MINERAL POLYMER BASED ON FLY ASH

J. Wastiels; X. Wu, S. Faignet, G. Patfoort

Dept. of Civil Engineering
Vrije Universiteit Brussel
Pleinlaan 2
1050 Brussels
Belgium

ABSTRACT

The mineral polymer composition used in this study is basically a two-phase system composed of solid particles of fly ash and an aqueous silicate solution. The polymerization of these components can be realized at low temperature (<100°C) and atmospheric pressure, resulting in a solid network structure. Present study is related to the characterization of fly ash based mineral polymer. DSC, TGA, TMA, mechanical tests and acid resistance tests were carried out. The effect of the amount of NaOH and SiO_2 in sodium silicates on the strength of the material has been studied to optimize the composition. The results show that fly ash based mineral polymer has a high mechanical strength, low thermal shrinkage, and low thermal expansion coefficient in the range of 25-600°C. When using suitable filler materials with appropriate granulometry, Mineral polymer concrete with good properties can be made. Resistance of the concrete against sulfuric acid attack was tested, and the results show that fly ash based mineral polymer has a very good acid resistance.

Key words: Mineral polymer; Fly ash; Sodium silicate; Optimization; Mechanical strength; Acid resistance

1. INTRODUCTION

Pulverized coal fly ash is a by-product of the combustion of pulverized coal in thermal power plants. It is removed by the dust collection system as a fine particulate residue from the combustion gases before they are discharged into the atmosphere. As more and more power plants are being built in the world, fly ash production is increased every year, and more land is required for its landfilling. If the fly ash cannot be properly used, its disposal will certainly cause environmental contamination and affect our life in the long run.

Pulverized coal fly ash comprises mainly chemical compounds and glasses formed from the elements Si, Al, Fe, Ca, and Mg, where certain amount of the Si-Al compounds is present as meta-stable alumino-silicates which results in certain pozzolanic activity. Because of this, main application of the fly ash so far, is to replace part of Portland cement in blended cement composition(1), where fly ash to cement weight ratio is ca 0.2-0.4, and early strength of the material is said lower than that without using the fly ash.

On another approach, to get a reliable material from the fly ash, study of mineral polymer (MiP) system in Dept. of Civil Engineering, Vrije Universiteit Brussel (VUB, Belgium), has shown a route in which pulverized coal fly ash can react with alkali silicate aqueous solutions to form a solid mass(2,3). Reaction between fly ash and sodium silicate aqueous solution might yield a feldspatoid material (referred to as fly ash MiP hereafter) composed mainly of the inorganic macromolecules made up by SiO_4 and AlO_4 tetrahedra linked by sharing oxygen atoms(4). Because the technique takes advantage of existing meta-stable alumino-silicate macromolecular structure to promote the reaction, polymerization can be realized at low temperature and at atmospheric pressure in a limited duration. Strength of this material is found higher compared to that of normal Portland cement material. As a contribution to the fly ash waste management, this technique offers a good approach to explore the value of the pulverized coal fly ash, independent of the normal Portland cement compositions.

This paper studies the influence of NaOH and SiO_2 in sodium silicate on mechanical strength of MiP material, and the behavior of the material in acid condition. Differential scanning calorimetry (DSC), thermal gravimetry analysis (TGA), thermal mechanical analysis (TMA), and mechanical tests were carried out. For the optimized composition, efflorescence and acid resistance tests were performed. Mainly compressive strength of the material was used as criterion to evaluate the material. It will be shown that the easy processing and raw materials availability of MiP permits to produce an engineering material with energy saving, which provides a base for a world-wide application.

2. PROCESSING AND MECHANICAL TESTING

Fly ash MiP studied in this paper was composed of pulverized coal fly ash and sodium silicate aqueous solution. The pulverized coal fly ash was obtained from thermoelectric power plant in Langerlo, Belgium. Oxide analysis and granulometry of the fly ash are presented in Table 1 and Figure 1 respectively.

Three series of sodium silicate aqueous solutions were used which results in three series of fly ash MiP material. Compositions of fly ash MiP and their corresponding sodium silicate are presented in Table 2. M is molar ratio of SiO_2/Na_2O of sodium silicate.

Mixing of the composition was performed in a planetary mixer until all components were homogeneously distributed. The resulting mixture is castable. Vibration was applied during cast molding. Curing of the composition was carried out at 60°C in a covered condition at atmospheric pressure for 24 hrs. Then the sample was taken out of oven, left in an environmental condition and cooled down to room temperature.

Compressive strength of the sample was tested by an INSTRON 1195 universal machine. Both dry (dried at 40°C for three days) and wet (immersed under water at room temperature) specimens were used. Specimen size was approximately 20mm x30mm x40mm. Loading surface was 20mm x40mm except specially mentioned. Each property shown in tables is a mean value of three test results.

3. INFLUENCE OF AMOUNT OF REACTIVE ON STRENGTH OF MATRIX

3.1 Exothermic Reaction

The reaction between the pulverized coal fly ash and sodium silicate is exothermic, which results in a solid mass with high strength. A typical DSC thermogram of the reaction is shown in Figure 2, with composition C1 as an example. The reaction enthalpy is $\Delta H=59.2$ J/g; and peak temperature is $T_{peak}=114.9$°C. It demonstrates that the polymerization can be carried out at low temperature.

3.2 Influence of NaOH and SiO2 in Silicate on Strength of Matrix

Three series of MiP composition were designed. Optimal composition can be obtained by investigating the influence of the amount of NaOH and SiO_2 in sodium silicate on strength of the material, as shown in Table 3. The VA in the table means the pulverized coal fly ash.

Series A studies the effect of the amount of NaOH in the sodium silicate on the compressive strength of MiP by fixing the amount of SiO_2; series B investigates the influence of the amount of NaOH and SiO_2 in the sodium silicate on the strength of the material by fixing M=1; while series C demonstrates the effect of the amount of SiO_2 in the reactive on the strength of MiP by fixing the amount of NaOH. Through this study, a composition with good mechanical strength can be obtained (C1). Compositions B3 and C3 are cross points of the three series compositions.

For series C, it is found that its strength, specially C1 and C2, are higher than normal Portland cement for a corresponding sand/cement ratio. Wet strength is lower than dry strength, but their difference is limited, and is not a sign of degradation under humid conditions.

3.3 Behavior at High Temperature

Weight loss and dimensional change of the fly ash MiP matrix were measured by Thermal gravimetry (TGA, Figure 3) and thermal mechanical analysis (TMA, Figure 4).

Figure 3 shows that the total weight loss of the material in the range of 25-1000°C is ca 12%. The majority of the weight loss occurs below 200°C. The weight loss is due to evaporation of H_2O employed in the composition.

Figure 4 shows that the thermal shrinkage in the range of 25-600°C is ca 4%. The first shrinkage occurs in the range of 150-250°C, and is caused by dehydration. The second shrinkage occurs at ca 600°C; this might be due to transformation of the silicate structure since there is no significant weight loss observed. By reheating the sample from 25°C to 600°C, no further shrinkage occurs. This shows that, once heated to high temperature, the structure of fly ash MiP is stable at high temperature. Thermal expansion coefficient is about 8-9 $\times 10^{-6}$/°C in the range of 25-600°C.

4. FLY ASH MIP CONCRETE

4.1 Strength of Fly Ash MiP Concrete

MiP concrete was made by adding extra quartz sand and gravel into the matrix C1. Composition and other properties of the MiP concrete are shown in Table 4 and Table

TABLE 1
Oxide Analysis of Fly Ash Used

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	Na_2O	K_2O	P_2O_5	SO_3
wt%	42.99	39.37	3.58	4.90	1.75	0.25	0.19	0.35	0.57	3.70

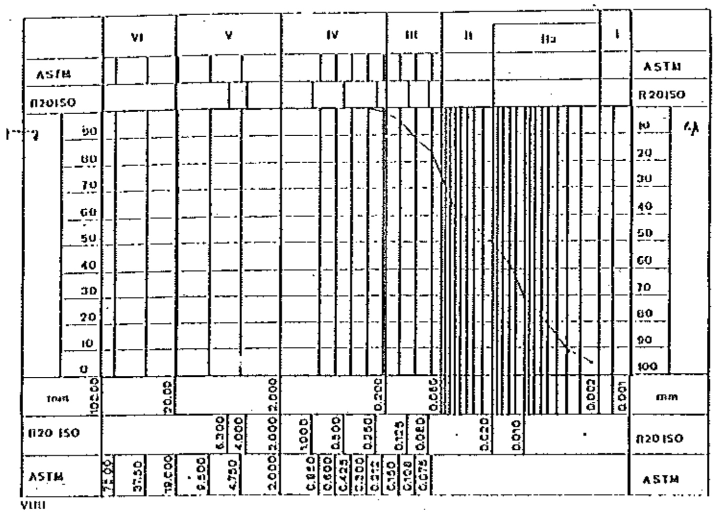

FIGURE 1
Granulometry of Fly Ash

TABLE 2
Composition of Fly Ash MiP Matrix

Sample		*Sodium silicate solution*			*Fly ash*	*Quartz sand 0-0.6 mm*
	M	*NaOH* g	SiO_2 g	H_2O g	g	g
A1	1.7	5.3	6.8	37.0	100.0	100.0
A2	1.4	6.4	6.8	37.0	100.0	100.0
A3	1.0	9.0	6.8	37.0	100.0	100.0
A4	0.7	13.8	6.8	37.0	100.0	100.0
B1	1.0	5.3	4.0	37.0	100.0	100.0
B2	1.0	6.4	4.8	37.0	100.0	100.0
B3=A3	1.0	9.0	6.8	37.0	100.0	100.0
B4	1.0	13.5	10.1	37.0	100.0	100.0
C1	1.2	13.5	12.2	37.0	100.0	100.0
C2	1.1	13.5	11.1	37.0	100.0	100.0
C3=B4	1.0	13.5	10.1	37.0	100.0	100.0
C4	0.8	13.5	8.1	37.0	100.0	100.0

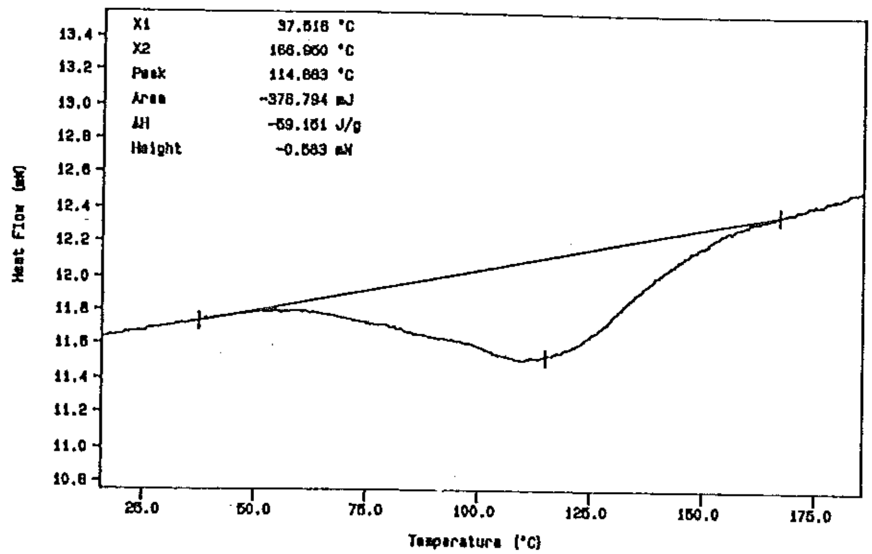

FIGURE 2
DSC Thermogram of Sample C1

TABLE 3
Compressive Strength of Matrix

Sample	*NaOH/VA wt %*	*SiO_2/VA wt %*	*Dry compressive strength MPa*	*Wet compressive strength MPa*
A1	5.3	6.8	6.1	3.5
A2	6.4	6.8	10.1	6.3
A3	9.0	6.8	28.4	17.8
A4	13.8	6.8	44.3	29.2
B1	5.3	4.0	3.1	1.5
B2	6.4	4.8	8.2	5.6
B3=A3	9.0	6.8	28.4	17.8
B4	13.5	10.1	48.1	35.6
C1	13.5	12.2	63.1	51.5
C2	13.5	11.1	53.8	46.9
C3=B4	13.5	10.1	48.1	35.6
C4	13.5	8.1	35.2	28.4

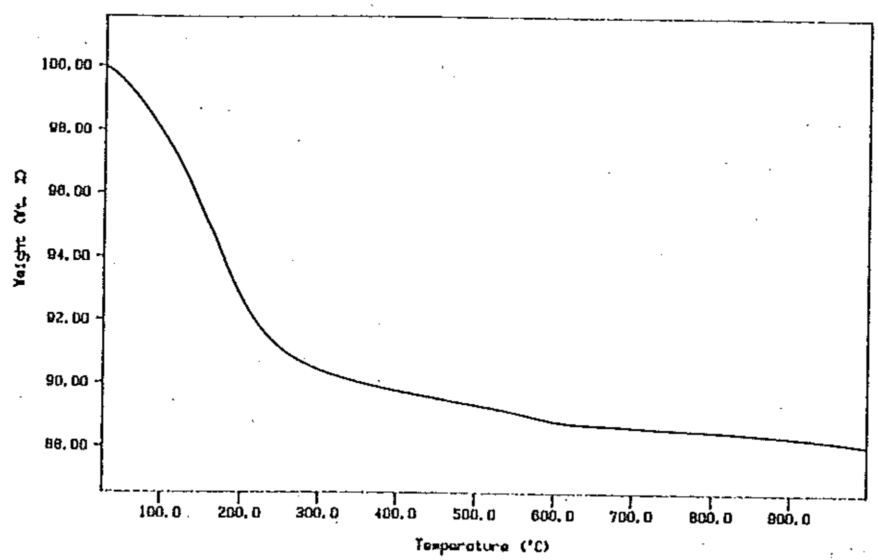

FIGURE 3
TGA Curve of the Fly Ash MiP (Sample C1)

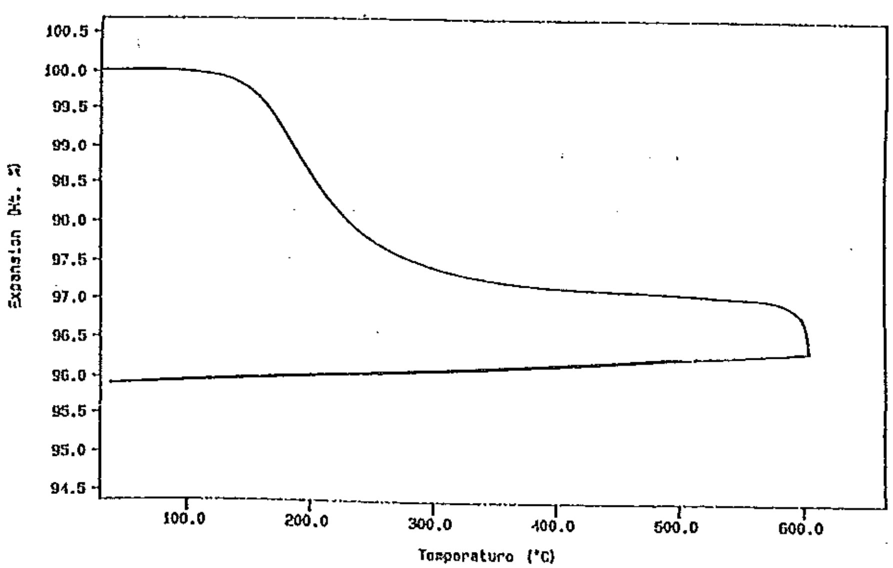

FIGURE 4
TMA Curve of the Fly Ash MiP (Sample C1)

TABLE 4
Composition of Fly Ash MiP Concrete

Component	*Kg per m³*
MiP matrix C1	532.3
Quartz sand (0-3 mm)	687
Gravel (7-14 mm)	1373

TABLE 5
Compressive Strength of MiP Concrete

Sample	*Dry density g/cm3*	*Porosity vol %*	*Compressive strength Dry, MPa*	*Compressive strength Wet, MPa*
MiP concrete	2.30	11.24	56.4	52.7

5 respectively. Cylindrical specimens (70mm xΦ45mm) were used for the measurement.

It is seen that strength difference between dry and wet fly ash concrete is not large (Table 5). Compared to that in Table 3, the strength of MiP concrete is comparable to that of MiP matrix. By examining the fractured surface of the concrete, it is seen that the fractured surface runs through the gravel. This shows that increasing strength of the fly ash concrete depends on using a gravel with higher mechanical strength.

4.2 Acid Resistance Test

Resistance against sulfuric acid attack was tested using fly ash MiP concrete by immersing the specimen in 20% H_2SO_4 solution for 14 weeks. Cylindrical specimens (70mm xΦ45 mm) were used. Compressive strength (according to ASTM C39-83b), weight loss and length change of specimens were monitored every two weeks (except for the 12th week). Accuracy of the length measurement is ±0.5%. Dry density and porosity (according to ASTM C642-82) before and after the test was measured. The results are presented in Table 6. Weight loss and linear shrinkage were calculated according to:

$$\frac{Property(0\ week)-Property(n\ week)}{Property(0\ week)}$$

The strength of the concrete is reduced as the test continues, but after six weeks, it becomes nearly constant. No significant sample swelling was observed, which shows a remarkable difference with Portland cement based concrete. The dimensional change is within the range of the accuracy (±0.5%). The weight loss of the sample is very small; this is reflected by the small change of the porosity and dry density values before and after the test. Weight loss is mainly due to residual alkali silicate in the concrete. The results indicate that the fly ash MiP concrete has a very good resistance against sulfuric acid.

5. DISCUSSION OF RESULTS

1. A technical route is established to use pulverized coal fly ash as primary reactive raw material for low temperature setting composition (fly ash mineral polymer). Attention must be drawn to its raw materials availability and economical cost.
2. Fly ash mineral polymer has a higher strength compared

TABLE 6
Properties of MiP Concrete During Acid Test

Duration	*Compressive strength, wet*	*Porosity*	*Dry density*	*Weight loss*	*pH of solution*	*Linear shrinkage*
week	*MPa*	*vol. %*	*g/cm3*	*wt %*		*%*
0	52.7	11.24	2.30	--	0	--
2	48.3	--	--	0.75	0	0.0
4	44.9	--	--	0.79	0	0.4
6	38.4	--	--	0.83	0	0.0
8	40.5	--	--	0.94	0	0.1
10	38.5	--	--	1.02	0	0.4
14	37.4	12.73	2.21	1.13	0	0.3

to that of normal Portland cement. Specially, it is shown that the composition has an excellent resistance against acid attack.

3. The quality of fly ash mineral polymer will be influenced by the quality of the pulverized coal fly ash supplied. Suitable techniques of quality control needs further study.

ACKNOWLEDGEMENT

The authors wish to thank the Dept. of Physical Chemistry of VUB for DSC, TMA and TGA measurement; and are grateful to VUB Research Council for financial support.

REFERENCES

1. Malhotra, V.M. (Ed.), *Supplementary Cementing Materials for Concrete*, CANMET, 1987.
2. Wastiels, J. and G. Patfoort, *Minerale Polymeren en Hergebruik van Afval*, Studiedag KVIV "Industriële afval als bouwmateriaal," Brussel, 1988 (in Dutch).
3. Patfoort, G. and J. Wastiels, *Verwerking van Vliegassen tot Konstruktiematerialen door Minerale Polymerisatie*, 9th Seminarie Beheer van Afvalstoffen, Brussel, 1989 (in Dutch).
4. Wu, X. and J. Wastiels, *Detoxification of Fly Ash from Incineration Plants*, Proc. of 13th Annual Conf. of Waste Prevention, Reduction & Recycling, Brussels, 1993.