

Research Article

Study on Hydration and Mechanical Property of Portland Cement-Blended Recycled Plaster Materials

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In this work, Portland cement- (OPC-) blended recycled plaster materials (R-CP) were prepared to find out their hydration and mechanical properties. It was found that the hydration of R-CP was accelerated by the rapid rehydrated ettringite (AFt), and the strength of R-CP was decreased by the reduced hemihydrate content and low strength of rehydrated AFt and CaCO₃. On the contrary, consistent with the previous studies, the strength of OPC-blended plaster of Paris materials (POCP) was improved by the formation of AFt, Ca(OH)₂, and CaCO₃ that filled pores in the pastes. Therefore, a different strength development could be seen in POCP and R-CP. In principle, these findings will lay a solid ground work for the utilization of recycled plaster.

1. Introduction

Plaster of Paris is widely used in the production of building products [1–3] and ceramic gypsum model [4, 5], and thus, a large amount of waste gypsum (WG) is produced after their utilization. The amount of gypsum wallboards produced annually is 80 million tons, and the amount of gypsum dumped in landfills is 15 million tons per year [6]. When the WG is mixed with organic waste, it can not only produce hydrogen sulfide gas but also when the WG is landfilled into the inert landfill, the sulfate will leach into the groundwater. In short, the production of WG has harmed human health in addition to aggravating disposal problems [7, 8]. Therefore, the recycling of WG and the utilization of its recycled plaster are necessary to reduce the plaster of Paris consumption, reduce cost, save energy, and protect the environment. However, the recycling of WG is insufficient, and a great loss of resources considering the gypsum is only limited as an auxiliary material for producing cement [6], reinforcing soft soil [9–12], and ceramic products [13].

Furthermore, large plate gypsum is prepared from WG by a wet process [14], which is too complicated to use on a large scale. The β -hemihydrate of calcined WG (recycled plaster) as a low-energy material can be produced by the

reversible reaction between gypsum dihydrate and gypsum hemihydrate in an electric oven at 180°C [14]. For example, Ren [15] investigated the macroscopic properties of the neat recycled plaster, such as water requirement for normal consistency, setting time, and mechanical strength. Bardella and Camarini [16] reported the physical properties of the neat recycled plaster, such as particle size distribution, fineness modulus, specific gravity, and bulk unit weight. Camarini et al. [17] studied the thermal properties of the neat recycled plaster. Pinheiro and Camarini [18] described the characteristics (fineness modulus, bulk unit weight, specific gravity, and specific surface area) of the neat recycled plaster under different regeneration cycles. Gladis Camarini studied the effect of citric acid on the setting time and mechanical properties of recycled gypsum plaster to build components [19]. Indeed, OPC is always added to the plaster of Paris to improve its strength, abrasion resistance, corrosion resistant, and durability [20–22]. Moreover, the hydration products of neat plaster of Paris are extremely different from OPC-blended plaster of Paris materials (POCP), which are obtained by the hydration of tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A), tetracalcium aluminoferrite (C₄AF), and hemihydrate (HH). However, the role of OPC is always neglected

after OPC-blended recycled plaster materials are reutilized. Residual cement or its hydration products can affect the performances of OPC-blended recycled plaster materials (R-CP), which may be different from the effect of directly adding OPC to improve the properties of plaster. Although there have been several investigations on the applications of WG and the hydration and mechanical properties of neat recycled plaster, little research is carried out about the hydration and mechanical properties of Portland cement-blended recycled plaster materials (R-CP). With respect to OPC-blended plaster of Paris materials, the researches on R-CP are largely lagged behind. In addition, no study describing the hydration and mechanical properties of Portland cement-blended recycled plaster materials has been published in the common sources by the scholars, which seriously hinder the utilization of WG.

In this work, the hydration and mechanical properties of Portland cement-blended recycled plaster materials were systemically studied by internal addition, and their working mechanism was also discussed. This research no doubt will lay a solid ground work for the utilization of recycled plaster.

2. Experimental Details

2.1. Materials and Preparation of R-CP. The virgin gypsum (VG) was purchased from Yingcheng in China. The OPC cement used was the Fuhuang Cement, OPC. 42.5R. Their chemical compositions are shown in Tables 1 and 2, respectively. Their grain size distributions are shown in Figure 1. The flowchart of preparing R-CP and its hardened R-CP was shown in Figure 2. In detail, the procedures were as follows: VG was grounded with a laboratory steel ball mill for 2 min, then calcined in an electric oven at 180°C for 3 h, and aged in air for 2 d to obtain POP. POP was added into different dosages of OPC to gain OPC-blended plaster of Paris materials (POCP). According to the standard consistency, POCP were mixed with water to convert it into gypsum dihydrate, which was called hardened POCP. The hardened POCP was then dried at $45 \pm 2^\circ\text{C}$ till mass stabilization and did as the same process above. To the end, R-CP and its hardened R-CP were produced. The water-plaster ratio (W/P), setting time, and strength were determined according to GB 9776-2008 [23]. The experimental details have been introduced in our earlier research [24].

Mixing different amount of OPC into plaster of Paris will result in different POCP and R-CP. According to the amount of OPC, POCP are named as follows: 0% (POCP-0), 3% (POCP-3), 5% (POCP-5), 10% (POCP-10), and 15% (POCP-15). R-CP are named as follows: 0% (R-CP-0), 3% (R-CP-3), 5% (R-CP-5), 10% (R-CP-10), and 15% (R-CP-15).

2.2. Experimental Techniques. The internal addition method was used to study the effect of OPC on the hydration and mechanical properties of Portland cement-blended recycled plaster materials. It is a kind of experimental methods, and the extra addition method can also be used in this work. The internal addition means that it is a plaster of Paris substitution by OPC, and the sum of plaster of Paris and

TABLE 1: Chemical composition of VG used.

Virgin gypsum	SO ₃	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	SrO
Chemical composition (%)	47.57	38.73	1.15	0.42	0.13	0.07	0.04

OPC is 100%. The experimental process is to add OPC to the plaster of Paris, which was then calcined into R-CP after hydration.

To facilitate understanding of the on-going work, a figure for describing the testing program was presented in Figure 3. Briefly, the water-solid ratio of POCP was measured first, and then the setting time was determined according to its water-solid ratio. Afterwards, the compressive strength was tested after the determination of the flexural strength. And the specimens for compressive strength were the divided specimens after the flexural strength measurement. As for R-CP, the testing program was the same with the process above.

To facilitate understanding of the scope of the work, a figure for the experimental program of R-CP was presented in Figure 4. Briefly, the hydration and mechanical properties of R-CP were measured first, and then the hemihydrate content of R-CP was determined by DSC/TG curves and triphase composition analysis. Next, the temperature evolution during the hydration reaction of R-CP was measured. Finally, the morphology and composition of hardened R-CP were tested.

2.3. Materials Characterization. The hemihydrate content of R-CP was determined by the triphase composition analysis (TCA) of gypsum and simultaneous differential scanning calorimetry/thermogravimetric analysis (DSC/TG) instrument (SMP/PF7548/MET/400W). The grain size distributions of plaster and OPC were carried out using a laser particle size analyzer. The composition of hardened R-CP was also analyzed by simultaneous DSC/TG instrument (SMP/PF7548/MET/400W). The morphological investigations of hardened R-CP were observed by the scanning electron microscope (TESCAN VEGA III LMH) equipped with energy dispersive X-ray spectroscopy (EDS). Temperature evolution during the hydration was measured by laboratory self-made insulation device. First, mix the plaster with water according to the standard consistency, and then inject the slurry into the thermos bottle which has been inserted a thermometer into the stopper. Finally, the temperature changes of the slurry were read.

3. Results and Discussion

3.1. Consistency and Hydration of Portland Cement-Blended Recycled Plaster. The effect of OPC on the W/S (ml water/300 g solid powder, water-solid ratio), setting time, strength, and strength decrease rate of R-CP was measured (Figure 5). Figure 5(a) compared the W/S of R-CP to POCP when OPC was added to plaster of Paris. It can be clearly seen that the W/S of R-CP was much higher than that of POCP under the same dosages of OPC, and the W/S of R-CP

TABLE 2: Chemical composition of OPC cement.

OPC cement	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	P ₂ O ₅	N ₂ O	SrO	MnO	ZrO ₂	Cl	ZnO	Cr ₂ O ₃	CuO
Chemical composition (%)	58.11	23.88	6.17	3.12	3.10	2.98	1.22	0.71	0.20	0.17	0.12	0.06	0.05	0.04	0.03	0.02	0.01

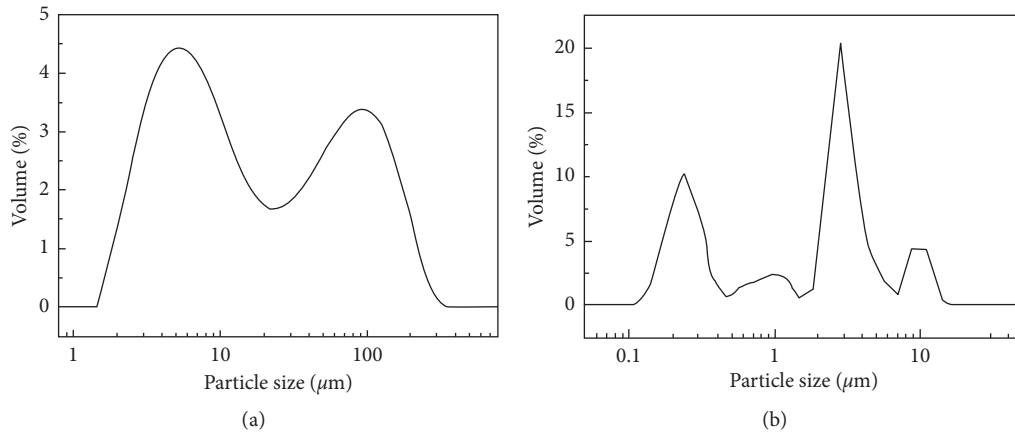


FIGURE 1: The grain size distributions of (a) plaster and (b) OPC.

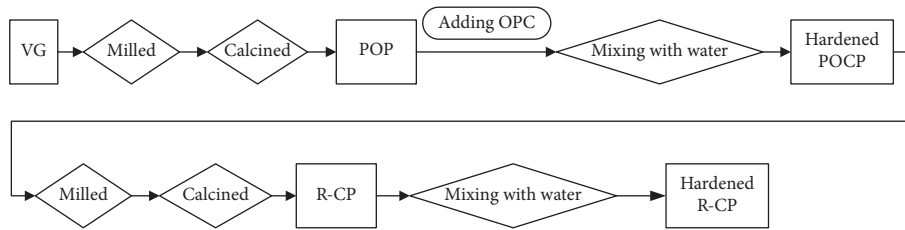


FIGURE 2: The flowchart of preparing R-CP and its hardened R-CP.

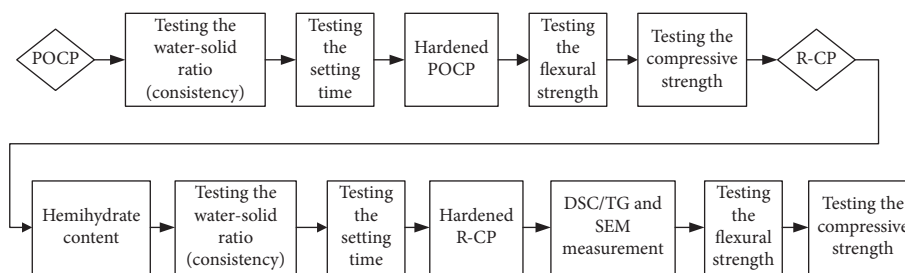


FIGURE 3: The testing program.

was also increased. Without OPC, R-CP-0 has a W/S of 0.85, which means that each 300 g plaster powder blends 255 ml water for its normal consistency, which is in harmony with the previous findings [15]. When the OPC content is 3%, this number of R-CP-3 increased drastically to 0.91, which may be related to the fact that the quick formation of recycled Aft reduces its fluidity, and this Aft was produced by the calcined Aft. Such a phenomenon that involved the quick formation of recycled Aft has been reported by Wang and Liu [25] and Ouyang [26]. Then, this trend began to level

out. In contrast, the W/S of POCP-0 was 0.63 in the absence of OPC, and the W/S of POCP-5 increased to 0.66, at which this began to decrease and dropped to 0.62 at the dosage of 15%. Although the W/S of POCP increased at low dosages, there was still an overall downward trend. It is well known that C₃A in cement can react with gypsum in the aqueous phase and rapidly forms Aft [20], which reduced the fluidity of POCP. On the contrary, the W/S of POCP could be greatly reduced by the addition of cement due to the low water demand of cement. The fluidity of POCP was affected by the

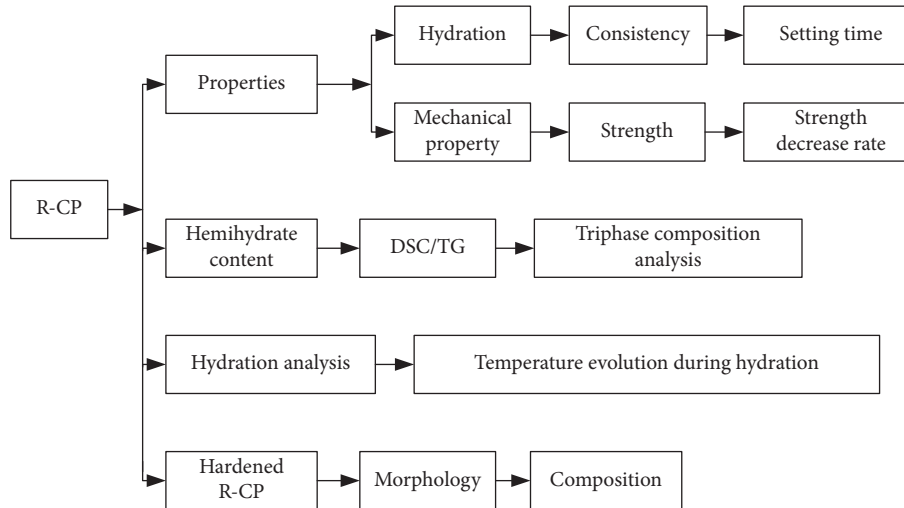


FIGURE 4: The experimental program of R-CP.

two aspects. The former plays a major role at low dosages; however, at high dosages, the latter has a great effect. Therefore, it can be concluded that the effect of OPC on W/S of R-CP was different from that of POCP, and the W/S of R-CP was also increased compared with R-CP-0 when the OPC was added.

In Figure 5(b), it can be seen that there was a downward trend in the setting time for both POCP and R-CP. The initial setting time of R-CP-0 was 33 min, and its final setting time was 13 min longer than the initial setting time; this agrees with the well-known findings of Ren [15]. However, there was a steep decline in the presence of 3% OPC, at which R-CP-3 was at a peak, and then continued to decrease but more steadily. In contrast, the setting time of POCP was very short, the initial setting time of POCP-0 was 8.5 min, and then it decreased gradually to 5 min at the dosage of 15%, which is consistent with Zhao et al. [20]. So, it can be concluded that a sharp decrease of setting time can be seen in R-CP and a corresponding steady decrease in POCP. The shortening in setting time of POCP and R-CP was caused by the rapid formation of AFt, which speeded up their hardening. To our surprise, the formation mechanisms of their AFt were not exactly the same. The AFt of POCP was formatted by the hydration of C_3A and gypsum, while the R-CP was formed by the recycling of calcined AFt immediately upon addition of water, which had been confirmed by other workers [25].

3.2. Mechanical Property of Portland Cement-Blended Recycled Plaster. Figures 5(c) and 5(d) show the addition of OPC and its amount on how to affect the strength and decline law of R-CP. It can be clearly seen that there has been a slight decrease in strength for R-CP. Without OPC, the flexural strength (FS) and compressive strength (CS) of R-CP-0 were 2.70 MPa and 4.80 MPa, respectively, and the numbers of R-CP-10 were gradually reduced to 2.48 MPa and 4.43 MPa, respectively. The strength continued to decrease but more steeply to 2.30 MPa and 3.77 MPa at the dosage of 15% OPC, respectively. In contrast, the strength of POCP showed

a considerable rise and increase in strength with the increase of OPC dosages. It can also be seen from Figure 5(c) that the strength of R-CP was reduced compared to POCP. Therefore, it was necessary to study the decrease law of R-CP for mastering their strength development. The decrease law meant the strength decrease rate of R-CP compared to POCP at the same OPC dosages, which could be calculated by the following equation (1); namely, the strength difference between POCP and R-CP was divided by the strength of POCP under a certain dosage of OPC. In the absence of OPC, the strength decrease rate of R-CP-0 was about 50% compared to POCP-0, and this number rose rapidly with the increase of OPC (Figure 5(d)). So, it can be drawn that when the OPC was added to plaster of Paris, an opposite strength development trend was exhibited between R-CP and POCP, and the strength decrease rate of R-CP was also much higher than that of R-CP-0:

$$\text{decrease rate} = \frac{\text{strength}_{\text{POCP}} - \text{strength}_{\text{R-CP}}}{\text{strength}_{\text{POCP}}} \quad (1)$$

3.3. Microanalysis. The temperature evolutions of R-CP-0 and POCP-0 during the hydration reaction are shown in Figure 6. As can be seen, for R-CP-0, the main peak of temperature appears after 75 min, while the maximum temperature in POCP-0 is rapidly reached, and the main peak is also shifted to 55 min, pointing out that the hydration of POCP-0 is slightly accelerated.

The hemihydrate content of R-CP-0 and R-CP-10 was measured by DSC/TG and triphase composition analysis (TCA). Figure 7(a) shows the DSC/TG curve for R-CP in the absence of OPC, where the peak at 141°C is due to the dehydration of hemihydrate to anhydrate, and the weight loss is $0.5 \text{ H}_2\text{O}$. Figure 7(b) shows the DSC/TG curve of R-CP in the presence of 10% OPC, where the peak at 141°C is also due to the dehydration of hemihydrate to anhydrate. The appearance of the endothermic peak at 430°C is because of $\text{Ca}(\text{OH})_2$. And the formation peak at 739°C was attributed to the decomposition of CaCO_3 , which may be due to the

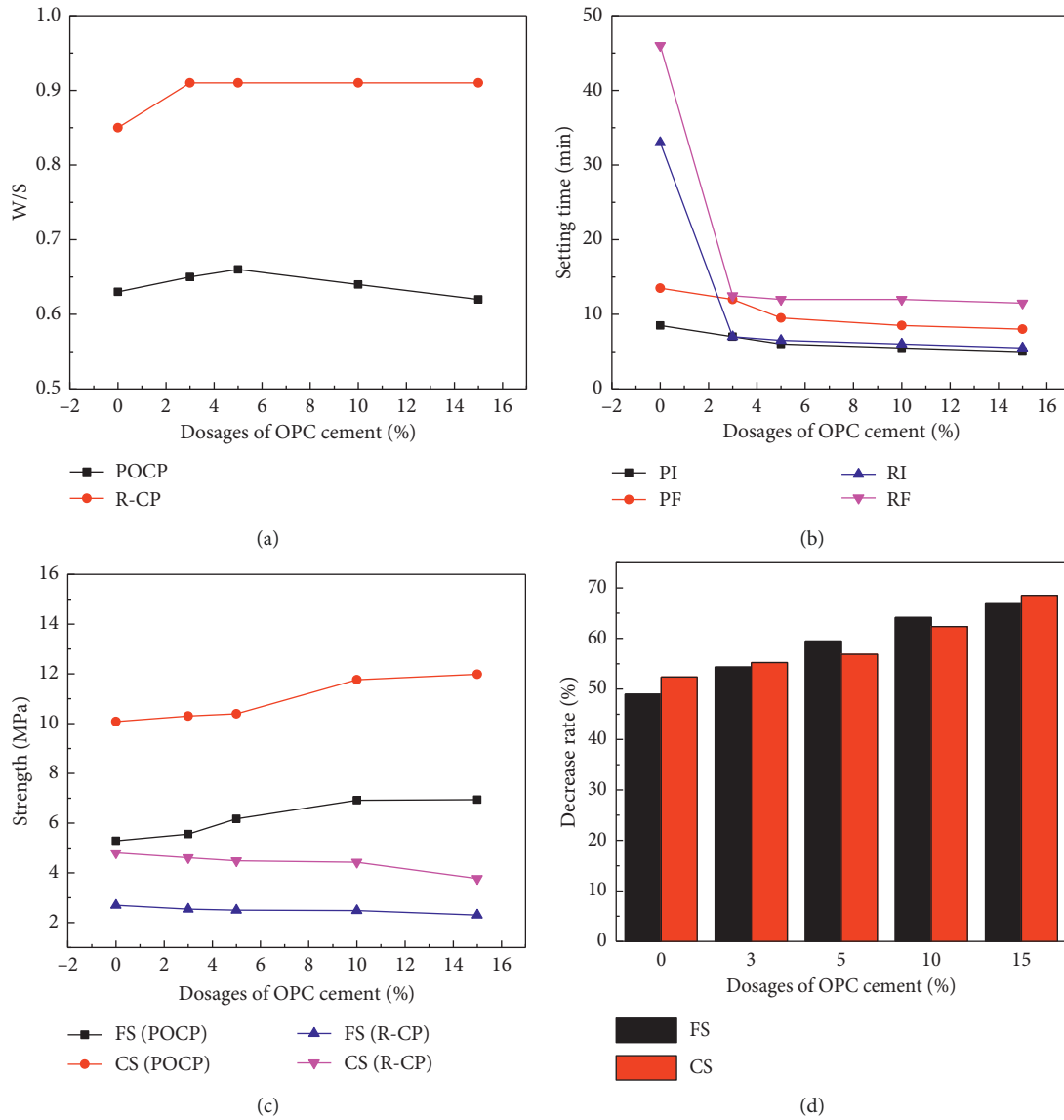


FIGURE 5: Macroproperties of R-CP: (a) water-solid ratio of R-CP; (b) setting time of R-CP; (c) strength of R-CP; (d) strength decrease rate of R-CP. PI: initial setting time of POCP; PF: final setting time of POCP; RI: initial setting time of R-CP; RF: final setting time of R-CP; FS: flexural strength; CS: compressive strength.

carbonization of $\text{Ca}(\text{OH})_2$ and gypsum. Based on the following equation (2), the hemihydrate content can be determined. Compared to R-CP-0 (92.44%), R-CP-10 displayed a low hemihydrate (82.34%):



The estimation of the hemihydrate amount of R-CP was also calculated by TCA. Figure 7(c) shows the TCA results. It can be clearly seen that the hemihydrate content is currently declining. Compared to R-CP-10, R-CP-0 has a high hemihydrate amount in the absence of OPC. The amount decreases linearly as a function of the dosages and is reduced to 76.69% at the dosage of 15%, so it can be concluded that the addition of OPC reduces the hemihydrate content of R-CP due to the existence of calcined cement hydration products, such as $\text{Ca}(\text{OH})_2$, calcined Aft.

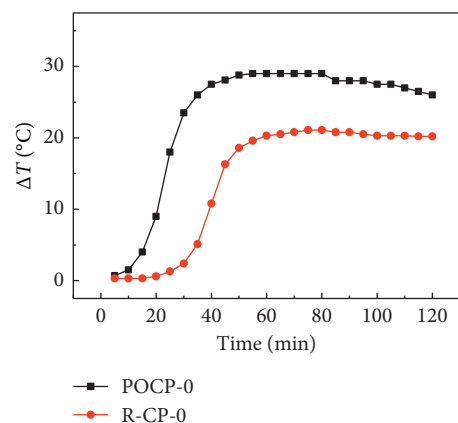


FIGURE 6: Temperature evolution rate curves of R-CP-0 and POCP-0.

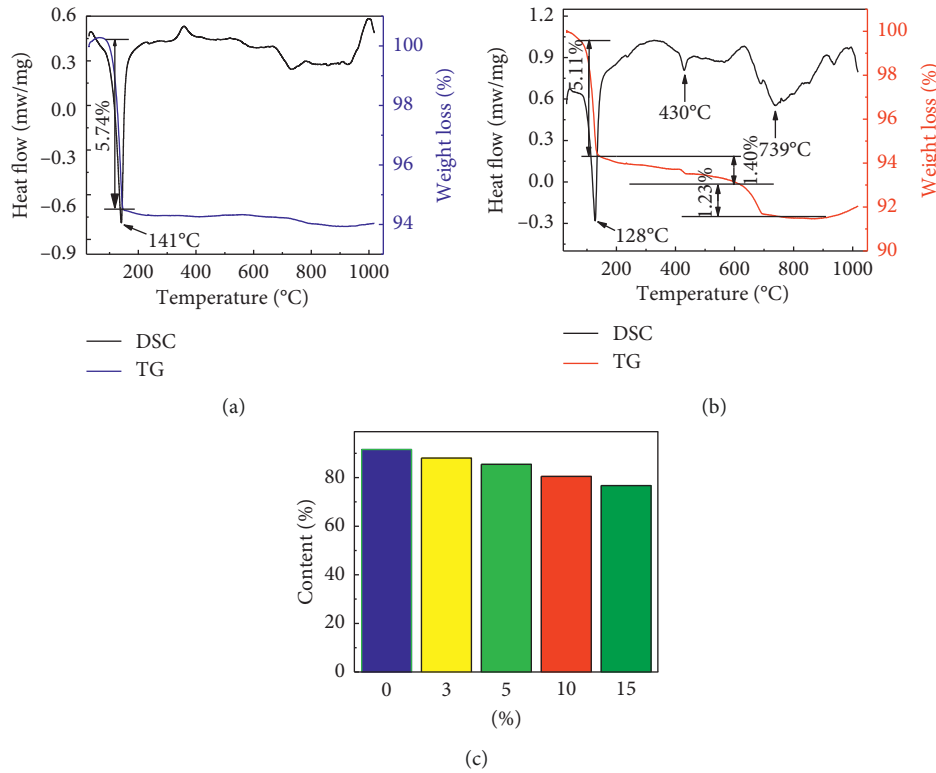


FIGURE 7: The hemihydrate content of R-CP: (a) DSC/TG of R-CP-0; (b) DSC/TG of R-CP-10; (c) TCA results.

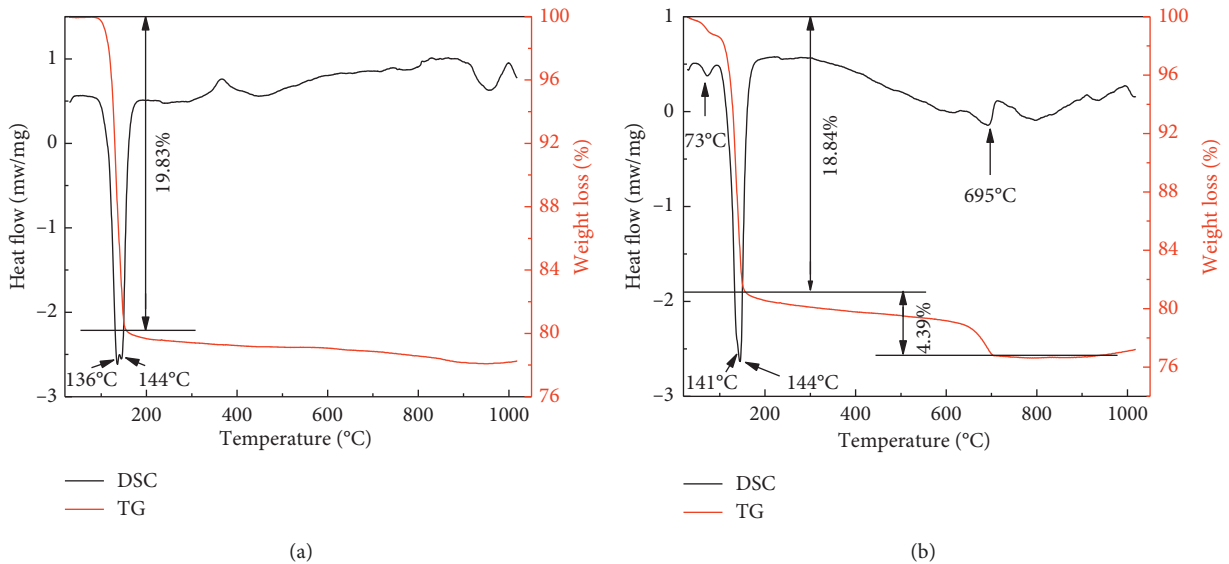


FIGURE 8: The constituent of hardened R-CP-0 and R-CP-10: (a) DSC/TG of hardened R-CP-0; (b) DSC/TG of hardened R-CP-10.

The DSC/TG of hardened R-CP-0 and R-CP-10 hydrated for 28 days is shown in Figure 8. Figure 8(a) shows the endothermic peaks at 136°C and 144°C due to dehydration of the hardened R-CP-0. However, the peaks of hardened R-CP-10 at 141°C and 144°C (Figure 8(b)) are reduced with the addition of OPC, and this is due to the existence of rehydrated AFt endotherms at 73°C. Moreover, the

appearance of an endothermic peak at 695°C is the formation of CaCO₃. This indicates that the hydration products of cement are also existed in the hardened R-CP, but their formation and existence mechanisms are not exactly the same as hardened POCP. Early researches which have been carried out on the strength development of rehydrated AFt proposed that AFt calcined at low temperature can be

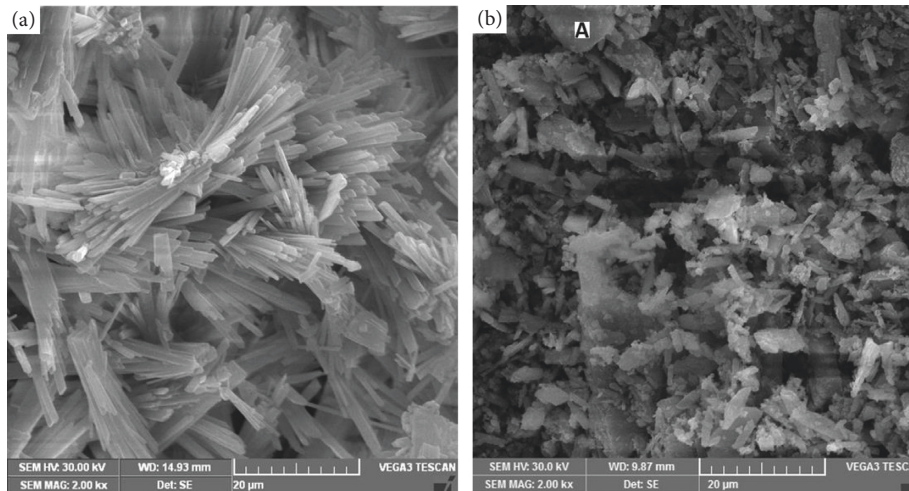


FIGURE 9: The microstructure of hardened (a) R-CP-0 and (b) R-CP-10.

rehydrated immediately upon addition of water, but its X-ray diffraction peaks are reduced and its strength is very low [25, 26]. Therefore, it can be concluded that although CaCO_3 and AFt existed in the hardened R-CP as well, low strength of CaCO_3 and rehydrated AFt reduce the strength of R-CP.

SEM images of hardened R-CP-0 and hardened R-CP-10 hydrated for 28 days are shown in Figure 9. In Figure 9(a), many cluster crystals existed in the hardened R-CP-0, but there are still a lot of crystals with relatively long length-radius intertwined. For hardened R-CP-10 (Figure 9(b)), the crystals turned into plate-like and rod-like crystals with low dimension, which weaken the complete development of crystals and their close overlapping of gypsum, thus leading to the worse performances with low strength results of R-CP-10. This change of crystals in the hardened R-CP-10 is caused by the interweaving of rehydrated AFt, CaCO_3 , and gypsum, which is also confirmed by the EDS of crystal A including the element of O, Al, Si, Ca, Fe, and S (Table 3). EDS is calculated based on the peak area and correction factor. It is found that the elements are essentially identical after performing several EDS points, and thus, the region A was chose. Briefly, the strength of R-CP is closely correlated with the microstructure of the hardened R-CP. The hardened R-CP-10 has a loose structure compared to the hardened R-CP-0, thereby decreasing their strength.

4. Conclusions

The hydration and mechanical properties of Portland cement-blended recycled plaster materials have been investigated. Clearly, the hydration of R-CP is accelerated by the formation of AFt. To our surprise, the strength of R-CP is decreased, which is not consistent with the conventional role of OPC in improving the strength of plaster of Paris. The reduced strength of R-CP is caused by their low hemihydrate content, low strength of rehydrated AFt and CaCO_3 , and poor crystals of hardened R-CP, as confirmed by SEM and DSC/TG. In principle, the research on Portland

TABLE 3: EDS of region A.

Element	Percentage of weight	Percentage of atom (%)
O K	48.27	64.81
Al K	9.86	7.85
Si K	16.64	12.72
S K	10.03	6.72
Ca K	13.55	7.26
Fe K	1.65	0.63

cement-blended recycled plaster materials will provide a theoretical basis of efficient utilization of waste gypsum.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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