PROCEEDINGS, Fourtieth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 22-24, 2016
SGP-TR-209

Influences of PLA on Properties of the CMC Self-degradable Temporary Sealing Materials for Geothermal Wells

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Keywords: poly lactic acid, self-degradation, temporary sealing material, geothermal wells

ABSTRACT

To deal with lost circulation during construction of geothermal wells, Brookhaven National Laboratory (BNL) has developed a temporary sealing material, which plugs fractures during drilling operations and opens them later by disintegration when the drilling is completed, by introducing carboxymethyl celluloses (CMC) into alkali-activated slag/fly ash cementitious material. Poly lactic acid (PLA) not only has been widely used in medical industry as additive for degradation of biocompatible bone cements, due to its biocompatibility and biodegradability; but also applied to fluid-loss control, fluid diversion, filter-cake removal in oil and shale gas fields for its degradability, in recent years. This paper aims at studying potential of PLA to further promote degradation of the temporary sealing material, by introducing PLA to the material. Thermo Gravimetric Analysis (TGA) was employed to study thermal decomposition behavior of PLA and effects of alkali-activated slag/fly ash cementitious material on it, the thermal decomposition temperature declined after PLA was treated by filtrate of the cement. Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS) was employed to study main products derived from the thermal decomposition of PLA. And the main products, gamma-butyrolactone, o-xylene, hexyl alcohol and 3-ethyl-3-buten-2-ol are in gaseous state at about 200℃. The addition of PLA could increase the material's fluidity, reduce specimens' surface cracks, and generate much more pores in specimens after 200℃-heated, compared with the temporary sealing material without PLA. Compressive strength of the 85℃-cured specimens declined as content of PLA increased, it was 6.76 MPa when the content reached 5%. The preliminary conclusion is: PLA has an ability of further promoting the self-degradation of the temporary sealing material.

1. INTRODUCTION

The researchers of Brookhaven National Laboratory (BNL) developed a temporary sealing material, consisted of a sodium silicate activator, slag, Class C fly ash and sodium carboxymethyl cellulose (CMC), has an ability of plugging the fractures at 85℃, and self-degrading after 200℃-heated and contact with water. They obtained conclusions that CMC of high molecular weight rendered two important features to the water-catalyzed self-degradation of heated cement: one was the high heat generated in exothermic reactions in cement; the other was the introduction of extensive porosity into cement (Sugama and Butcher, 2010; Sugama, Butcher, Brothers and Bour, 2011; Sugama and Pyatina, 2014; Sugama and Pyatina, 2015). It was also mentioned that the ideal sealer must not only plug the fractures at a low temperature of 85℃,but also it must self-degrade at the well temperature ⩾200℃.

PLA is sensitive to heat, it will degrade obviously when temperature is above 200℃ (Feng, Zhang and Ren, 2011). In medical operations, PLA was applied as additive in bone cement, when it comes in contact with body fluids, it will degrade to create high porosity of cements, thereby providing inter-connective channels for the bone (Zuo, Yang, Wolka, Li and Jansen, 2010; Habraken, Liao, Zhang, Wolke, Grijpma, Mikos, Feijen and Jansen, 2010; Groll, 2013). In our daily life, it was also used as the raw material to manufacture disposable articles, for example the fresh-food packaging, shopping bags and bed sheets, as it is able to degrade completely to CO_2 and H_2O, in environment (Carlo, Caterina , Agnieszka, Agnieszka, Roberto and Rana, 2015; Dharmalingam, Hayes, Wadsworth, Dunlap, DeBruyn, Lee, Wszelaki, 2015).

In recent years, PLA has been widely applied in various shale gas field and oilfield applications. It was composited with other materials to form degradable particulates in temporary sealant slurry, to seal preexisting fractures in subterranean, then degraded to remove the seal after the re-fracturing operations was finished (Halliburton Energy Services Inc., 2014). It was also employed in self-degradable diverter materials to form a diverter plug, to reduce risk of premature setting of the fracturing plug and avoid the need to drill out the plug before production and reduce the time for fluid flow back, compared with the fracture plugs which set into place (Halliburton Energy Services Inc., 2014). These materials containing PLA have been applied in shale gas field, to avoid employment of mechanical packers (Potapenko, Tinkham, Lecerf, Fredd, Samuelson, Gillard, LeCalvez and Daniels, 2009; Arnold, Boulls and Fragachan, 2014).

This paper investigates the influences of PLA on properties of the CMC self-degradable temporary sealing material by evaluating effects of PLA on compressive strength, fluidity, water absorption, surface cracks and self-degradation of the material. This paper also tested thermal decomposition properties of PLA and the effect of alkali-activated cement on it, and discussed the potential ability of PLA to further promote self-degradation of the material.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The slag used in this paper was obtained from Longang Trading Co., Ltd. of Tangshan city, and the Class C fly ash was supplied by Luyuan Power Resource Development Groups Co., Ltd. of Shandong province, the sodium silicate was supplied by Qingdao Yousuo Chemical Technologies, Inc of Shandong province, the CMC was supplied by Yanxing Chemical Industry, Inc. And the PLA was obtained from Changsheng New Materials Technologies, Inc., which also supplied the typical values (Table 1).

Table 1: Typical values of PLA.

Typical values	
Density(g/cm^3)	1.25±0.05
Molten rate g/10min(190℃， 2.6kg)	2~10
T_g(℃)	155~165
T_m(℃)	56~60
Tensile strength (MPa)≥	5
Elongation at break (%) ≥	3.0
Impact strength (KJ/m^3, Izod)	1~3

The formula of dry pozzolana cements employed in this test depended on our earlier work (Li, 2015), had slag/Class C fly ash ratio of 80/20 by weight. A 6 wt% sodium silicate by total weight of pozzolana cements was added to prepare the cement which was termed as C in this paper. To study the fluidity of all of the cement slurries employed in this paper, water was added in the same water/blend (w/b) ratio 0.6 for preparation. The cement C containing 1 wt% CMC is termed as CC. And the cement C containing 2, 5 and 10 wt% PLA is termed as PC1, PC2, PC3, respectively. And the cement CC containing 2, 5 and 10 wt% PLA is termed as PCC1, PCC2, PCC3, respectively, Table 2 shows the mix proportions. As the ideal sealer should plug the fractures at 85℃ and self-degrade at 200℃. The slurries were left at room temperature in air for 72 h, and then all set cements were cured at 85℃ for 24 h, some of the 85℃-cured cements were further heated for 24 h in an oven at 200℃.

To evaluate influences of the alkali-activated cement on PLA, powders of 4 g PLA was immersed into 50 ml filtrate of the slurry of cement C obtained from experiments of filtration. The filtrate with PLA was left at room temperature in air at room temperature for 72 h and cured at 85℃ for 24 h, then filtrated, washed, dried for further testing.

Table 2: Mix proportions of cements.

Sample	Mix proportions (wt %)		
	CMC	PLA	Water/blend
C	0	0	0.6
CC	1	0	0.6
PC1	0	2	0.6
PC2	0	5	0.6
PC3	0	10	0.6
PCC1	1	2	0.6
PCC2	1	5	0.6
PCC3	1	10	0.6

2.2 Measurements

Compressive strength of cements was tested by servo universal test machine at a loading rate of 17.1 kN/min. Three cubes of size 50.8 × 50.8 × 50.8 mm in dimension of cements were casted for the tests of compressive strength, and all specimens were demolded after 72 h of casting. The compressive strength σ was evaluated by using the following equation:

$$\sigma = F/A \tag{1}$$

where F is the maximum load, A is the cross-sectional area of the samples, 50.8 × 50.8 mm.

A conical die with 36 mm upper diameter, 60 mm lower diameter and 60 mm height, a square glass plate with 400 mm length and 5 mm thickness, a stopwatch and a steel ruler were employed to test cements' fluidity in this investigation. The moist conical die without water stains was placed on the clean glass plate, the cement slurry was injected into the conical die, rapidly and vertically lift the conical die up, then measured the maximum diameter at vertical directions of cement slurry on the glass plate, took average value of them, after 30 seconds.

Thermo Gravimetric Analysis (TGA) was employed to test the filtrate-treated and untreated PLA. And the tests were carried out in a N_2 flow at the heating rate of 10℃/min from room temperature to 450℃.

Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS) was employed to identify and quantify the volatile derivatives emitted by the decomposition of PLA. The chromatographic peaks were identified by referencing them to the NIST MS library and data in the literature, and by comparing their chromatographic retention times to those of the available reference chemical compounds.

For the water absorption test, the specimens were weighed (W_0) after 85℃-cured, and then the specimens were immersed in clean water in three deferent ways, at room temperature for 15 min, at 85℃ for 15 min, and after cooled in air for 24 h then immersed in water at room temperature. After the immersion period, the specimens were taken out and wiped quickly with wet cloth, and then the mass was weighed (W_1) immediately. The water absorption (W_A) was calculated by using the formula:

$$W_A = \frac{W_1 - W_0}{W_0} \times 100\% \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Compressive strength

The compressive strength of the 85℃-cured cements containing CMC or/and PLA are presented in Fig 2. The cement containing 1 wt% CMC exhibited an enhancement of 29.90% in the compressive strength, and the cement containing 2 wt% PLA increased by 10.57%, compared with the cement without CMC or PLA. Although the compressive strength of cement with CMC and PLA declined as the content of PLA increased, the addition of 2 wt% and 5 wt% PLA respectively decreased by 18.76%、63.56%, compared with the cement with CMC. Even so, the compressive strength of the cement containing 1 wt% CMC and 2 wt% PLA still increased by 5.53%, compared with the cement without CMC or PLA, and when the PLA content reached to 5 wt%, the value of the compressive strength is 6.76 Mpa.

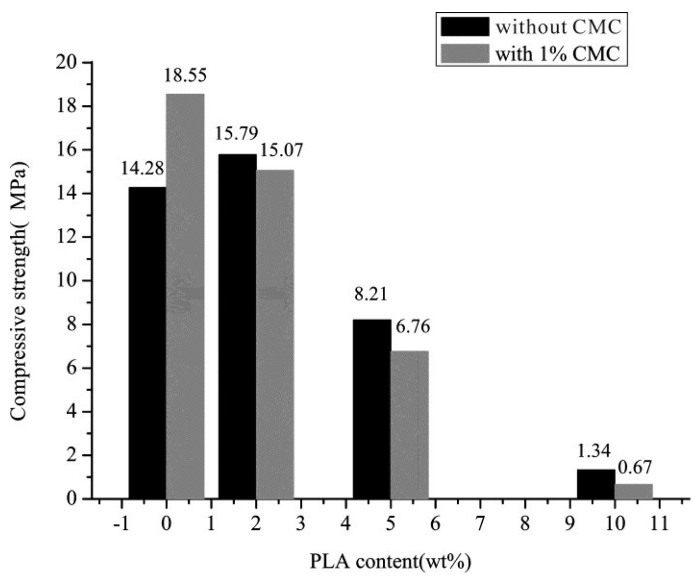


Fig 2: Compressive strength as a function of PLA content for 85℃-cured cements with and without CMC.

3.2 Fluidity

As the function of increasing the viscosity, the adding of 1 wt% CMC leaded to the fluidity of cement slurry declined from 17.7 cm to 16.2 cm. The effects of PLA on fluidity of cements with and without CMC were uniformed: a lower content of PLA enhanced the fluidity, but a higher content decreased the fluidity. The adding of 2 wt% PLA to the cement without CMC or PLA resulted to increase the fluidity from 17.7 cm to 18.6 cm. And the fluidity of the cement containing 1 wt% CMC increased from 16.2 cm to 18.6cm, resulted from the addition of 2 wt% PLA.

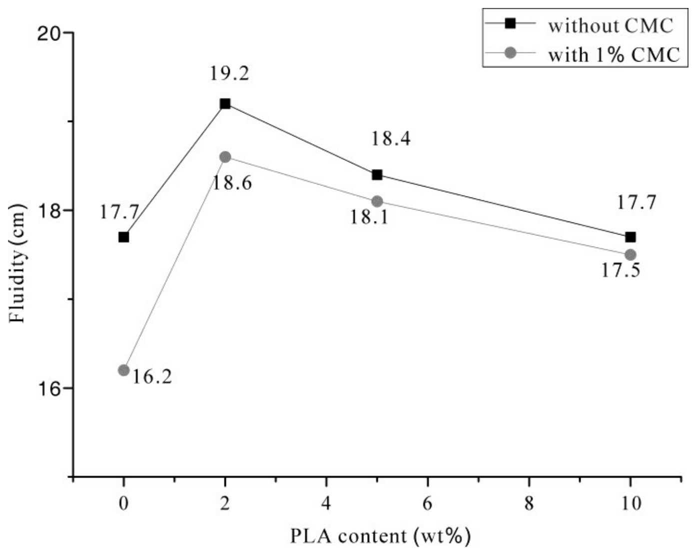


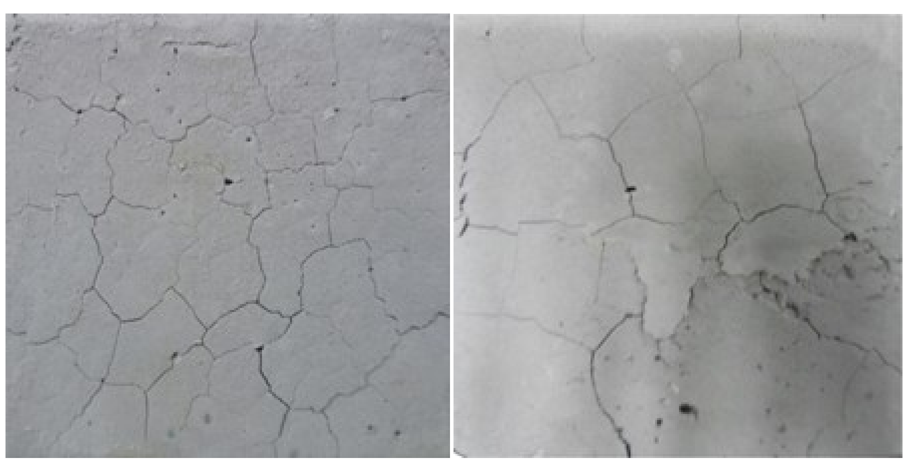
Fig 3: Influence of PLA content on fluidity of cement with 1% CMC or with no CMC

3.3 Water absorption and density

Table 3 shows that, although the water absorption of the 85℃-cured specimens immersed in three different ways displayed uniform variance trends that the water absorption decreased as PLA content increased, the decrease in the first immersed condition was not obvious as the second and third conditions. It can be also found that the water absorption of the samples tested in the water absorption experiment was declined, after the specimens were cooled in air at room temperature for 24 h. Fig 4 shows that the surface cracks of specimens reduced as the PLA content increased, and this leaded to the phenomenon that the water absorption of the cement with a higher content PLA was smaller than the cement with a lower content, in such a short time.

Table 3: Water absorption of 85℃-cured specimens and densities of the cement slurries.

Sample	Density (g/cm^3)	Water absorption (wt%) at different temperatures		
		85℃	Room temperature	Room temperature (after cooled)
CC	1.71	43.65	43.85	38.49
PCC1	1.71	43.55	43.10	37.83
PCC2	1.69	43.29	42.21	36.89
PCC3	1.68	42.62	34.58	25.96



(a) (b)

(c) (d)

Fig 4: (a) The surface cracks of specimens with 1% CMC and 0% PLA.

(b) The surface cracks of specimens with 1% CMC and 2% PLA.

(c) The surface cracks of specimens with 1% CMC and 5% PLA.

(d) The surface cracks of specimens with 1% CMC and 10% PLA.

3.4 TGA study

Fig 5: Comparison of the PLA in filtrate, before and after left at room temperature for 72 h and cured at 85℃ for 24 h.

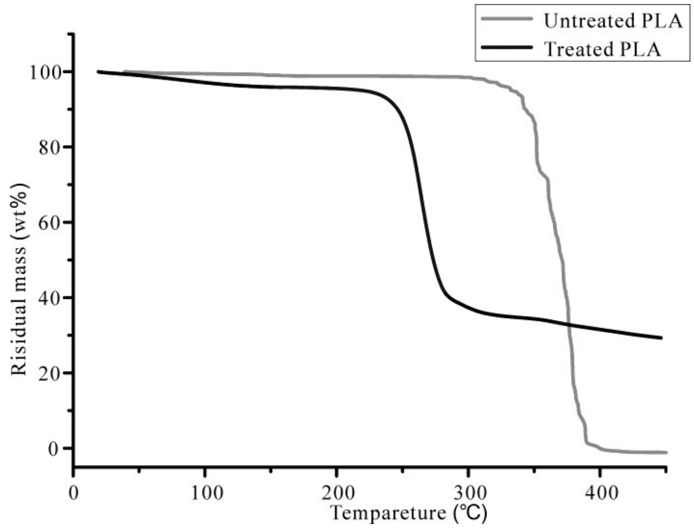


Fig 6: TGA curves for the filtrate-treated and untreated PLA.

After treated by the filtrate of cement C, the weight of PLA reduced from 4.06 g to 2.50 g. It can be observed in Fig 5 that particles of PLA powder became smaller. Fig 6 shows that the thermal decomposition temperature of PLA declined from 350℃ to 275℃, after treated by filtrate. This phenomenon properly resulted from the hydrolytic decomposition of PLA (Zhang, Maria, Alex and Lusiana, 2008; Zhang, Cui, Song and Qiu, 2008), as it was exposed to alkaline condition at elevated temperature.

3.5 Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS) study

Fig 7 and Table 4 show the main products, of which area account for more than 2.5% of total, derived from the thermal decomposition of PLA, gamma-butyrolactone, o-xylene, hexyl alcohol and 3-ethyl-3-buten-2-ol are in gaseous state at about 200℃. Although the boiling point of gamma-butyrolactone is 204℃, it can evaporate with water vapor; and the boiling point of o-xylene, hexyl alcohol and 3-ethyl-3-buten-2-ol is 144.4℃, 157℃ and 115.9℃, respectively. The gaseous products resulted in the more pores of cement, and thus promoted the self-degradation of cement, when the temperature was above 200℃.

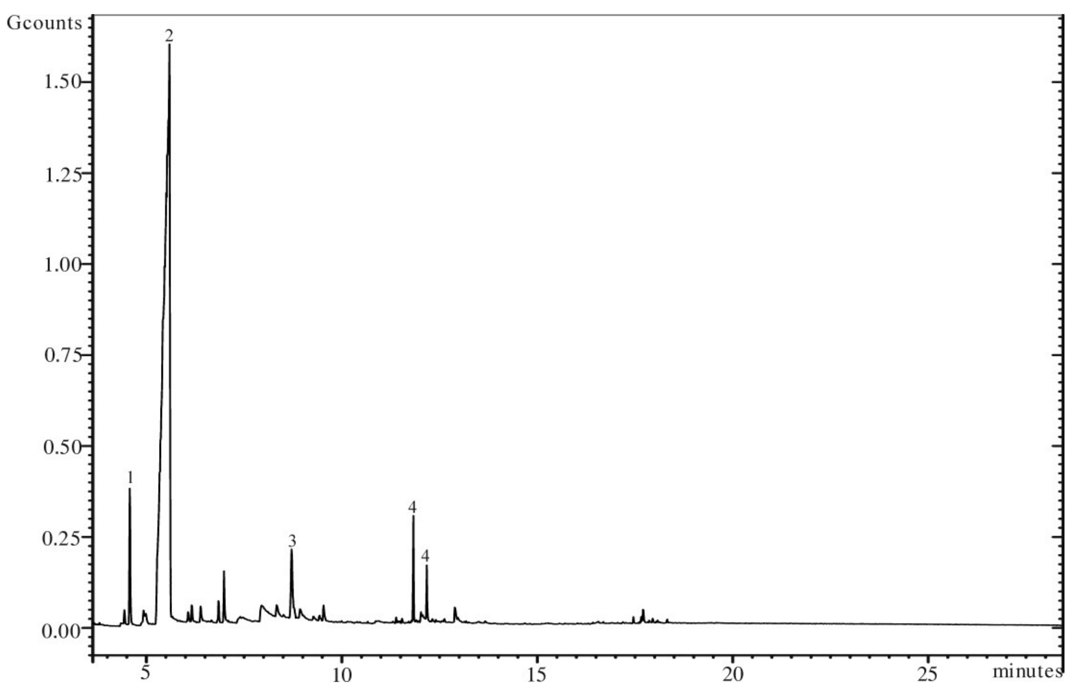


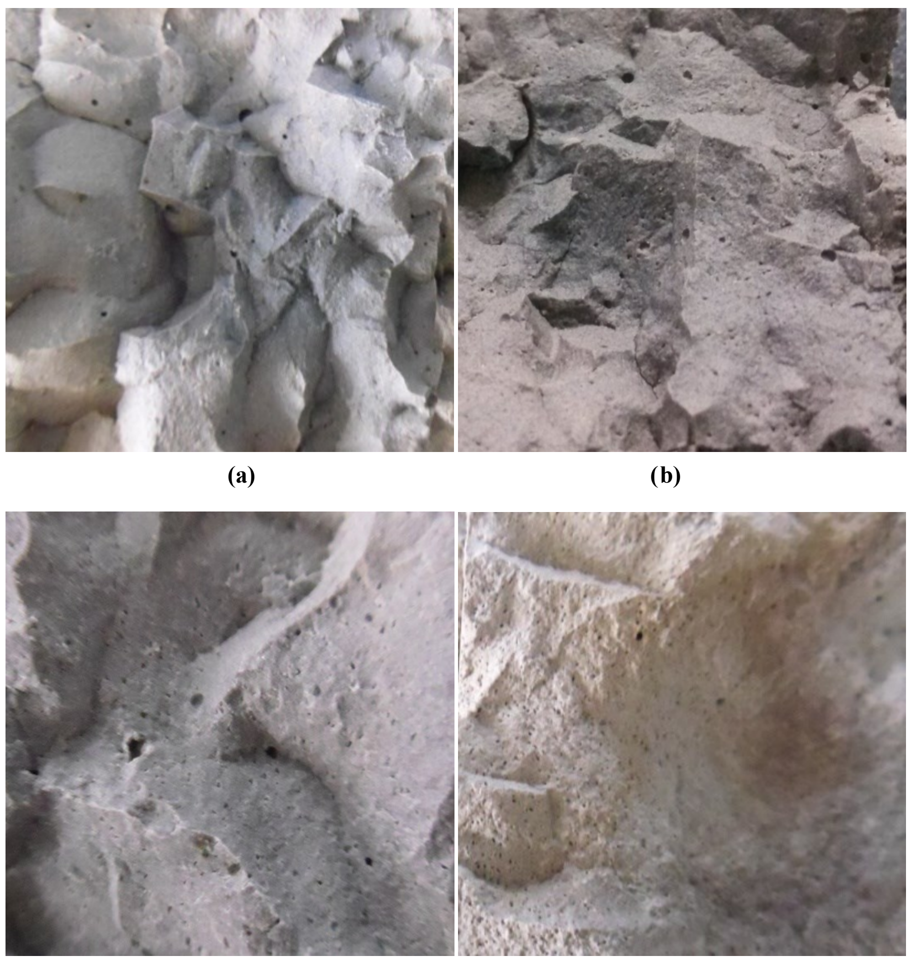
Fig 7: Py-GC/MS abundance-retention time curve of PLA.

Table 4: Pyrolysis derivatives along with their area %of total obtained from Py-GC/MS for PLA

ID number	Retention time(min)	Compound	Area %of total
1	4.577	O-xylene	3.286
2	5.514	Gamma-butyrolactone	82.907
3	8.717	Hexyl alcohol	2.952
4	11.829	3-Methylpent-1-en-3-ol	1.676
4	12.174	3-Methylpent-1-en-3-ol	2.644

3.6 Self-degradation

To observe the self-degradation of the cements, the specimens were immersed in water immediately at room temperature, after cured at 85℃ and heated in oven at 200℃for 24 h. All of these specimens could be broken by hand: the PCC3 could be broken very easily; CC specimens needed more pressure, and crumbled along the surface cracks. Fig 8 shows that the internal structures of specimens of CC, PCC1 and PCC2 were granular, and the granular structure made the cements harder, but the same structures were not found in specimens of PCC3. The amount of pores in specimens increased from CC to PCC1, PCC2 and PCC3 in order, revealed the more PLA was contained in cement, the more pores were generated. In addition, it predicted that the addition of PLA introduced more pores in the CMC self-degradable materials, thus promoted the self-degradation of the materials.



(a) (b) (c) (d)

Fig 8: (a) The pores in specimens with 1% CMC and 0% PLA.

(b) The pores in specimens with 1% CMC and 2% PLA.

(c) The pores in specimens with 1% CMC and 5% PLA.

(d) The pores in specimens with 1% CMC and 10% PLA.

4. CONCLUSIONS

This study aimed at studying the influences of PLA on properties of the CMC self-degradable temporary sealing material for geothermal wells by introducing PLA powders to the material. The conclusions obtained in the current study are as follows:

Although the compressive strength of the 85℃-cured PLA and CMC modified alkali-activated slag/fly ash cement decreased as the PLA content increased, the cement containing 1 wt% CMC and 2wt%PLA still increased by 5.53%, compared with the cement without CMC or PLA. This implied that a higher compressive strength could be still obtained by a low PLA content.

PLA was able to increase cements' fluidity, to relieve the problem that CMC reduced the fluidity and increased cement water demand. The increment of PLA content reduced the surface cracks of 85℃-cured cement, thus reduced the water absorption.

The thermal decomposition temperature of PLA declined after treated by filtrate of the cement, and the main products of the thermal decomposition were in gaseous states when the temperature was above 200℃, the introducing of PLA could generate much more pores in cement. In summary, PLA has an ability to further promote the self-degradation of the temporary sealing materials.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge Project 43572361 "Design and Preparation of Green Environmental- Friendly of Self-degradable Foamed Temporary Cementitious Sealing Materials for Geothermal Reservoir" supported by National Natural Science Foundation of China.

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