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Cement pastes with UV-irradiated polypropylene: fracture energy and the benefit of adding metakaolin

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Abstract

Adding fine plastic-based aggregates to cement pastes can allow for recycling waste while increasing the tensile strength and fracture toughness of the paste. However, the hydrophobicity of plastic causes poor cohesion with the cement paste, affecting the mechanical properties of the composite. Pre-irradiation with UV-C light reduces the hydrophobicity of the plastic, thus increasing the tensile strength of the paste while preserving compressive strength. This paper presents new experimental results, mainly showing that: (i) UV-C irradiated micro-sized polypropylene powder increases the tensile strength and fracture energy of CEM-I cement pastes; (ii) blending cement with metakaolin amplifies the positive effect of polypropylene addition in both untreated and UV-treated forms. These findings indicate that cement-metakaolin pastes containing UV-irradiated polypropylene may be an asset when crack resistance is key, such as in nuclear waste storage and oil/gas well cementing.

Keywords: Cement-plastic composites; UV irradiation; polypropylene; metakaolin; fracture energy; strength.

1. Introduction

The durability of cementitious materials depends largely on their ability to prevent crack propagation. This is quantified by the fracture energy G_F , which is the energy to grow a crack surface by a unit area [1]. Cement-based composites can be devised to have higher G_F compared to traditional pastes [2]. Common solutions involve adding plastic to the cement paste, either as fibres, crumb, or powder [3, 4, 5, 6]. Cement-plastic composites are particularly interesting because the plastic components can be sourced from waste, and under the right circumstances this can benefit the economy and the environment [7].

However, adding plastic typically reduces the compressive strength of hardened pastes [6]. This can be mitigated to some extent by using fine powders or fibres (micro-sized) and in small

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amounts, and by tailoring the plastic particle size distribution to minimise the porosity of the composite [8]. Nevertheless, some loss of compressive strength is likely to persist due to the hydrophobicity of plastic, which causes:

1. flocculation of the plastic particles in water and also in the cement solution, leading to low-quality composites with weak regions displaying locally high plastic–cement volume ratios;
2. poor cohesion between plastic particles and hydrophilic cement hydrates, and in particular the calcium–silicate–hydrate (C–S–H), which is largely made of structural water [9, 4, 10, 11].

Altering the surface chemistry of the plastic can reduce its hydrophobicity and improve the final composite without affecting the workability of the mix. Examples of surface treatments are: argon gas plasma discharges [12], mild gamma-ray irradiation [13], alkaline treatment [14, 15], and UV-ray irradiation [16, 17, 11].

Here we focus on UV-C irradiated plastic and present new experimental results on micro-sized polypropylene powder (PP: one of the most important and widely produced types of plastic) added to CEM-I cement pastes. The choice of UV-C irradiation is due to the simplicity and cost effectiveness of the method. Plastic powder was preferred over its fibres counterpart, despite the latter are known to provide more fracture toughness, in order to emphasise exclusively the role of the interfacial adhesion between plastic and cement paste, hence minimising the confounding effects that could stem from the geometry of the fibres. Literature results from atomic force microscopy on PP irradiated with UV light in an ozone-rich atmosphere, have shown a significant increase of adhesion forces [17]. Recent work on cement–rubber composites has shown that the ozone atmosphere can be avoided if UV-C radiation is used, which is sufficiently energetic to create ozone directly through air irradiation [11]. The first contribution of our work is to test the UV-C treatment for cement–PP composites. The second contribution is to explore the effect of plastic addition to a blend of portland cement and metakaolin. The rationale is that the aluminium provided by the metakaolin yields calcium–aluminium–silicate–hydrate (C–A–S–H) as the main hydration product of the cement–metakaolin paste. rather than the C–S–H of the original portland cement pastes. C–A–S–H may interact differently with the PP powder compared to C–S–H.

Figure 1: Pictures of the experimental campaign.

2. Methodology

2.1. Materials and UV treatment

A CEM I 52.5N portland cement by LaFarge-Holcim was used[18]; its composition is shown in Table 1. For the plastic, the micro-sized Icorene Polypropylene 1404-01 sourced by the A. Schul-

Table 1: Cement Composition

Compound	SO ₃	Cl ⁻	Eq Na ₂ O	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
%w	2.5-3.5	<0.10	<1.0	40-60	12.5-30	7-12	6-10

man company was used (see Fig. 1.a). This is a medium flow, high impact PP usually used for injection molded parts. Its specific weight is 0.902 g/cm³, its tensile strength is 22.1MPa, its tensile elongation at yielding is 10%, and its flexural modulus is 965MPa. The particle size distribution of the PP, measured by sieving [19], is shown in Fig. 2. More than 80% of the plastic was found to have maximum size below 1 mm: this ensures a sufficiently large area of plastic-cement interface to obtain well-discernible effects on mechanical properties. The metakaolin is the MetaStar 501, by Imerys Oilfield Solutions. This metakaolin was manufactured by calcining and micronising kaolinic clay, approximately 68.3% of it has maximum size below 2μm, and only a 0.0010% residue has size over 325μm.

Figure 2: Particle size distribution of the polypropylene plastic.

UV-C exposure of the PP was carried out in the light box shown in Fig. 1.b, built specifically for the purpose and fitted with two 18W bulbs (254 nm wavelength). Four 10 g PP samples were prepared by spreading the power inside the UV light box to form a layer with uniform thickness of *ca.* 1 mm, and irradiating them respectively for 0, 24, 48 and 72 hours without interruption. The samples were then allowed to cool down at room temperature for 10 minutes. The degree of surface modification induced by the UV treatment was measured in terms of hydrophilicity, quantified by water retention tests [11]. There are other possible ways to quantify hydrophilicity, *e.g.* the PP–water contact angle [15], but water retention provides a balance between accuracy and simplicity that is satisfactory for the purpose of this work. In a typical water retention test, a 10 g sample of PP was mixed with a volume $V_1 = 50$ ml of tap water and stirred continuously for 10 minutes. The suspension was then poured into a funnel, lined with filter paper over a measuring cylinder, and allowed to drain out for 10 more minutes. The volume of water in the cylinder V_2 was recorded as a function of time and the difference $V_1 - V_2$ is the measure of water retention. The temporal evolution of water retention is shown in Fig. 3.a. It clearly emerges that a longer exposure to UV-C leads to a larger degree of surface modification, reflected by increased water retention, as also illustrated in Fig. 3.b. Irradiation times longer than 72 hours were tested but these resulted in visible degradation of the plastic samples, which were discarded. Analogous results, including a 72–hours optimum irradiation time, were obtained in previous work on cement–rubber composites, where the increased water retention was explained in terms of surface polarity [11].

Figure 3: (a) Water retention curves starting with 50 ml of water added to the PP. (b) Increased hydrophilicity of PP after UV irradiation.

2.2. Mix design and sample preparation

Mixes consisting only of cement, PP, water and metakaolin were prepared. Other aggregates were not involved, in order to avoid confounding effects due to aggregates–PP interactions, and to focus only on the cement–PP interaction. The water–binder mass ratio was kept constant for all mixes: $w/c = 0.34$ [20]. All mixes were cast as: (i) cylinders with nominal base diameter of 40 mm and height of 100 mm, the latter to be then reduced to *ca.* 80 mm prior to compressive tests, (ii) small beams with square 38×38 mm cross section (nominal) and nominal length of 175 mm. These samples are smaller than typical samples of concrete (see *e.g.* ASTM C39 and ASTM E399 [21, 22]); such reduced dimensions were used for two reasons: (i) limited availability of PP, especially UV-treated; (ii) since pastes with good workability were tested (see slump tests below), the maximum size of heterogeneities is controlled by the largest particles of cement and plastic, both smaller than 1 mm (see Fig. 2): this is considerably smaller than the size of heterogeneities in concrete, which is controlled by aggregates in the order 10 mm. All our samples were cured underwater for 28 days at a temperature of $20 \pm 2^\circ\text{C}$.

The reference mix in this work is a pure portland cement (PC) paste. The mix containing only PC and metakaolin (PC-MK) was obtained by replacing 30%w of the cement with metakaolin; previous work suggests that optimum replacement percentages of PC with metakaolin are between 10%w and 40%w [23]. Adding metakaolin significantly affected workability, thus Sika ViscoCrete 35 RM superplasticiser was added to all samples containing metakaolin (a volume equal to 3.3%

111 of the volume of water in the mix): this sufficed to bring slump test results back to the 175 mm
 112 of the pure PC mix [24] (see Fig. 1.c). For the mixes containing plastic (PC-PP and PC-MK-
 113 PP) 15%vol of PP was added to the volume of binder (cement plus metakaolin) before mixing
 114 it with water. The objective was to obtain hardened samples with similar surface area of PP–
 115 paste interface per unit volume. We chose specifically 15% based on literature results showing
 116 that volume fractions between 10% and 20% should provide a discernible effect on mechanical
 117 properties without reducing excessively the compressive strength of the paste [8]. Adding PP
 118 without MK led to a slump of 178 mm, very similar to the original PC, so superplasticiser was not
 119 used for pastes containing PP. Table 2 shows the composition of the resulting mixes. Some mixes
 120 were prepared with untreated plastic, others with UV–treated plastic, indicated respectively as
 121 PP_{plain} and PP_{UV} .

Table 2: Mix compositions referred to 1000 grams of binder (cement plus metakaolin). PC = portland cement (CEM); MK = metakaolin; PP = polypropylene.

Name	Water (g)	CEM (g)	Metakaolin (g)	PP (g)	Superplast. (ml)
PC	340	1000	-	-	-
PC-MK	340	700	300	-	27
PC-PP	340	1000	-	85	-
PC-MK-PP	340	700	300	79	27

122 2.3. Density measurements

123 After 28 days of curing, the water–saturated cylindrical samples were removed from the
 124 hydration bath, their circular bases were immediately sawed and ground to obtain parallel end
 125 surfaces and prevent eccentric loads during the subsequent compressive tests (see Section 2.4).
 126 The resulting cylinders were weighed and their volume was calculated *via* multiple measures
 127 taken with a Vernier calliper. The actual diameter and height of the samples after demoulding
 128 and base–flattening were 39.0 ± 0.1 mm and 84.1 ± 4.78 mm respectively.

129 2.4. Compressive strength tests

130 The tests were conducted on the cylindrical samples using an Instron Universal Testing Sys-
 131 tem machine and following the ASTM C39 standard [21]. The contact surfaces of the machine
 132 were cleaned of any grit and the cylinder was centred on the lower platen. After contact with

the upper platen, the load was applied at a rate of 1 mm/min (see Fig. 1.d). The compressive strength was obtained from the maximum load experienced by the sample until failure.

2.5. Split tensile strength tests

Following the principles in the ASTM C496 standard [25], some of the cylindrical specimens were removed from the water curing basin at 28 days and were sliced into circular disc specimens with a thickness-to-diameter ratio t/d between 0.25 and 0.3, hence within the 0.2–0.75 range indicated in the standard. The dimensions of the discs were measured using a Vernier calliper and their averages were computed. The contact surfaces between disc and Instron machine platens were cleaned of any grit and the testing sample was centered on the lower platen (see Fig. 1.e). After contact with the upper platen, the load was applied at a rate of 1 mm/min. The maximum compressive load before failure, P_f , was used to compute the indirect split tensile strength $\sigma_{f,t,split}$ as [25]:

$$\sigma_{f,t,split} = \frac{2P_f}{\pi t d} \quad (1)$$

Eq. 1 assumes linear elastic behaviour until failure. Indeed, all samples displayed a linear load–displacement response before reaching P_f in the split tests, hence Eq. 1 is quantitatively reliable.

2.6. Flexural tensile strength tests

Some of the small beam samples were tested for tensile strength obtained from three point bending (3PB) tests [26]. The experimental setup is shown in Fig. 1.f. The distance L between the supports was a constant 130 mm for all tests. The load was applied as a vertical line load at the mid-span and normal to the surface of each specimen to avoid loading eccentricity, and at a low constant rate of 1 mm/min. The ultimate load of each sample at failure, P_f , was used to calculate the flexural tensile strength $\sigma_{f,t,flex}$:

$$\sigma_{f,t,flex} = \frac{3P_f L}{2bh^2} \quad (2)$$

b and h are the cross sectional depth and height, both averaged over three measurements near the midspan: the resulting values were closed to the previously mentioned nominal values of 38 x 38 mm. Eq. 2 assumes linear elastic behaviour until failure, but some samples, especially those containing PP, displayed marked non-linearities in their load–displacement response. Hence it is not recommended to consider the $\sigma_{f,t,flex}$ in this work as quantitatively precise measurements of tensile strength, but rather qualitatively as a way to evaluate the effects of adding PP and MK to the PC pastes, and to corroborate the results from the split tensile tests.

2.7. Fracture energy tests

The experimental setup for this test has been adapted from ASTM E399 [22] and is shown in Fig. 1.g. The setup is analogous to the 3PB tests to measure the flexural tensile strength, discussed above. The only notable difference is the presence of a straight notch culminating in a V-slot, which was sawed at mid-span under the point load (Fig. 1.g). The nominal ratio between notch length and cross sectional height h was 1/3, leading to reduced mid-span cross sectional areas $A_{red} = 1055 \pm 62 \text{ mm}^2$ (against the original nominal cross sectional area of $38 \times 38 = 1444 \text{ mm}^2$; the uncertainty on A_{red} includes the sub-millimetre accuracy of the notch depth). Load-displacement curves until full failure were obtained for all the samples subjected to the notched 3PB test. The tests were run in displacement control with 1 mm/min loading rate. Except for the samples without PP, the recorded post-peak behaviour was sufficiently ductile to provide stability in the softening regime (additional discussion in the Results section). Expectedly, failure occurred as a vertical crack propagation starting from the tip of the notch. The area under the load-displacement curves divided by A_{red} provided the desired estimation of fracture energy G_F .

3. Results

3.1. Density

Fig. 4.a shows that the pure portland cement paste (PC) has the highest density at 28 days. Its average value of 2.08 g cm^{-3} is consistent with the composition in Table 2 and with the fact that additional water is probably absorbed during underwater curing, to support hydration.

Adding untreated PP to the pure PC paste significantly decreases the density, to an average of 1.89 g cm^{-3} . UV-irradiated PP leads to a higher density compared to pastes with untreated PP, although still lower than the density of the original PC paste. This trend is probably the result of several effects of plastic addition to the mix: (i) PP is much less dense than dry PC powder and its hydration product, (ii) untreated PP may flocculate to some extent, forming clusters and leaving pores, (iii) untreated PP may generate low-density interfacial zones with the hydration product of the cement, and (iv) the hydrophobicity of PP may limit the access of additional water during underwater curing. The UV treatment of the PP is likely to mitigate all these effects, except for the intrinsically lower density of PP powder, leading to denser composites compared to pastes with untreated PP.

Replacing some PC with metakaolin (MK) decreases the density. It is often the case that density reduction due to MK addition is caused by lower workability and entrained air[27]. We

192 tried to minimise this effect by tapping the fresh mixes before curing and by fixing the same level
 193 of workability for all samples in this work, using superplasticizer (see Section 2.2). It is therefore
 194 likely that the MK-induced decrease in density is due to the MK and its hydration product being
 195 intrinsically less dense than PC and its product [27]. When PP is added, the PC-MK blends
 196 display the same trend of density as the pure PC pastes, *viz.* a decrease of density that can be
 197 mitigated by using UV-treated PP.

Figure 4: Density and strength of hardened pastes. PC = portland cement; MK = metakaolin; PP = polypropylene, untreated (“plain”) or UV-treated. The error bars indicate the maximum and minimum values obtained from three to five samples.

198 3.2. Compressive strength

199 Fig. 4.b shows that, expectedly [4, 28, 29], PP addition reduces the compressive strength of
 200 both PC and PC-MK pastes. The figure also shows that treating the PP with UV irradiation
 201 brings the compressive strength back to values that are comparable to the original pastes without
 202 PP. This reflects qualitatively the trends of density in Fig. 4.a.

203 Partial substitution of PC with MK causes a marked increase of compressive strength, even
 204 though the density decreases. This beneficial effect of MK addition may not be universal, as a
 205 decrease of compressive strength was recorded in previous experiments with a similar replacement
 206 of coarser metakaolin [23] (*ca.* 80 μm average metakaolin particle size compared to *ca.* 2 μm of
 207 the metakaolin used here). Since finer grinding typically leads to higher surface area and thus
 208 to higher reactivity, it is possible that the relationship between metakaolin particle size and
 209 compressive strength reflects the lower reactivity of metakaolin compared to PC [30]. In our

case, MK addition increases the compressive strength, hence our PC-MK-PP composites, both with and without UV treatment of the PP, end up having greater compressive strength than the pure PC paste. This shows that treating PP with UV irradiation and adding fine MK to the PC-PP composite can prevent losses of compressive strength without increasing the density. Indeed, the density of the PC-MK-PP_{UV} composite is *ca.* 10% lower than that of the original PC paste (1.88 g cm⁻³ *vs.* 2.08 g cm⁻³) whereas its average compressive strength is *ca.* 20% higher (67 MPa *vs.* 55 MPa).

3.3. Split and flexural tensile strength

This section discusses together split and flexural tensile strength, focusing on qualitative trends rather than on quantitative results. It is known that the two types of tests lead to different results and show different sensitivity to environmental conditions such as humidity [31]. Fig. 4.c suggests that adding MK to a PC paste (without PP) increases the split tensile strength. This increase is however within error bars and an opposite trend is instead shown by flexural tensile strength results in Fig. 4.d. On the other hand, literature data on flexural strength tests on similar PC-MK pastes show an increase of tensile strength [32]. It is therefore unclear whether MK addition improves or not the tensile strength.

The addition of untreated PP to whether pure PC or PC-MK pastes, markedly increases the split tensile strength. Some literature results show instead a decrease of tensile strength after addition of untreated plastic [28], but the PP in our experiment is much finer and this can explain the different result [33, 8]. The observed increase in tensile strength is not trivially related to the change of density: indeed density decreases when adding PP, whereas tensile strength increases. The increase in tensile strength is rather due to the composite behaviour with the ductile PP contributing with its superior mechanical performance in tension compared to the brittle cement hydrates. This is one of the desired results that motivated the addition of PP in the first place. Adding UV-treated plastic further increases the tensile strength: this is particularly visible from the split tensile test results on PC-MK-PP_{UV} pastes, in Fig. 4.c. This confirms that the increase in tensile strength stems from the composite behaviour of the PP-cement pastes, with UV irradiation improving the cohesion between PP and cement hydrates.

Fig. 4.c and, more clearly, Fig. 4.d, suggest that the increase in tensile strength due to PP addition is enhanced in pastes containing MK. This may point to a better interaction between PP and the hydration product in MK-PC pastes, which differs in part from the hydration product

in pure PC pastes. However, more research on the interaction between PP and these different hydration products is needed before drawing definite conclusions in this respect.

Figure 5: Force-displacement curves from notched-beam flexural tests on cement (PC) – polypropylene (PP) composites, (a) without, and (b) with partial substitution of metakaolin (MK). The PP can be untreated (plain) or UV treated. The solid lines represent average curves from three tests; shaded areas indicate standard deviations. (c) Average fracture energy G_F , related to the area under the force-displacement curve, with error bars indicating the minimum and maximum values out of three tests.

3.4. Fracture energy

The strength results in Fig. 4 address the behaviour of the pastes until the onset of macroscopic damage at peak load. Part of the rationale for adding PP, however, is to counteract the brittleness of cement hydrates and improve the large-deformation, post-peak behaviour, limiting damage propagation and increasing the energy required for the material to completely fail. In order to quantify this, Fig. 5 shows force-displacement curves from flexural tests on notched small-beam samples, which characterize the entire mechanical response of our pastes, both before and after the peak load.

Qualitatively, the curves in Fig. 5 show a similar trend as the tensile strength results in Fig. 4, *viz.* that PP, especially when UV-treated, significantly increases the tensile strength, in particular if the PC is partially substituted with MK. The different strength ratios between Figs. 4 and 5, respectively *ca.* 2 and 5 between samples with UV-treated PP and samples without PP, is not surprising because failure is controlled by crack propagation with characteristic size of defects that may be different in the unnotched samples, whereas the notch length is the same for all samples in the fracture energy tests. The curves in Fig. 5.a, for composites without

metakaolin, are very consistent, with only small error bars. The error bars are larger for the composites containing MK, in Fig. 5.b, with large fluctuations especially around the peak force. This caused the apparent double-peak in the error regions, whose origin is merely statistical, is not displayed by individual datasets, and would disappear over further averaging. However, despite the large error bars, the curves in Fig. 5.b already clearly show the beneficial impact on strength and ductility (post-peak deformability) of adding PP, especially if UV-treated. The force-displacement curves also show that composites containing MK are slightly stronger and significantly more ductile than composites without MK.

Fig. 5.c shows the fracture energy G_F of the pastes, computed from the load-displacement curves as explained in Section 2.7. Typical values of G_F for cement and concrete range between 10 and 100 J/m² [34, 35]. The average G_F of our PC pastes is at the lower end of this spectrum ($G_F = 8.3$ J/m²), similar to the G_F of the PC-MK paste. Adding plain PP increases G_F by almost one order of magnitude: a quantitatively similar result as previously obtained with polymer impregnated cements [36]. If UV-treated PP is added instead, G_F increases even further, well above 100 J/m².

The Young modulus, measured during the compression tests using strain gauges in the middle third of the samples, was *ca.* 14 GPa for the PC pastes and *ca.* 20 GPa for the PC-MK pastes. Changes induced by PP addition were not significant when compared to the error bars. This, along with the limited change in tensile strength in Fig. 4, indicates that the fracture energy trends in Fig. 5.c reflect also trends in ductility, *e.g.* quantified by Hillerborg's characteristic length [37]. It is finally worth pointing out that the values of G_F in Fig. 5.c may be imprecise for several reasons: (i) possible friction between beam and supports in Fig. 1.g, (ii) because the failure of the samples without PP was brittle and thus the displacement-control tests overestimated their G_F , and (iii) because some samples failed suddenly in their advanced post-peak regime, leading to underestimated G_F , *e.g.* the PC-MK-PP_{UV} curve in Fig. 5.b at 1.2 mm displacement. Nevertheless, the clear trends in Fig. 5.c and the orders of magnitude differences from one sample type to another outweigh the error that may stem from the just mentioned sources.

4. Conclusions

The experimental results in this work have shown that:

- Adding untreated polypropylene powder (PP) to cementitious pastes (PC) reduces the

compressive strength, irrespective of whether part of the PC is or is not substituted by metakaolin (MK). This detrimental effect on strength is largely mitigated using UV-treated PP, despite a lower density of the composite compared to the original paste.

- Partial substitution of PC by MK increases significantly the compressive strength while slightly reducing the density. The MK used in this paper is very fine, and literature results suggest that the increase of compressive strength relies on the MK being sufficiently fine to compensate its lower reactivity compared to PC.
- Adding PP significantly improves the tensile strength, especially if the PP is pre-treated with UV irradiation.
- MK substitution without PP does not change significantly the tensile strength. On the other hand, combining MK substitution with PP addition leads to improved tensile strength, especially if the PP is UV-treated.
- The fracture toughness G_F of pastes without PP is not affected by partial substitution of PC by MK. Addition of untreated PP increases G_F by approximately one order of magnitude, especially for pastes that also contain MK. If the PP is UV-treated, the increase of G_F is even larger.

These results indicate that adding UV-treated PP plastic to a cement paste may be a relatively economical and clean solution to obtain slightly lighter composites with enhanced tensile strength and fracture energy. The improved adhesion between plastic and cement provided by the UV treatment seems thus sufficiently promising to test it further in more complex mortar and concrete formulations, *e.g.* using plastic fibres instead of powder. The benefits of adding PP are amplified if part of the cement binder is substituted with MK, possibly due to a better interaction between PP and the hydration product of MK-PC blends, which differs from the hydration product of PC-only pastes. All these findings points to the opportunity of leveraging the composite behaviour of portland cement, metakaolin, and UV-treated PP in cementing applications that require a large margin of safety against crack propagation, for example oil/gas well isolation and nuclear waste disposal.

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