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Modification of Recycled Cement with Different Additives

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Abstract. *The unmodified recycled cement (RC) paste has unfavorable properties (like fast setting, high water demand and low strength) restricting application. This paper intends to rectify these shortcomings and improve RC with different additives. A comprehensive experimental program combining flowability, setting time, isothermal calorimetry and mechanical tests of modified recycled cement (M-RC) paste with different proportions were conducted. The results indicate that adding TEA and pectin could significantly improve the early flowability of RC and delay its setting, but it will have adverse effects on the mechanical properties of RC paste. Adding 0.5% TEA or 0.075% pectin can increase the fluidity by 240% and 293%. For the 0.5% TEA and 0.075% pectin groups, the 3-day compressive strengths were reduced by 44.3% and 49.5%, respectively.*

Keywords: *recycled cement; TEA; pectin; modification.*

1 Introduction

The disposal of a huge amount of cement-based solid waste occupies a significant amount of valuable resources and causes secondary pollution to the environment. The hardened cement pastes, and unhydrated cement particles in the waste concrete all actually have the potential for recycling. The hardened cement pastes can be ground into a fine powder, then dehydrated, and finally activated at high temperatures to restore its cementitious properties, thus obtaining low-carbon recycled cement (RC), which can effectively dispose of construction waste and turn it into a valuable resource (Xu et al. 2022).

For thermal-activated RC, it is now widely accepted that the early stage of rehydration results in a high rate and amount of heat release. However, the total heat of rehydration of RC is generally lower than that of ordinary Portland cement (OPC). Moreover, the reactions involved and the explanation for the heat release rate are still subject to debate.

Another notable feature of RC is its high-water demand. Previous research has shown that even when the water-cement ratio reaches 0.85, the fluidity level may not reach that of OPC at a water-cement ratio of 0.45 (Baldusco et al. 2019). The high content of CaO and large specific surface area are believed to be the reasons for the high-water demand. When the w/b is high, it would lead to low strength in the RC system, so it is necessary to reduce the w/b to increase the compressive strength.

Overall, there may be potential impacts on the performance of RC at every stage of the recycling process. For example, in the precursor materials, the degree of hydration and carbonation of waste hardened cement paste, particle size during separation and grinding steps, temperature, heating and cooling rates during the thermal activation step, and w/b during the rehydration process can all affect the fresh properties, mechanical performance, hydration product composition, and microstructure evolution of the RC paste. As for the mechanical performance of the hardened RC paste, the compressive strength reported in the literature ranges from 3-32 MPa at 28 days, which may be attributed to the differences in precursor materials, w/b ratio, and other factors (Xu et al. 2022).

Based on a comprehensive analysis of the research status, there are still several issues in the study of RC, such as low compressive strength (3-32 MPa), high water demand (over 0.85), and short setting time (presented a rapid workability loss within 3 min and lost all workability at the age of 12 min) of RC obtained by conventional procedures (Xu et al. 2023c), which may affect its practical engineering application. It is necessary to conduct modification studies on the optimal RC obtained in the first step using common solid waste, SCMs, or chemical additives to regulate and optimize its various properties. This article is based on the research on the modification of RC using different additives to increase its workability due to its fast setting, providing possibilities for future engineering applications.

2 Materials and methods

2.1 Raw Materials

The anhydrous RC is obtained by crushing, grinding, and high-temperature activation at 750 °C. The specific waste OPC pastes and subsequent preparation steps can refer to our previous research (Xu et al., 2023a, Xu et al., 2023b). The type of superplasticizer used in this experiment is commercial BASF PCE410 (the solid content measured at 150 °C is 50.55%). Analytical grade of chemicals including triethanolamine (TEA) and pectin (P) were used as received (over 98% purity). Deionized water was used in all experiments in this study.

2.2 Mix Design and Specimen Preparation

The w/b of all groups was fixed at 0.5, and the dosage of PCE in pastes was fixed at 4% bwob. Blank represents the addition of only PCE. In isothermal calorimetry test, the dosages of TEA in M-RC pastes were fixed at 0.05%, 0.1%, 0.5%, 1.5%, 3% and 4.5% bwob, and the dosages of pectin in M-RC pastes were fixed at 0.01%, 0.075%, 0.1%, 0.5%, 1.5% and 5% bwob. According to the results of the isothermal calorimetry test, TEA doses of 0.05%, 0.5% and 1.5% and pectin doses of 0.01%, 0.075% and 0.5% were selected for the tests of setting time, flowability and mechanical properties.

2.3 Experimental method

2.3.1 Isothermal calorimetry

The isothermal calorimetry was carried out upon pastes prepared outside the calorimeter according to EN 196-11: Method A (external mixing) specification using the TAM Air micro-calorimeter (Thermometric AB, Sweden) at 25 °C for 120 hours. Samples were prepared by mixing dedicated amounts of each group with deionized water in a 20 ml glass ampoule with a stirrer for 1 min to achieve paste with a w/b of 0.5.

2.3.2 Flowability and setting time

The setting time and flowability of M-RC pastes with a w/b ratio of 0.5 was determined according to the Chinese standard GB/T1346-2011 by using a Vicat apparatus.

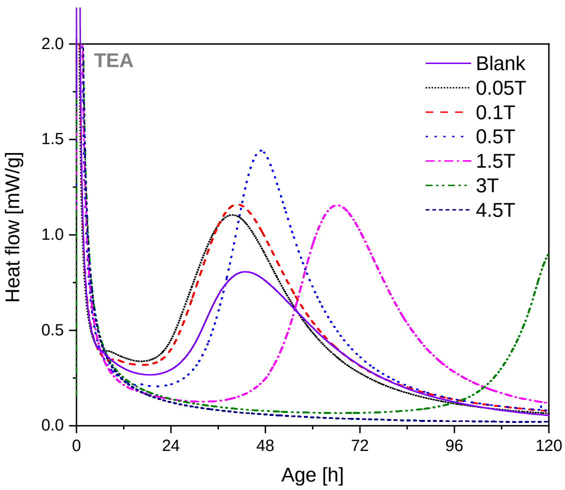
2.3.3 Mechanical property

The compressive strength of the specimens was carried out at 3 days of age according to GB/T 50081-2019. For each composition of M-RC pastes, three 40×40×40 mm samples were produced and kept in a standard curing room.

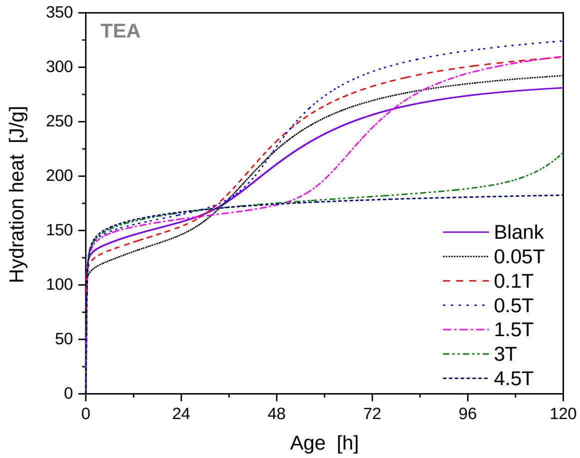
3 Results and analyses

3.1 Hydration heat

The hydration of M-RC with the addition of TEA at different dosages containing differential curves and cumulative curves are shown in **Figure 1**. Overall, the heat flow curves show that the different doping levels of TEA have a significant effect on the rehydration of the M-RC. 3%, 4.5% doping significantly inhibits the rehydration, and no exothermic peaks appear or appear later in the measured time range. The doping of 0.05% and 0.1% will advance the appearance of the exothermic peak to some extent, and the doping of 0.5% and 1.5% will delay the appearance of the exothermic peak to some extent. From the total exothermic curve (Figure 1(b)), 3%, 4.5% doping is much lower than the Blank due to the inhibition of hydration development. The remaining doping amounts of each group are higher than the Blank. Therefore, we selected 0.05%, 0.5% and 1.5% as pre-experiments for the subsequent mechanical properties, flowability and setting time tests.



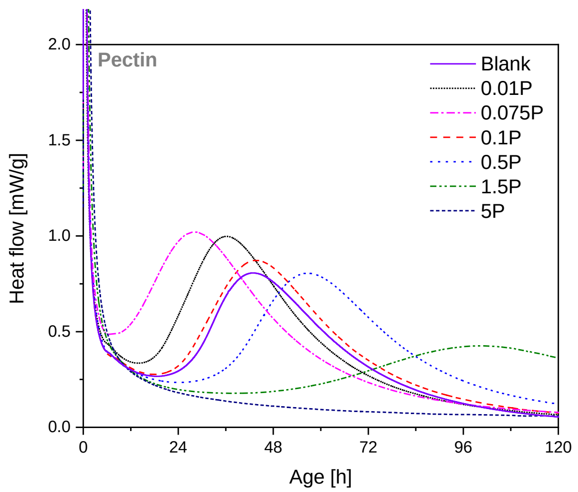
(a)



(b)

Figure 1. Hydration of M-RC with different dosages of TEA, (a) differential curves; (b) cumulative curves.

The hydration of M-RC with the addition of pectin at different dosages containing differential curves and cumulative curves are shown in **Figure 2**. Overall, it can be found from the heat flow curves that pectin at different doping levels has a large effect on the rehydration history of recycled cement, but with the magnitude of the change in doping level, the magnitude of the effect on the rehydration heat of hydration is smaller compared to TEA. 1.5%, 5% doping significantly inhibits the rehydration and no exothermic peak appears or appears later in the measured time range. The doping of 0.01%, 0.075%, and 0.1% will somewhat advance the appearance of the exothermic peak, and the doping of 0.5% will somewhat retard the emergence of the exothermic peak. From the total exothermic curve (Figure 1(b)), the doping of pectin significantly reduces the early exotherm regardless of the doping amount. Therefore, it also reduces the total heat to a certain extent. Of course, from the subsequent response, the 0.075% doping group still has a great advantage. Therefore, based on the results of this experiment, we selected 0.01%, 0.075% and 0.5% doping for the subsequent mechanical properties, flowability and setting time tests



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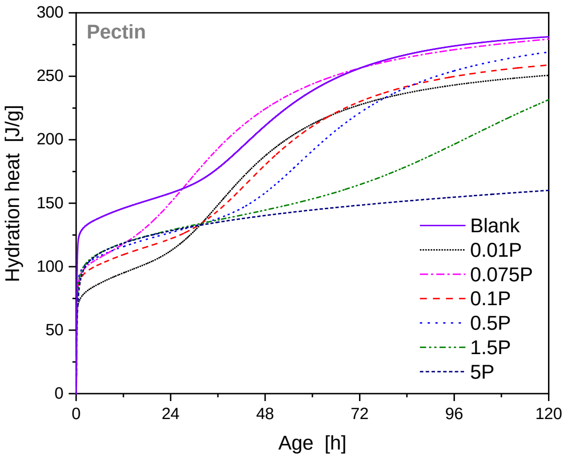

(b)

Figure 2. Hydration of M-RC with different dosages of pectin, (a) differential curves; (b) cumulative curves.

3.2 Flowability and setting time

The setting time of M-RC pastes is shown in **Table 1**. The initial and final setting time of Blank pastes were 55 and 260 minutes respectively, however, the flowability is only 75mm, which caused by the reunion and impoundment of RC particles. Although the setting time of Blank-RC basically meets the standard (GB/T 175-2015) for setting time (initial setting time ⩾ 45 minutes, final setting time ⩽ 390 minutes), its poor workability will limit its practical application. It can be seen that the addition of TEA and pectin delays the setting time and increases the early workability. For TEA, the initial and final setting time first decreased and then increased with the increase of dose, but the flowability gradually increased. Compared with the Blank group, 0.5% TEA could increase the flowability by 240%. The initial and final setting time of the pectin group decreased with the increase of the dosage. In addition, the flowability of pectin significantly increased at low doses and expanded to 300% compared to the Blank group.

Table 1. The setting time of M-RC pastes.

Paste Designation	w/b ratio	Setting time (min)		Flowability(mm)
		Initial	Final	
Blank		55	260	75
0.05TEA		90	420	170
0.5TEA		70	375	180
1.5TEA	0.5	85	390	195
0.01P		125	330	225
0.075P		95	295	220
0.5P		80	275	90

3.3 Mechanical property

The compressive strength of M-RC pastes at 3 days are shown in **Table 2**. The compressive strength continued increasing as the hydration progressed, also demonstrating the rehydration. The early 3-day strength of Blank could reach 19.2 MPa. Both the amount of TEA and pectin, either more or less, adversely affected the 3-day compressive strength, and the higher dose group had a serious adverse effect. For the 0.5% TEA and 0.075% pectin groups, the 3-day compressive strengths were reduced by 44.3% and 49.5%, respectively.

Table 2. The compressive strength of M-RC pastes.

Paste Designation	3d Compressive strength (MPa)	Variance of the strength
Blank	19.2	1.67
0.05TEA	9.6	0.43
0.5TEA	10.7	0.45
1.5TEA	1.2	0.05
0.01P	8.6	0.14
0.075P	9.7	0.40
0.5P	2.0	0.08

4 Conclusions

The results obtained in this study provide a knowledge on fresh and mechanical behaviors of the M-RC binder system. The findings of the present study can be summarized as follows.

- TEA and pectin could significantly improve the early flowability of RC and delay its setting. Adding 0.5% TEA or 0.075% pectin can increase the fluidity by 240% and 293%.
- For the 0.5% TEA and 0.075% pectin groups, the 3-day compressive strengths were reduced by 44.3% and 49.5%, respectively.

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