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Transition from brittle to ductile behavior of fly ash using PVA fibers

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Abstract

In this study, short polyvinyl alcohol (PVA) fibers are employed to improve the mechanical properties of brittle fly ash samples, which are solidified by a small amount of sodium hydroxide (NaOH) and by a hydrothermal hot-pressing process. The mechanical properties of the PVA fiber reinforced fly ash composites are evaluated by splitting tensile test. Several key factors such as fiber content, processing temperature, and processing duration are investigated. The effect of different types of fly ash (Class C vs. Class F) is also studied. The experimental results demonstrate that the addition of short PVA fibers can significantly improve the ductility of the fly ash composites. The optimum fiber volume content is estimated to be 1.0% with Class C fly ash.

Keywords: Fly ash; Fiber reinforcement; Splitting tensile test; Hydrothermal hot-pressing

1. Introduction

1.1. Fly ash production, utilization and problems

In the United States, over 50% of the electricity is produced by coal fired electric utilities and almost 90% of the coal used in this country is burned to generate electricity [1]. Fly ash is the main residue from coal burning. As a result, million tons of fly ash are produced annually. However, only a limited portion (less than 35%) of fly ash is recycled at present. Fig. 1 shows the production and use of fly ash from 1995 to 2002 [1]. The majority of fly ash is disposed of at landfills, which creates environmental problems. In addition, a surcharge of landfill is overwhelmingly required in many areas. Therefore, new recycling strategies are necessary to produce value-added products from fly ash instead of considering it as waste material that needs disposal.

Among the current limited use of fly ash, application in the field of cement and concrete production accounts for a large portion of over 50%. Other applications include structural fill, waste stabilization, mining, soil modification and stabilization, and artificial aggregates [2]. In addition to these traditional applications, emerging technologies to make high performance inorganic polymers from fly ash are under investigation in many countries, such as Australia [3,4], the United States [5], Spain [6], and South Africa [7].

1.2. Activation of fly ash

Fly ash has pozzolanic property, but its reactivity is very low in its as-received conditions. To date, several approaches are used to activate, or accelerate, the reactivity and pozzolanic reaction of fly ash. These approaches include (1) mechanical treatment (grinding) [8], (2) accelerated curing, hydrothermal and autoclaving [6,9–13], and (3) chemical activation [6,9–12]. In summary, the following conclusions can be reached from the various activation methods:

- The reactivity of fly ash is very low under as-received conditions from power plants.

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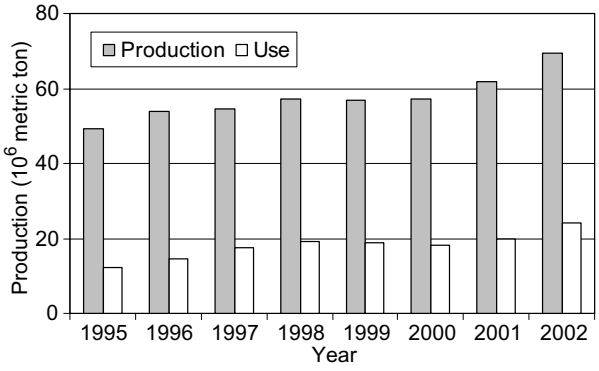

Fig. 1. Fly ash production and use in USA (1995–2002, reproduced from [1]).

- The reactivity of fly ash increases with the increase of curing temperature and time.
- Chemical activation is more efficient for increasing the reactivity of fly ash than grinding and autoclaving.
- The combined use of some chemical activators shows better results than the individual constituent alone. The pH value of the chemical environment is a significant determinant for fly ash activation.
- Class F and Class C fly ash show different response to the same chemical activator. In general, Class C is more reactive than Class F under the same conditions.

It is found that a synergistic use of chemical activation and hydrothermal hot-pressing produces very strong fly ash samples compared to mixes of inactivated fly ash [19]. Hydrothermal process involves hot water under pressure to carry out dissolution, leaching, and precipitation reaction. Fly ash can be solidified and shows splitting tensile strengths of 0.96–1.24 MPa by hydrothermal hot pressing alone. With a small amount of chemical activator (sodium hydroxide), the tensile strength can reach as high as 5.4 MPa [19]. However, these fly ash samples are very brittle.

1.3. Short fiber reinforcement of brittle materials

For brittle materials, such as cement, concrete, fly ash, etc., increasing their ductility and toughness has been a major motivation for many research works in recent years [2]. By using fibers in a relative weak (in tension) brittle matrix is one of the effective ways. Reinforcing fibers in a brittle–matrix composite serve mainly three functions [14]: (1) increase toughness of the composites by providing energy absorption mechanism related to de-bonding and pull-out of the fibers that bridge cracks, (2) increase ductility of the composites by permitting multiple cracking, and (3) may increase strength of the composites by transferring stresses and loads across cracks.

When a brittle composite is loaded up to its first cracking strength under uniaxial tensile loading, a first macroscopic crack is formed in the composite. The composite load across the crack will then be shared by the bridging fibers. These fibers then transfer the load via their interface back into the matrix. If enough load is transferred, the matrix may crack again and the process repeats until the matrix is broken by a series of sub-parallel cracks [15]. Because of opening of each individual crack and a large numbers of such parallel cracks, the tensile deformation (ductility) of composites can be significantly increased. During the process of multiple cracking, the composite load can even rise and exceed the first cracking strength of the composite [16]. When a macroscopic crack starts to open, the bridging stress increases as fiber/matrix interfaces de-bond and the de-bonded segments of fibers stretch. Eventually either fiber pull-out or fiber rupture occurs leading to final failure of the composite.

Typical fibers used could be metallic, polymeric or ceramic. Metallic fibers have high modulus and high strength. Their behavior is ductile but they are heavy and susceptible to corrosion. Polymeric fibers are strong and ductile but their modulus is relatively low. Ceramic fibers are generally strong and stiff but brittle. In addition to the commonly used virgin fibers, some recycled fibers can also be used for engineering purposes [17].

1.4. Research approach

In a previous study [19], the properties of the fly ash (both Class C and F) samples made from a synergistic combination of chemical activation and hydrothermal hot-pressing were evaluated, and the following conclusions have been drawn:

- Hydrothermal condition had a positive effect on the splitting tensile strength of fly ash specimens. But its effect was much less evident in the case when the chemical activator (sodium hydroxide) was used. In other words, sodium hydroxide was so effective that it dominated the strength gain.
- Mechanical pressing during hydrothermal process could favor chemical reaction between sodium hydroxide and fly ash, and could achieve more compact microstructure. The splitting tensile strength was improved significantly by mechanical pressing.
- Both high temperature and high dose of sodium hydroxide enhanced reactivity of fly ash, hence higher splitting tensile strength was reached.
- Class F showed lower reactivity in strength development under the same hydrothermal hot-pressing conditions than Class C.

In the second phase of the research program, short reinforcing fibers are used to further improve the brittle properties of the plain fly ash specimens, especially the ductility of the specimens. The research findings are reported in this paper.

2. Experimental program

2.1. Materials

Both Class C and Class F fly ash (provided by American Electric Power Energy Services) per ASTM C618 [18] are studied, and their chemical compositions are listed in Table 1. Sodium hydroxide flakes from Fisher Scientific are used as chemical activator. The short PVA fibers (Fig. 2) are produced by Kuraray Company in Japan and the properties of the fiber are listed in Table 2.

2.2. Sample preparation

The starting materials used in this study include fly ash (Class C or F), water, a small amount of sodium hydroxide (NaOH) serving as chemical activator, and short PVA fibers if used. The content of NaOH is expressed by the concentration (Molarity) of the NaOH solution and the weight ratio of the NaOH solution to raw fly ash (L/S ratio). And the fiber content is expressed as the volume fraction of the fiber in the composite.

Table 1
Chemical compositions (% mass) of Class C and Class F fly ash used in this study (from American Electric Power Energy Services)

Component	Class C	Class F
Silica	38.6	57.8
Aluminum oxide	21.1	29.5
Iron oxide	6.2	2.9
Titanium oxide	1.6	1.5
Calcium oxide	22.0	0.7
Magnesium oxide	4.4	0.7
Sodium oxide	1.3	0.2
Potassium oxide	0.6	2.3
Sulfur trioxide	1.1	0.3
Phosphorus pentoxide	1.1	0.1
Barium oxide	0.7	0
Manganese oxide	0	0
Strontium oxide	0.4	0
Total carbon	0.5	3.3
Other	0.1	0.4
Total (%)	99.7	99.7
Loss on ignition (%)	0.66	3.66
Specific gravity	2.52	2.09

Table 2
Properties of the PVA fiber used in this study (from Kuraray Company)

Diameter (μm)	Length (mm)	Specific gravity	Modulus (GPa)	Tensile strength (MPa)
37	15.0	1.30	40	1800

The NaOH solution is first prepared and cooled to room temperature before use. The starting materials are mixed for 5 min and then filled in the cylinder chamber of a specifically designed mold, which can achieve both hydrothermal and hot-pressing conditions at the same time when mounted on a MTS machine. The structural detail of the mold has been described elsewhere [19]. The mold is mounted on a MTS 810 machine. The MTS hydraulic piston compresses the mold, permitting a pressure built-up at a rate of 1.0 MPa/min until a specified value (20 MPa is used in this study).

After the pressure reaches the set value, an AVS Series 3210 Split Tube Furnace (305-mm outside diameter and 406-mm high), also mounted on the MTS machine, is then closed to heat the sample at specified temperature. While the sample inside the sealed mold is held under pressure and at an elevated temperature, hydrothermal hot-pressing condition is achieved.

When a specified heating time is reached, the power of the furnace is turned off. With the decrease of the temperature, the pressure on the sample reduces due to sample shrinkage. After the pressure is diminished almost completely, the mold is removed from the MTS machine, and cooled further in air. Fig. 3 shows a typical load history curve.

After the mold cools completely, the cylindrical sample of 25.4 mm diameter is demolded and cut into 50.8 mm

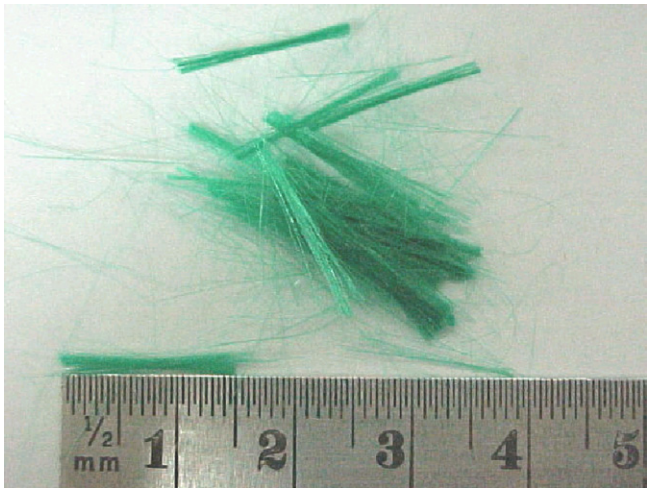

Fig. 2. Short PVA fiber used in this study (15 mm length).

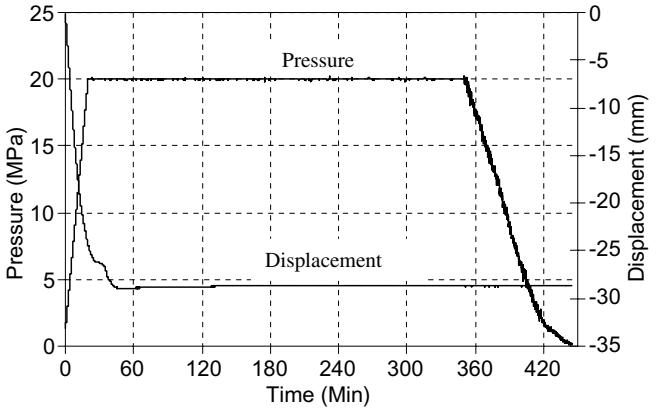

Fig. 3. Pressure on the sample and the displacement of the MTS piston with time (the furnace is shut down after 360 min).

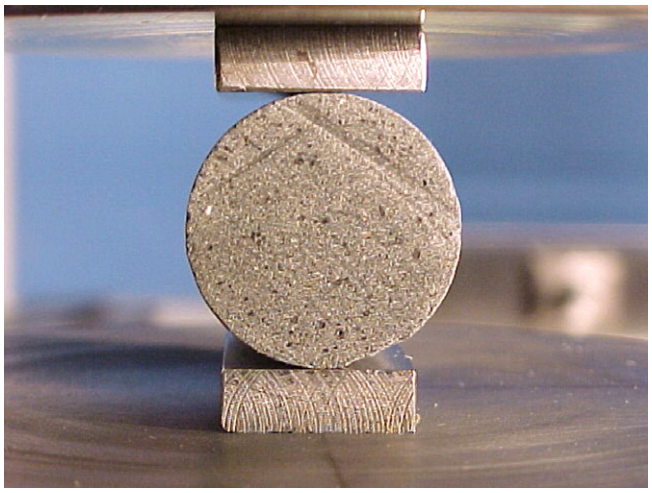

Fig. 4. Splitting tensile test setup.

long specimens. All specimens are stored in air for further drying until the specified age of 2 days at testing.

2.3. Splitting tensile test

Splitting tensile test (Fig. 4) is employed to evaluate the properties of each specimen prepared as described above and the splitting tensile strength of the specimen is determined as follows:

$$T = \frac{2P}{\pi DL}, \tag{1}$$

where T is the splitting tensile strength (MPa), P the maximum load on the sample (N), D the diameter of the sample (mm), and L is the length of the sample (mm).

Although Eq. (1) is valid only up to first crack strength, it is also used to characterize the tensile response beyond the first crack strength for comparison in this study (i.e., beyond the first crack strength, T is interpreted as an effective tensile stress).

3. Results and discussion

Several dominant factors such as fiber content, processing temperature, and processing time are investigated. In addition, the different behavior of Class C and Class F fly ash reinforced with fibers is studied. The mix compositions and processing parameters of all the specimens for each specific study are listed in Table 3.

3.1. Transition from brittle to ductile behavior with fiber additions

Two series of specimens, series 1 and 2, as listed in Table 3, are prepared. When short fibers are used to reinforce fly ash matrix, several properties, especially the ductility of the composites are enhanced significantly. The effects of fiber reinforcement on Class C fly ash specimens are shown in Figs. 5–7.

Table 3
Sample mix design and processing parameters

Series no.	Type of fly ash	Temperature (°C)	Time (h)	Fiber volume ratio (%)
1	C	130	5.5	0, 1.0
2	C	150	2.5	0, 1.0
3	C	150	2.5	0, 0.5, 1.0, 1.5
4	C	20	5.5	0
5	C	130, 200	5.5	1.0
6	C	150	0.5, 1.0, 2.5, 5.5	1.5
7	C, F	150	1.0	1.5

Note: The concentration of NaOH solution is 10 M and the L/S ratio is 0.62 for all samples.

Figs. 5 and 6 show the strength and ductility improvements when the fibers are added. In series 1, the plain fly ash specimen is brittle, and the first crack strength, also the ultimate strength, is 5.44 MPa (all strength values reported in this paper are the average of 3 tests unless otherwise mentioned). With the addition of 1.0% PVA fibers, the specimen shows excellent ductility, and the ultimate strength (the highest load registered) is 7.68 MPa,

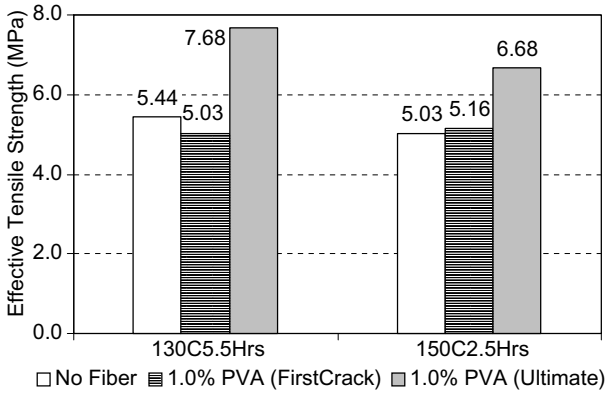

Fig. 5. Fiber effect on the splitting tensile strength of Class C fly ash specimens.

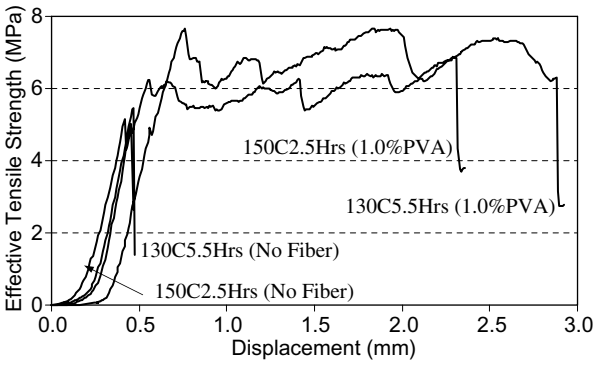

Fig. 6. Fiber effect on the ductility of Class C fly ash specimens.

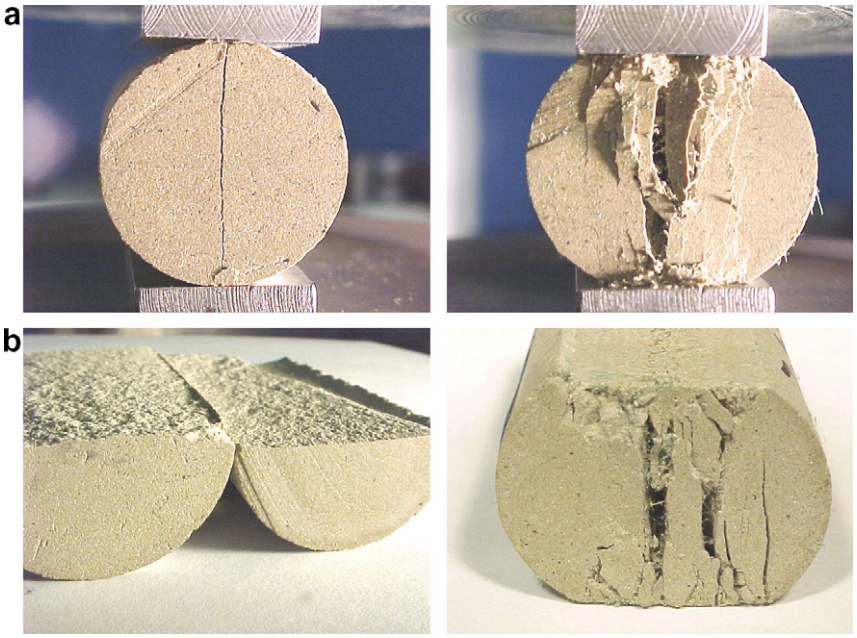

Fig. 7. Different failure modes of Class C specimens without fiber (left) and with 1.0% PVA fiber (right): (a) during test and (b) after test.

almost a 50% increase from 5.44 MPa. Although the first crack strength of the fiber reinforced fly ash sample is 5.03 MPa, slightly less than that without fibers. The reason is yet to be discovered but likely due to additional voids formed as a result of the somewhat poor workability of the sample with fibers. Similar results are also observed in series-2 samples. The first crack strengths are 5.16 MPa with 1.0% PVA fibers and 5.03 MPa without fibers. Both the ultimate strength and the ductility are significantly increased when the fibers are employed.

Fig. 7a and b shows direct comparison of the failure modes between two specimens during and after the splitting tensile tests, one of which has no fibers and the other has 1.0% PVA fibers. It can be seen clearly the brittle failure of the plain specimen and the ductile failure of the specimens with fibers.

3.2. Effect of fiber content

In order to further understand the effect of fiber, the influence of fiber content is investigated, and the results are illustrated in Figs. 8 and 9. Four batches of Class C fly ash specimens are prepared with different fiber volume fractions of 0.0%, 0.5%, 1.0%, and 1.5%, listed as series 3 in Table 3.

The plain specimen without fibers is brittle, and its first crack strength, also its ultimate strength, is 5.03 MPa. For other specimens with fiber contents from 0.5% to 1.5%, they demonstrate extensive ductility and their failure modes are ductile. The first crack strengths vary between 5.2 and 5.4 MPa, slightly higher than 5.03 MPa of the plain specimen. It is evident that the ultimate strengths of the specimens with fibers are much higher than that of the plain specimen. When the fiber content is 1.0%, the ultimate strength reaches the highest value of 6.90 MPa (Fig. 8), and the ductility is the best among the specimens

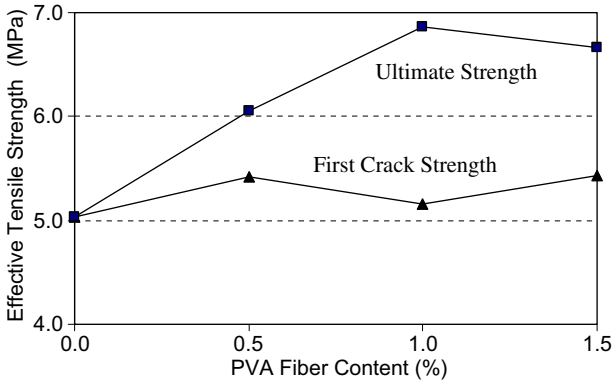

Fig. 8. Fiber content effect on the strength of Class C fly ash specimens.

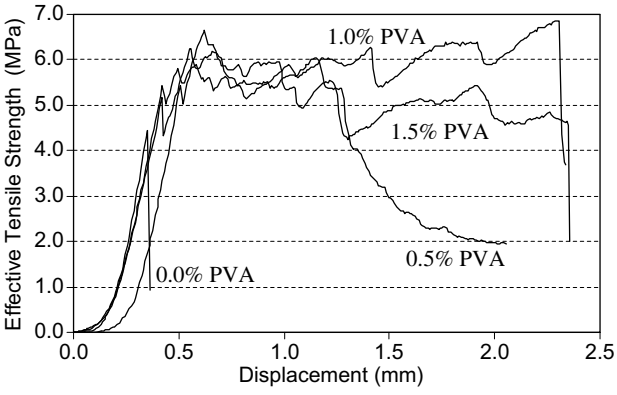

Fig. 9. Fiber content effect on the ductility of Class C fly ash specimens.

under investigation. As fiber content increases to 1.5%, there is no further property improvement largely because of poor workability of the fiber composite resulting in mixing difficulty. In other words, 1.0% is the optimum fiber volume fraction for Class C fly ash under the current investigation.

It should be noted that optimum fiber content could vary depending on the compositions of composite. To guarantee excellent ductility, the optimal fiber content must be greater than the critical fiber content, V_f^{crit}. The critical fiber content is defined as the minimum amount of fiber required for the composite to exhibit pseudo strain hardening property. For example, based on micromechanical theory dealing with matrix crack extension and crack bridging by random discontinuous fibers, the critical fiber content is shown to be a function of the properties of fiber, matrix, and the fiber–matrix interface [15]. It is therefore possible to optimize fly ash compositions to reduce the critical fiber content so that the optimize fiber content can be further reduced. This aspect is currently under investigation.

3.3. Processing temperature effect

Because polymer fibers have low temperature resistance, it is important to investigate temperature effect on the properties of the fly ash samples with PVA short fiber reinforcement. The processing temperatures investigated are room temperature (20 °C, 130 °C), and 200 °C. The volume fraction of PVA fiber is 1.0% for the specimens made at 130 and 200 °C. The specimen made at room temperature is prepared as control and no fiber is used. The mix compositions and processing parameters of the samples are listed as series 4 and 5 in Table 3.

The test results are shown in Figs. 10 and 11. The splitting tensile strength of the plain specimen prepared at room temperature (20 °C) is very low (1.01 MPa) and it is brittle. For the specimen processed at 130 °C and reinforced with 1.0% PVA fibers, its tensile properties are greatly enhanced. The specimen shows ductile behavior, with a first crack strength of 5.03 MPa and an ultimate strength of 7.68 MPa. However, as the processing temperature increases further to

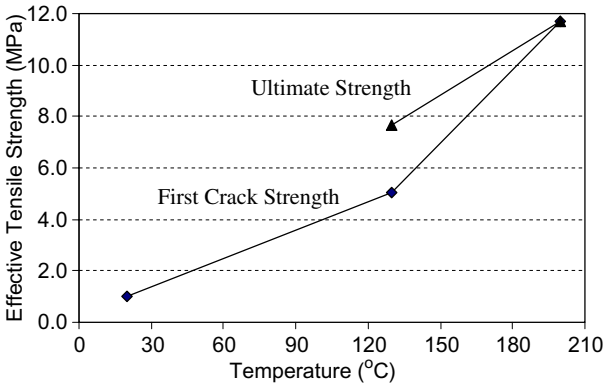

Fig. 10. Temperature effect on the strength of Class C fly ash specimens.

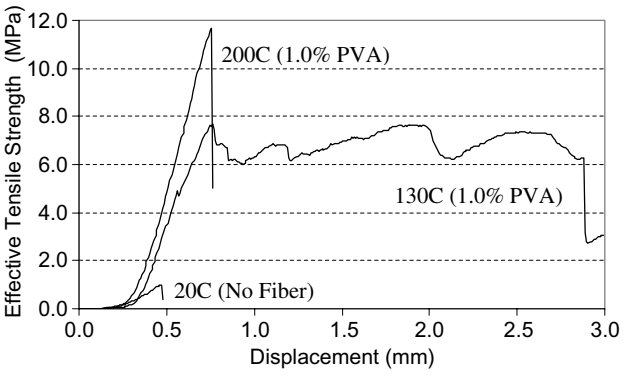

Fig. 11. Temperature effect on the ductility of Class C fly ash specimens.

200 °C, the fiber-reinforced specimen becomes very brittle with a very high strength of 11.7 MPa (Fig. 11). No trace of PVA fibers can be found on the fracture surfaces of the sample after the 5.5 h treatment at 200 °C, indicating the PVA fibers have decomposed due to the heat treatment. Nevertheless, owing to the high temperature treatment, a very high strength develops.

3.4. Processing duration effect

The effect of heating duration on the tensile properties of Class C fly ash specimens reinforced with fiber is also investigated. The heating durations investigated are 0.5, 1.0, 2.5, and 5.5 h, respectively, while the temperature is kept at 150 °C, as listed as series 6 in Table 3. Figs. 12 and 13 illustrate the test results.

It is confirmed that all the specimens show ductile behavior in Fig. 12, and the ductility of the specimen with 1.0-h heating time is the best among all the specimens. As the heating duration increases from 0.5 to 1.0 h, the first crack strength increases from 4.15 to 5.40 MPa (Fig. 13). Further increase to 2.0 h, the first crack strength, 5.43 MPa, remains almost the same as that of 1.0 h. Prolonged heating (5.5 h) causes a reduction in the first strength. Similar trend is also observed for the ultimate

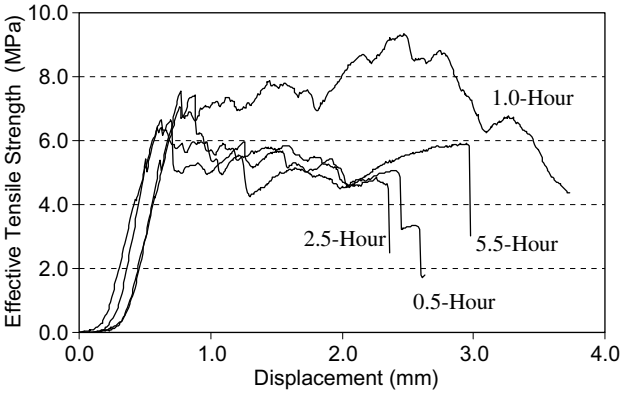

Fig. 12. Heating duration effect on the ductility of Class C fly ash specimens.

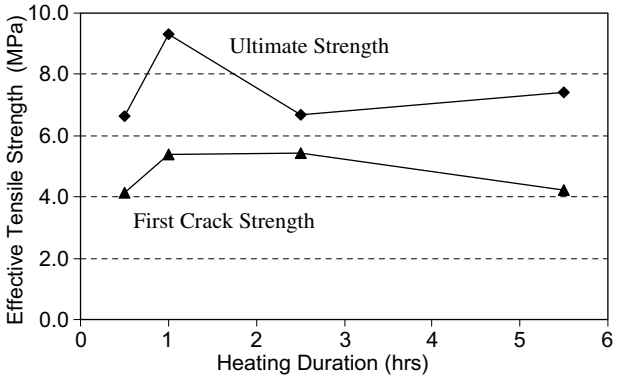

Fig. 13. Heating duration effect on the strength of Class C fly ash specimens.

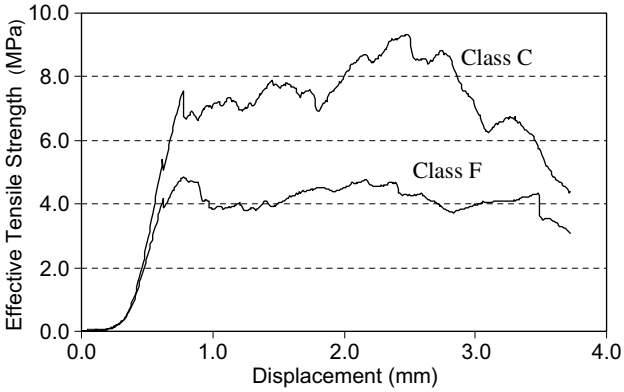

Fig. 15. Ductility comparison of Class C and Class F fly ash specimens.

strength. The weakening effect after excessive treatment at 150 °C appears to come from the degradation of the fibers at such heat environment. Therefore, in terms of processing cost, ductility, and ultimate strength, 1.0 h of heating appears to be the optimum.

In a previous study [19], it has been already demonstrated that the optimum hydrothermal hot-pressing (130 °C) process time for plain Class C fly ash with NaOH is also 1.0 h.

3.5. Comparison of Class C and Class F fly ash

In a previous study, it was found that Class C and Class F fly ash without fiber reinforcement behave differently in terms of mechanical properties, volume change, and setting property under identical treatment conditions, largely due to difference in reactivity of the ash [19]. In order to investigate the reinforcement effect of PVA fiber on Class F fly ash and the difference between fiber-reinforced Class C specimen and fiber reinforced Class F specimen, Class F specimen and Class C Specimen both reinforced with 1.5% PVA fiber are prepared, listed as series 7 in Table 3. The results are shown in Figs. 14 and 15.

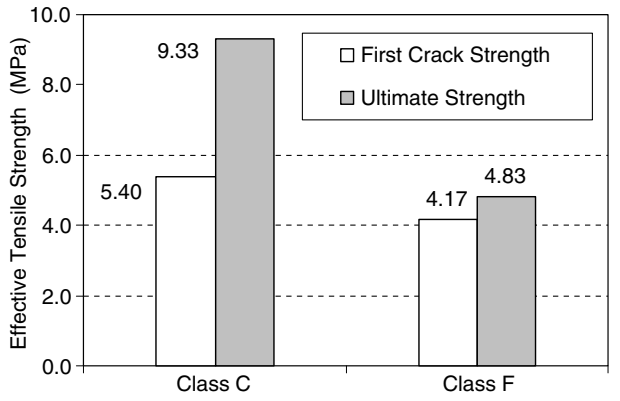

Fig. 14. Strength comparison of Class C and Class F fly ash specimens.

The Class F specimen develops moderate strength and excellent ductility when short PVA fibers are used to reinforce the matrix. Compared to the Class C specimen processed with the same parameters, Class F shows 23% and 48% reduction in first crack strength and ultimate strength, respectively, which follows the same trend of the plain matrices without fiber reinforcement. In terms of ductility, Class C specimen and Class F specimen are almost the same, as shown in Fig. 15.

4. Conclusion

In this study, short PVA fibers are employed successfully to improve the brittle properties of Class C fly ash samples produced under chemical activation and hydrothermal hot-pressing. It is confirmed that fiber reinforced fly ash composites can exhibit very high tensile strength and excellent ductility. The current conclusions are drawn in comparison of fiber-reinforced fly ash with regular plain concrete and unreinforced fly ash. Comparisons with other fiber reinforced concrete or inorganic matrix will be reported in a future publication. It is also discovered that an optimum fiber volume fraction of 1.0% is established in terms of composite properties and processing cost. Since the PVA fibers will decompose at high temperature (such as 200 °C) the composite processed at that temperature shows very high strength but brittle behavior again. Regarding processing time, the composites follow the same trends as plain fly ash, and it is found that 1.0 h is the optimum when processed at 150 °C. With fiber reinforcement, Class F fly ash composites exhibit ductile behavior as well. But both the first crack strength and the ultimate strength are lower than those of Class C fly ash produced under the same conditions.

Acknowledgement

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