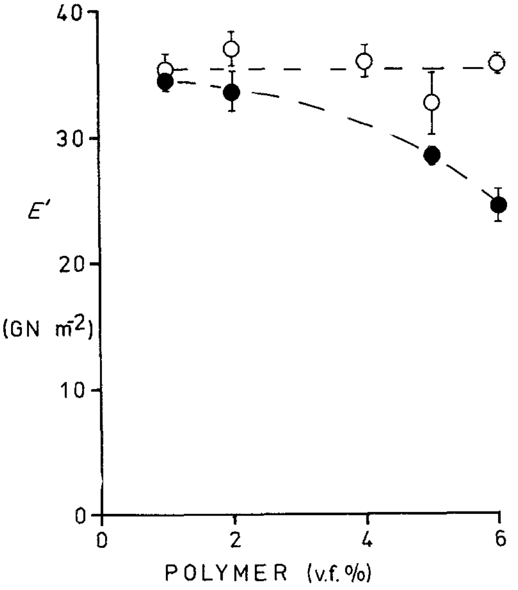

Figure 4 The effect of polymer content on the wet and dry initial tangent modulus. Volume fraction of cement, 66.7%. 3 day cure; ● wet; ○ dry.

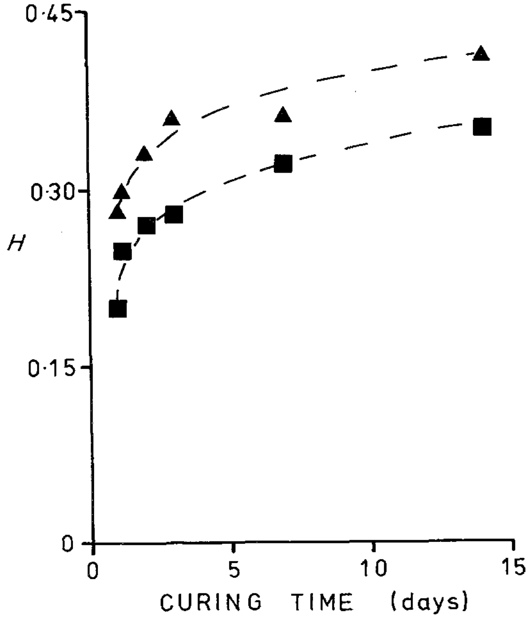

Figure 5 The degree of hydration of a 2% and a 6% polymer content mix (64% v.f. cement) cured under water at 20° C. ▲ 2% polymer; ■ 6% polymer.

relationship. This indicates that the true rupture stress plotted in Fig. 2 should actually reduce with polymer content for the 3 day cure.

The initial tangent modulus, Fig. 4, is also affected by moisture state and polymer content through not in an identical manner to the flexural strength. In the dry state, polymer content has virtually no effect upon initial tangent modulus. Where the load–deflection behaviour is nonlinear, the modulus quoted is the slope of a tangent to the curve at the origin (see Fig. 3).

It can also be seen from Fig. 3 that the polymer addition has a considerable effect upon the strain to failure. At 6% polymer content the strain to failure is approximately 0.19%. This compares to normal, polymer-free cement pastes which fail at about 0.06% strain [3].

3.2. Effect of curing and drying time

The two mixes numbers 7 and 9 (64% cement 2% and 6% Celacol respectively) were examined in more detail for the effects of curing time on wet and dry modulus and strength and also for degree of hydration and moisture content. The effect of drying time was also examined to confirm the validity of the 7 day standard drying period.

During underwater curing the plates absorbed up to about 4% of their total weight in water. Although the effect on bulk density was negligible, this represented a substantial amount in relation to the original mixing water, and had to be taken into account when calculating the degree of hydration.

The bulk density calculated from the mix proportions (Table I, mixes 7 and 9) was 2.39×10^3 kg m^{-3} for 2% v.f. polymer and 2.41×10^3 kg m^{-3} for 6% v.f. polymer. After 24 h curing (i.e. before water submersion) the measured density of the former mix was 2.39×10^3 kg m^{-3} and that of the latter 2.42×10^3 kg m^{-3}, indicating that air had successfully been excluded during the processing.

The total water content after curing was calculated from the original mix proportions and the gain in weight during curing. The moisture content, i.e. weight lost at 105° C, gave a measure of the uncombined water, the remainder being taken as water chemically bound during the process of hydration. Assuming that, on average, 1 g of cement reacts with 0.23 g of water [7], the fractions of combined water could be converted to "degree of hydration". This is shown in Fig. 5. The curves are similar in form to those observed in normal cement preparations [8] and the rapid fall-off in the rate of hydration after the first day appears to be due to the lack of water or space for continued hydration.

Porosity levels can be calculated from the saturated moisture content. In the case of the 2% polymer content this was 9.6% (by weight) after 24h curing, rising to 10.6% after 14 days curing. For the 6% polymer content these figures were 9.3 and 10.1% respectively. In normal cement pastes, the volumetric equivalents of these would be taken as at least a reasonable [7] if not absolute [9] measure of porosity. They are 20.8% rising to 23.0% for the 2% polymer content and 20.6% rising to 22.2% for the 6% polymer cement. It is uncertain whether or not the "volume" of the polymer, in the wet state, should be added to this to obtain the total porosity (i.e. total volume of non-solid).

Upon drying for 7 days in the laboratory atmosphere, the specimens lost varying amounts of water, depending upon curing time. This varied from about 3.3% of the total weight for the 24h cure to 2.2% for the 14 day cure. The specimens cured for longer period thus had a somewhat higher moisture content when tested "dry".

The degree of hydration after drying was calculated as above, correcting for the loss of weight during drying and the resultant moisture content. It was assumed that carbonation during this stage would be negligible, due to the relatively high density and low degree of hydration. Fig. 6 compares the degree of hydration before and after drying. It can be seen that there is very little hydration during the drying period, and the separation of the process into a "curing period", where water saturation is maintained, and a "drying period", where water is removed, is reasonable.

The shapes of the load–deflection curves remained similar to those in Fig. 3 (save that 2%, rather than 1%, polymer was used in this instance for the lower polymer content), but there was a marked reduction in degree of curvature in the wet specimens, especially at the higher polymer content, as the curing time was increased. For example, total strain to failure varied form 0.1% at 24h to 0.08% at 14 days at the low polymer content, and from 0.23% at 24h to 0.16% at 14 days for the higher polymer content. This reduction in total strain to failure was not reflected in the development of the initial tangent modulus, which is shown in Fig. 7.

The development of wet flexural "strength", insofar as it can be estimated from the nonlinear load–deflection curves, is also shown in Fig. 7, and follows broadly the same trend as modulus.

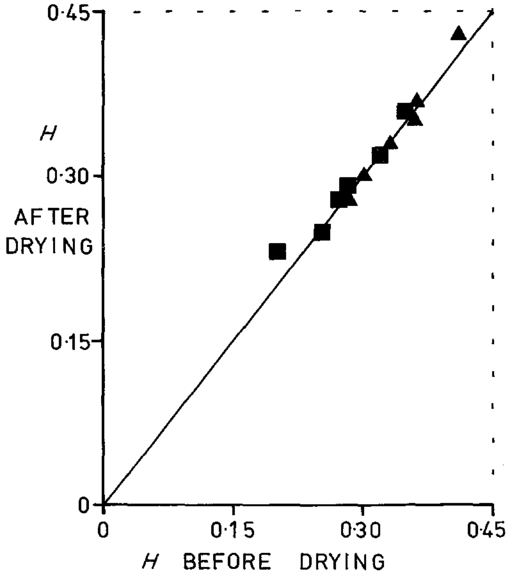

Figure 6 The effect of the 7 day drying period on the degree of hydration. ▲ 2% polymer, ■ 6% polymer.

In Fig. 8 the dry modulus and strength, respectively, have been plotted against curing time for the same series of mixed as Fig. 7. The wet curing time does not appear to affect the dry properties after about 28h curing, as indicated in Section 3.1.

It can be seen from the foregoing that, with regard to wet properties, these materials have not reached equilibrium within the time span studied here; they cannot be described as "mature". However, Fig. 7 indicates that the gains in wet strength

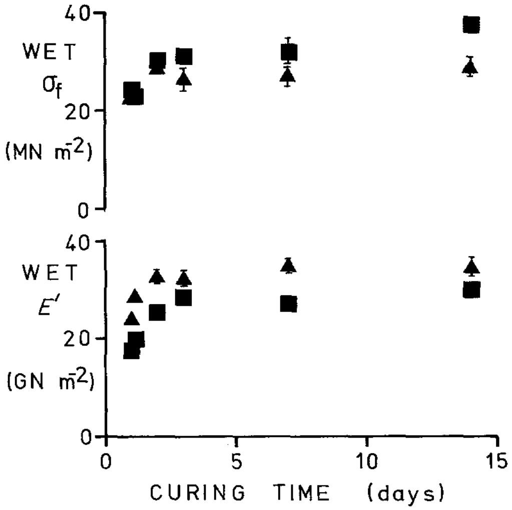

Figure 7 The development of wet flexural strength and initial tangent modulus during underwater curing at 20° C. ▲ 2% polymer, ■ 6% polymer.

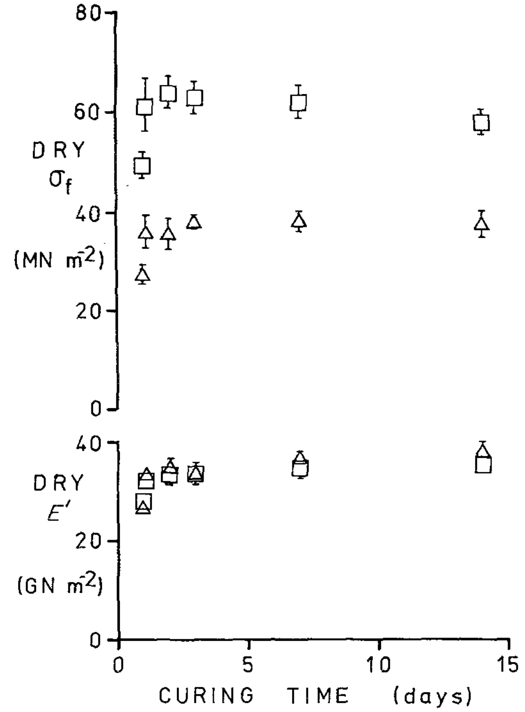

Figure 8 The effect of wet curing time upon the flexural strength and modulus, of polymer modified cements dried for 7 days at ambient humidity immediately after curing. △ 2% polymer; □ 6% polymer.

and stiffness have slowed down considerably by 3 days' curing time. For practical purposes any further work not directly involving examination of this parameter was carried out at a curing period of 3 to 5 days.

Flexural tests were also carried out on specimens dried for various times less than the standard 7 days, and the results confirmed the observation of Alford *et al.* [6] that the strength and modulus essentially stop increasing within 7 days. The load–deflection behaviour had become linear within the first day of drying. Moisture lost during this period is shown in Fig. 9.

3.3. Fracture mechanics tests

The three mixes 7, 8 and 9 (64% cement, 2, 4 and 6% Celacol respectively) were examined for fracture toughness, using both K_{1c} measurements at notch/depth ratios between 0.2 and 0.5 and slow-bend work of fracture (γ_F) tests at a notch/depth ratio of 0.65. The size effects associated with these measurements on cement pastes, particularly K_{1c}, have been described elsewhere [2, 10] and the values for small beams quoted here were taken as comparative rather than absolute.

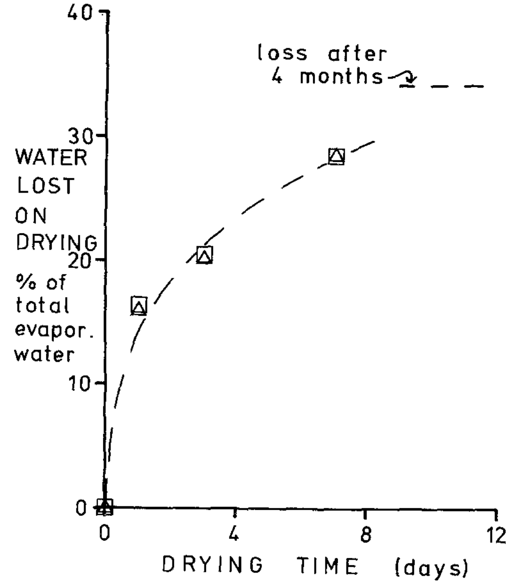

Figure 9 Loss of "evaporable" water on drying at ambient humidity. Curing time 5 days, v.f. cement 64%. △ 2% polymer; □ 6% polymer.

Wet tests were carried out at 3 to 4 days after fabrication, and dry tests were carried out on specimens which had been allowed to dry for 3 days after this, notched (using a water-cooled diamond saw), and allowed to re-dry for a further 6 days. The amount of water absorbed by the dry specimens during notching was small and was lost rapidly, and it was considered that this would not disrupt the normal curing and drying process.

Both K_{1c} and γ_F, Fig. 10, were found to increase with increasing polymer content in both wet and dry specimens. Furthermore, the values of γ_F, wet and dry, do not show any simple relationship to one another. This would appear surprising in view of the much higher flexural strengths of the dry materials which have failure strains comparable to those of the wet materials. It should be noted that the apparently higher value of γ_F in the wet specimens at high polymer content was due to a much higher beam deflection (i.e. strain) and not to an increased peak load which was actually lower in the wet specimens. The critical stress intensity factor for the wet materials has not been included, since it is obviously not valid to use linear elastic fracture mechanics on highly nonlinear materials.

In the dry state, the work of fracture gives an overestimate of K_{1c} from the equation

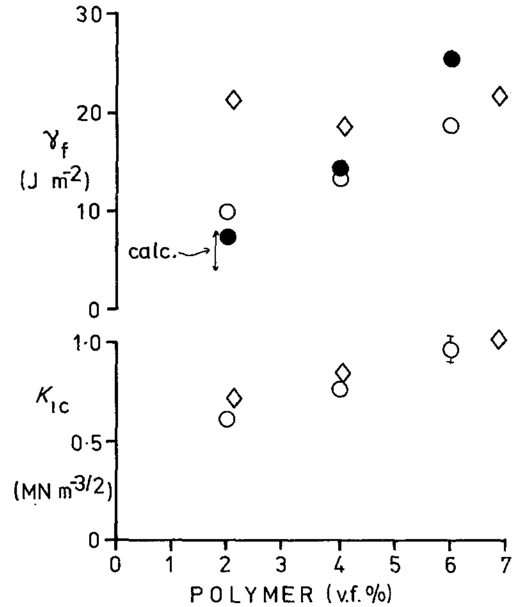

Figure 10 Fracture surface energy, γ_F, and critical stress intensity factor, K_{1c}, as a function of polymer content. Curing time 4 days, v.f. cement 64%. This study: ● wet, ○ dry; ◇ dry [5].

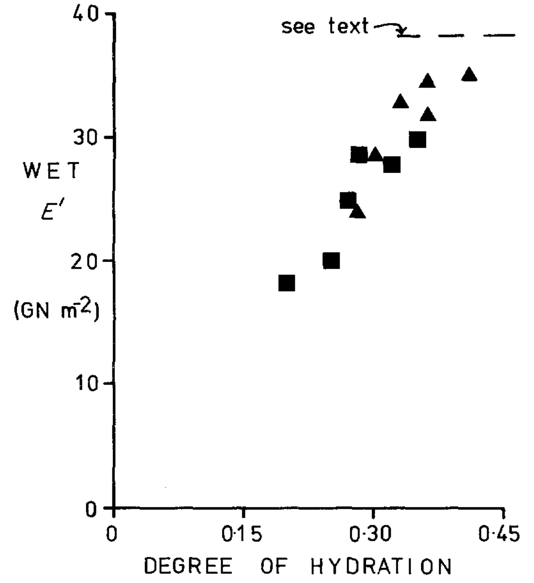

Figure 11 The effect of the degree of hydration on the initial tangent modulus of water saturated materials. ▲ 2% polymer; ■ 6% polymer.

$$K_{1c} = (2E\gamma) \qquad (1)$$

This varies between 30% and 70% and is to be expected from testing such small specimens [3]. General agreement was found between this study and that of Alford *et al.* [6] for K_{1c}, though values for work of fracture did not correlate, possibly due to different stability criteria in the two studies.

4. Discussion

One of the most important aspects of these results is that, as observed before [3], much of the high strength is gained upon drying; this can clearly be seen in Fig. 2. Furthermore, the gain is dependent upon the quantity of organic polymer used. As already pointed out [3], this behaviour is in marked contrast to normal Portland cement paste, which tends to lose strength upon drying due to the effect of shrinkage cracking.

The wet and dry behaviour will therefore be discussed separately below.

4.1. Wet properties

The initial tangent modulus, E' is dependent upon the volume fraction of polymer present (Fig. 4), and a simple interpretation of this result might be that the presence of the low-modulus polymeric material is the cause.

However, Fig. 5 indicates that there are differences in the extent to which the cement has reacted with water in the different mixtures. It is possible that this effect is due to chemical retardation of the hydration process, but it is equally likely that it is due to a reduction in the amount of water available for reaction (see water/cement ratios in Table I), since similar results have been obtained on normal cement pastes without polymer additives [8].

Given the similarity of Figs. 5 and 7, the degree of hydration is clearly important in determining wet modulus. Indeed, it is found that there is a direct correlation between the degree of hydration and the initial tangent modulus in the wet state (Fig. 11) regardless of the polymer content. Since the apparent porosity deduced from the saturated moisture content in these materials remains virtually unchanged with increasing degree of hydration (see Section 3.2) it is not possible to invoke simple porosity–modulus relationships to explain this result.

However, it is interesting to note that the limiting value (i.e. on mature pastes) of Young's modulus for these materials is close to that predicted from the expression obtained by Helmuth and Turk [11]

$$E = E_1(1-p)^3 \qquad (2)$$

where E_1 is the zero porosity elastic modulus (about 80 GPa by extrapolation) and p is the volumetric porosity measured in the same way as the present study. Inserting a porosity of 0.22 yields a value of ≈ 38 GPa for elastic modulus (see Fig. 11).

Although not investigated here, the original packing density should be reflected in the porosity at a given degree of hydration, and it would be envisaged, therefore, that the initial tangent modulus in the wet state is governed by degree of hydration and packing density, in a similar way to normal pastes, and is independent of polymer content.

The strain to failure, ϵ, at the lowest polymer content was 0.075%, only slightly greater than that observed in normal cement pastes, i.e. $\approx 0.06\%$. Since, in this case $\sigma \approx E\epsilon$, it might be expected that the flexural strength σ is governed by the same factors as modulus. That is to say that, corresponding to the modulus–porosity relationship quoted above, there is an equivalent strength–porosity relationship for mature pastes in the absence of gross flaws. In this sense the packing density and degree of hydration are controlling the wet flexural strength and there is direct experimental evidence for this view [12]. Alford [13] obtained a similar wet strength (about 28 MPa) by pressing Portland cement paste to a w/c ratio of about 0.15 without a polymer addition.

Thus the wet strength and modulus of elasticity of a polymer modified cement using the minimum amount of polymer necessary to facilitate fabrication, correspond to those which would be expected from a polymer-free cement compacted to the same degree by other means. The process has enabled the production of a high quality paste of a higher packing density (i.e. lower w/c ratio) than otherwise obtainable without high pressure compaction, and to this extent it can be said that a small amount of polymer (about 1% of the weight of the cement) is acting as a rheological aid.

Further replacement of the original mixing water by water-soluble polymer does not lead to any improvements in wet strength at curing times at least up to 3 days (Fig. 2). There is some evidence that flexural strength increases slightly with increasing v.f. of polymer at longer curing times (Fig. 7); however, as discussed previously (Section 3.2) the nonlinear behaviour at high v.f. leaves such an interpretation questionable.

Nonlinearity of the type shown in Fig. 3 is not observed in normal cement pastes without the polymer and it is clear from the above discussion that it must be the polymer content, not any changes in packing density, porosity or degree of hydration, that is responsible for this. On the basis of this observation alone, it must be concluded that the polymer is modifying the apparent deformation characteristics of the calcium silicate hydrate (CSH) gel. The observed constancy in flexural strength with increasing polymer content, whilst the strain to failure increases, will be discussed in Section 4.3.

4.2. Dry properties

A further important observation of this study is that, in the dry state, the initial tangent modulus is apparently unaffected by the volume fraction of polymer (Fig. 4). This, in effect, means that the change in E' upon drying increases with increasing polymer content. As can be seen from Fig. 6, which indicates very little increase in degree of hydration upon drying, this change in modulus cannot be accounted for in terms of an effectively increased curing time. It must therefore be deduced that there is a small but significant enhancement of the modulus due to the removal of water in the presence of the polymer, which we have already concluded is modifying the deformation characteristics of the CSH gel.

The drying process also removes the greater part of the curvature in the load–deflection behaviour observed in the wet specimens (Fig. 3). Since the strain to failure has remained unchanged on drying, and the modulus slightly increased, the strength is considerably increased, in proportion to the polymer content. A model for the strength of this material that will account for these observvations is developed in Section 4.3.

It should be noted that only between a quarter and a half of the available water, about 5 to 9% of the dry weight of cement, has reacted with the cement (see Fig. 5). This leaves much of the original mixing water, together with some water absorbed from the curing bath, in a relatively unbound state. However, the drying process, which produces significant changes in the mechanical properties, removes only about 30% of this "free" water (Fig. 9).

It is interesting to consider the reasons for this high moisture retention after "drying". Powers [7] observed that the hydration products of

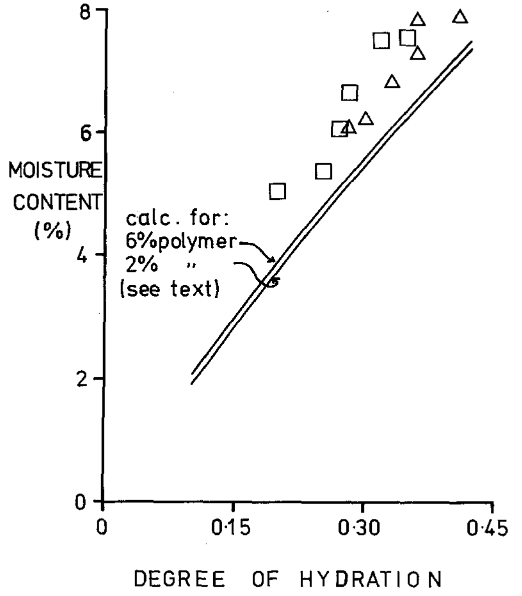

Figure 12 Moisture content after drying at ambient humidity (55% r.h.) for 7 days. △ 2% polymer; □ 6% polymer.

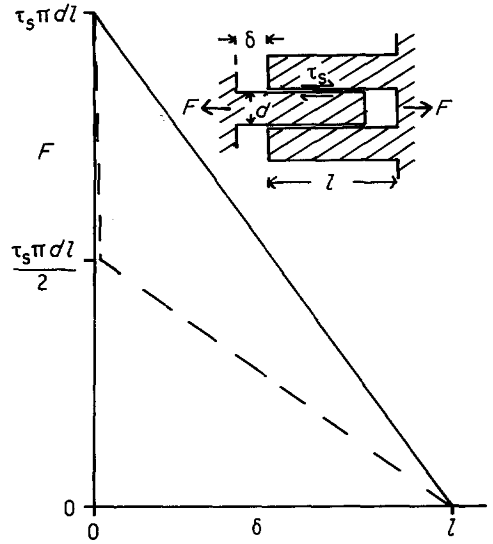

Figure 13 Simple force–separation relationships for the pull-out of calcium silicate hydrate fibrils.

Portland cement appear to have a "characteristic" fine scale porosity of about 28% of their saturated volume. The water residing in this porosity was observed to remain until the relative humidity dropped below about 45%. From the degree of hydration, it is thus possible to calculate the expected moisture content, at 45% r.h., of the polymer modified cements, correcting for the small amount of water left if the polymer dries to its equilbrium moisture content. Allowing for the relative humidity of the laboratory being somewhat higher, at about 55%, and the specimens not being at complete equilibrium after 7 days' drying (Fig. 9), the agreement, shown in Fig. 12, is good.

This accounts for the moisture retention after "drying", and suggests that the polymer is not residing in the finest pores of the CSH gel (i.e. it is not displacing the "gel water"). It can be seen therefore that since the water lost on "drying" has been removed from the polymer gel, and not from the CSH gel, there has been a very large change in the moisture content of the relatively small amount of polymer present.

It should be noted that the above calculations are made using Powers' [7] experimental observations, and are independent of any arguments relating to their interpretation with regard to a microstructural model [8].

4.3. A model for the tensile strength of Portland cement with and without polymer modification

It has been shown experimentally [3, 10] that Portland cement paste behaves as a comparatively notch–insensitive material, essentially because its intrinsic strength, i.e. in the absence of gross flaws, is low. It was suggested [10] that failure occurs by the pulling apart of calcium silicate hydrate (CSH) fibrils. One can therefore envisage a model in which the tensile strength, σ_y, results from the pulling out of the fibrils by shear, the interface having a shear strength τ_s and an area of contact πdl (Fig. 13). Therefore

$$\sigma_y \approx \pi d l \, \tau_s N \tag{3}$$

where N is the number of fibrils per unit area of failure surface. The geometry of this rudimentary model can be deduced from the size of CSH fibrils [14], for which l is of the order of 0.5 to 1 μm and d about 0.3 μm. It should be noted that the use of a single value of τ_s is of a somewhat approximate nature, since the fibrils are irregularly shaped [14] and will have less than perfect contact between each other. τ_s is thus an average value for the notional contact area πdl. As discussed later (Section 4.5) any change in the real contact area will lead to an apparent increase in τ_s.

The effect of, for instance, w/c ratio (i.e. cement packing density) and degree of hydration upon this model would be to vary the parameter N. Unless the average distance between the initial cement grains is less than $\approx 1\,\mu$m, it is unlikely that the packing density will greatly affect the morphology of the fibrils in this interfacial region, where bonding between particles occurs. Thus N will increase with increased packing density (i.e. lower w/c ratio) and increasing degree of hydration.

If it is assumed that, to a first approximation, the flexural strength depicts the intrinsic strength [2, 10], then N can be deduced from the flexural strength data.

In order to estimate N, we need a value for τ_s; in the absence of direct values, we have taken an average value deduced from fibre and rod pull-out tests on cement pastes [15], of about $10\,\mathrm{MN\,m^{-2}}$. Note also that the value of l deduced from the microstructure is the same as the observed critical crack opening displacement in a three-point bend test [10, 16].

Using the wet strength of the low polymer content mix, of about 28 MPa (Fig. 7), inserting the above values in Equation 3 yields a value for N of $\approx 3 \times 10^{12}$ fibrils $\mathrm{m^{-2}}$. Since fibrils are pulling apart in both directions, i.e. two failure surfaces, the total number of fibrils required is about $6 \times 10^{12}\ \mathrm{m^{-2}}$.

It is also possible to estimate N from the degree of hydration (Fig. 5) which in the case of the lower polymer content has levelled off at about 40%. Since the volume of the hydrates of a unit volume of unhydrated cement is about 2.2 times its original volume [7], then at an original packing density of 0.64, the total volume of hydration products will be $0.64 \times 0.4 \times 2.2 = 0.49$. The volume of CSH fibrils will be somewhat less than this, since part of the products will be crystalline calcium hydroxide (CH). Let us take a reasonable value as being ≈ 0.4.

In a unit volume, then, the number of fibrils will be given by

$$\mathrm{N_v} = \frac{0.4}{0.25\,\pi d^2 l} = 6 \times 10^{18}\ \text{fibrils}\ \mathrm{m^{-3}} \qquad (4)$$

i.e. over a unit area

$$2N = \mathrm{N_v^{2/3}} = 3 \times 10^{12}\ \text{fibrils}\ \mathrm{m^{-2}} \qquad (5)$$

The agreement between the figures above is remarkably close, bearing in mind the assumptions made in the model. The value of N obtained from the degree of hydration will be an underestimate, since the fibrils are foil-like rather than rod-like [14], and the value obtained from the flexural strength will be the number of effective, stress carrying, fibrils. The average number of fibrils over a unit area would be somewhat higher, and the relationship between total and effective numbers will depend upon the number of near-neighbour distances between original cement grain surfaces less than about 1 to $2\,\mu$m. Clearly this latter is a complex function of the packing density and particle size distribution, and is beyond the scope of the present discussion.

This model does not infer that the CSH gel is "weak". Indeed, it is implicit in the model that, for fibres with an aspect ratio of $\approx 3:1$ to pull out without breaking across their bases, the material of which they are made (CSH gel) must be "strong" compared with the observed failure strength. From the figures used, the lower limit of the strength of the gel is

$$\frac{\tau_s\,\pi d l}{0.25\,\pi d^2} \approx 140\,\mathrm{MPa} \qquad (6)$$

In the case of plain Portland cement pastes, one might expect a degree of nonlinearity in the stress–strain curve as the material parts. However, it is unlikely in a material as inhomogeneous as cement paste that general yield will be seen. Fracture may be initiated at a large inhomogeneity (e.g. a large calcium hydroxide crystal), grow stably by pull-out of CSH fibrils and finally propagate unstably to failure when the crack opening displacement reaches its critical value of about $1\,\mu$m. It might reasonably be expected that the spacing of these inhomogeneities is large, so that the total additional strain will be below resolution in a typical three-point bend test. These inhomogeneities would also account for the size effect seen in Portland cement paste even after gross visible flaws have been removed [3].

This model also provides a basis for understanding the effect of the polymer on the mechanical properties discussed above.

We can envisage that the polymer interacts with the surfaces of the CSH fibrils that bond adjacent particles together, and that the shear strength of the interface, τ_s, is changed. Clearly the nature of the stress–strain curve, in the presence of the polymer, will depend upon the altered characteristics of the CSH–polymer–CSH fibrillar interface.

The wet properties observed above suggest that the interface may have viscoelastic properties, and the high degree of nonlinearity at high polymer content in the wet state might be expected to be strain-rate dependent.

The increase in strength upon drying can be interpreted as an increase in τ_s on removal of water from the polymer-rich interface region. The higher shear strength is associated with less nonlinearity in the stress–strain curves, and the dried materials might be expected, therefore, to show less strain rate dependence. This is supported by the work of fracture tests, which suggests that the strain around the notch tip in slow fracture is considerably higher in the wet state, at high polymer content, than expected from the dry work of fracture (see Section 4.4).

Clearly the CSH–polymer interaction envisaged above will depend upon the type of polymer, of which only one has been studied here. The interface would also be moisture sensitive, and the effect of other drying conditions will need further investigation.

The conclusion that the CSH fibrils grow through the polymer gel, and are then bonded together by the dried polymer, is supported by the earlier observation (Section 4.2) that the polymer was not taking up any of the pore space in the gel, i.e. within the fibrils themselves.

It may also be noted that the appearance of fracture surfaces of polymer modified cements is not visibly different from that of polymer-free cements [6]. This suggests that there has been no change in the fundamental fracture mechanism.

A further difference between normal and polymer modified cements is the distribution of CH crystals. In normal pastes, of relatively low packing density, these crystals become large and can act as crack initiators. The situation is less clear for polymer modified cements, in which the CH exists in part as a microcrystalline form [6], and it is possible that CH is less likely to be the site of crack initation. The stress–strain curve is therefore expected to show more nonlinearity, and the strength to show less dependence on volume tested. The former point is observed for the wet specimens; however, inhomogeneities may still exist in the form of large (100 μm) unhydrated grains of cement [1].

Although the model is based upon the rupture characteristics of Portland cement paste, it can be seen that the term N will also govern the initial tangent modulus, since it characterizes the number of bonds over which the applied stress is carried. The large net (internal) volume increase on hydration, noted earlier, means that, even though the porous hydration products have a lower modulus than the original cement grains [11], the effect of the relative fractions of unhydrated and hydrated material is of only secondary importance, and the modulus would probably be governed primarily by number of bonded fibrils, N, as seen in Fig. 11.

Since the initial modulus is not dependent upon the value of τ_s, it is not expected to change markedly when τ_s is increased. However, if the polymer is filling space between fibrils, in the wet state as a wet gel and in the dry state as an adhesive, then it will act in the latter as part of the solid structure, and hence contribute to the elastic modulus, producing the small increase in modulus already noted (Fig. 5).

4.4. Fracture mechanics

On the basis of the model of rupture proposed, it is now possible to examine the fracture mechanics measurements.

The pull-out of each fibre will have an amount of energy, w, associated with it, which depends upon the fibril geometry and force–separation characteristics. This latter will in the simplest case take a triangular form (Fig. 13), since, as the fibres pull out, the remaining contact area decreases in proportion to the pull-out distance or separation δ. However, there may be an initial de-bond, as suggested by Higgins and Bailey [17], indicated by the dotted line in Fig. 13.

If the upper bound is set at the force calculated using Equation 3, and the lower bound at about half this, then the pull-out energy per fibril (the area under the curve, Fig. 13) will be between $Fl/2$ and $Fl/4$. The force, F is given by

$$F = \tau_s \pi d l \tag{7}$$

Hence

$$\tau_s \pi d l^2/4 < w < \tau_s \pi d l^2/2 \tag{8}$$

The total energy per unit crack area will be wN, and the fracture surface energy $\gamma_F = wN/2$. Thus

$$\tau_s \pi d l^2 N/8 < \gamma_F < \tau_s \pi d l^2 N/4. \tag{9}$$

Inserting the values used in Section 4.3, then for the wet, low polymer content material (2% v.f.), we have

$$4 < \gamma_F < 8\,\mathrm{J\,m^{-2}} \tag{10}$$

The observed value of $7.4\,\mathrm{J\,m^{-2}}$ (Fig. 10) is in close agreement with this expression.

Comparison of Equations 3 and 9 shows that according to this model there is a direct relationship between σ_y and γ_F, i.e.

$$\sigma_y = k\gamma_F/l \tag{11}$$

where $4 < k < 8$.

For a normal paste of w/c ratio 0.3 there is close agreement with experimental evidence. Inserting a flexural strength of $15\,\mathrm{MN\,m^{-2}}$ and fracture surface energy $3.8\,\mathrm{J\,m^{-2}}$ [3] and $l \approx 1 \times 10^{-6}$ m yields a value of $k \approx 4$.

In the case of the polymer modified cements we do not as yet have sufficient knowledge of the microstructure to ascribe values to l and d. However, as noted in Section 4.3 there appears to be no major change in the appearance of the fracture surface when compared with normal paste. If the fibrill length has not been changed then Equation 11 would still apply, with $l = 1 \times 10^{-6}$ m and $k \approx 4$.

A plot of the dry fracture surface energy of the three mixes shown in Fig. 10 against their flexural strengths yields a linear relationship passing through the origin with $k = 3.5$. Allowing for the small overestimation of γ_F by using small beams [3], the agreement with the above value of k is very close.

The situation is more complex in the wet specimens since, although the flexural strength remains approximately constant (Fig. 2), there is a marked increase in fracture surface energy (Fig. 10). It has already been suggested that, in the wet state, the CSH–polymer–CSH interface may have viscoelastic properties. This would imply that at least some of the stress–strain curve is inelastic, and hence fracture, particularly at low speed, will be accompanied by energy absorbing processes on either side of the crack plane, hence increasing the work required to open up a unit of crack area. Obviously, further information on the stress–strain behaviour is required before a more detailed interpretation of the fracture mechanics in the wet state is possible.

4.5. General

It is clear from the model set out above that for a constant fibril size, there are two factors principally governing the mechanical properties: the number of fibrils, N, which affects strength, modulus and fracture surface energy, and the interfacial shear strength, τ_s, which affects strength and fracture surface energy. Now, since the degree of hydration and hence the value of N has not changed during drying, the apparent value for τ_s increases upon drying to about $12\,\mathrm{MN\,m^{-2}}$ for the 1% polymer level and to about $22\,\mathrm{MN\,m^{-2}}$ at 6% level.

The polymer has considerable adhesive properties on its own, when dried [4], and an increase in τ_s is therefore reasonable. However, it is less easy to see why the amount of polymer should affect τ_s, since it is not normal to observe a change in strength of an adhesive joint with increasing thickness of glue. The average nature of τ_s has already been noted, and it seems likely that the polymer is filling in the spaces in the uneven interface between the irregular fibrils. In this case, the model would predict a maximum in the dry strength with increasing polymer content, when all the available spaces or sites for polymer adhesion between fibrils have been filled up. On this basis, the upper limit of tensile strength would occur when τ_s reaches the yield point of the polymer. Taking this to be about half the tensile strength of polymer film (70 MPa), i.e. about 35 MPa, it can be seen that the upper limit of strength will occur at $35/10 \times 28\,\mathrm{MPa} \approx 100\,\mathrm{MPa}$. Furthermore we deduce a modified lower limit for the strength of the CSH gel of $35/10 \times 140\,\mathrm{MPa} \approx 500\,\mathrm{MPa}$.

The model proposed above accounts for the salient features of the mechanical properties measured in this study. It suggests ways in which the mechanical properties might be further improved, for instance by optimisation of the number of CSH fibrils and the adhesive strength capacity of the CSH–polymer–CSH fibrillar interface. Further work must be directed towards these objectives, as well as a more detailed study of the nonlinear wet materials in direct tension, particularly as regards the possible viscoelastic effects and also the role of crystalline CH.

5. Conclusions

1. A polymer content of about 1% of the weight of the cement is required as a rheological aid in producing a well-made paste without gross flaws.

2. In the wet state, an increase in the polymer content has no effect upon the ultimate value of the initial tangent modulus. At best, ultimate flexural strength increases only slightly with

polymer content. It does however increase both the nonlinearity in the stress–strain curve and the failure strain, hence increasing the fracture surface energy.

3. In the dry state, an increase in the polymer content produces a marked increase in flexural strength and fracture toughness, but leaves the elastic modulus relatively unchanged.

4. The high flexural strength is only obtained on removal of water from the microstructure, indicating that the removal of pores, either large or colloidal, is not the principal mechanism by which this high strength is attained.

5. A fibrillar pull-out model, based upon the observed fracture behaviour, is proposed, by which it is possible to explain the major features of the mechanical properties. The principal effect of the polymer, when dried, appears to be as an adhesive between the calcium silicate hydrate fibrils.

References

1. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, *Nature* 289 (1981) 388.
2. J. E. BAILEY and D. D. HIGGINS, *ibid.* 292 (1981) 89.
3. N. B. EDEN and J. E. BAILEY, *J. Mater. Sci.* 19 (1984) 150.
4. COURTAULDS ACETATE LTD., private communication.
5. J. D. BIRCHALL, K. KENDALL and A. J. HOWARD, European Patent Publication No. 0 021 682.
6. N. McN. ALFORD., G. W. GROVES and D. D. DOUBLE, *Cem; Concr. Res.* **12** (1982) 349.
7. T. C. POWERS, Proceedings of the Fourth Symposium on the Chemistry of Cement, Washington, 1960 (National Bureau of Standards, Washington, 1962) Monograph 43, pp. 577–613.
8. J. H. TAPLIN, *Aust. J. Appl. Sci.* **10** (1959) 329.
9. R. F. FELDMAN and P. J. SEREDA, *Mater. Struct.* **1** (1968) 509.
10. D. D. HIGGINS and J. E. BAILEY, *J. Mater. Sci.* **11** (1976) 1995.
11. R. A. HELMUTH and P. H. TURK, Symposium on Structure of Portland Cement (Highways Research Board S.P. 90, Washington DC, 1966) pp. 135–144.
12. N. B. EDEN and J. E. BAILEY, to be published.
13. N. McN. ALFORD, *Cem. Concr. Res.* **11** (1981) 605.
14. H. R. STEWART and J. E. BAILEY, *J. Mater. Sci.* **18** (1983) 3686.
15. R. C. de VEKEY and A. J. MAJUMDAR, *Mag. Concr. Res.* **20** (1968) 229.
16. D. D. HIGGINS and J. E. BAILEY, Proceedings of the Conference on Hydraulic Cement Pastes, Sheffield (Cement and Concrete Association, UK 1976), pp. 283–96.
17. D. D. HIGGINS and J. E. BAILEY, *J. Mater. Sci. Lett.* **12**, (1977) 2350.

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