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MACRO DEFECT FREE CEMENTS: A REVIEW

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The usage of polymers in different sectors has been increasing in recent decades, and even our current age may have been defined as polymer age. When concrete is considered polymers are also widely used to modify the properties of both mortar and concrete and the usage of polymers in concrete dates back to 1920's. On the other hand, Macro-defect free (MDF) cements are one particular type of cement-polymer composites and developed and patented by scientists at Imperial College at the beginnings of 1980's. MDF cements are produced by mixing cement (commonly calcium aluminate cement) with small amounts of polymer (usually polyvinyl alcohol acetate) and water. High shear, relatively low pressure (about 5 MPa) and moderate temperature (about 80-100 °C) are applied during the production of this material. MDF cements, although consist of more than 80% by weight of cement, show 20-30 times higher flexural strength comparing to ordinary Portland cements. However, MDF cements show a considerable reduction in strength when they are exposed to water even for a short time. Many studies have been conducted to solve the water sensitivity of MDF cements for over 30 years. In this study, production, basic properties and the current state of the art of MDF cements are explained, and the future research works are suggested.

Keywords: MDF composites, cement, polymer, calcium aluminate cement, PVA, Water sensitivity.

1 INTRODUCTION

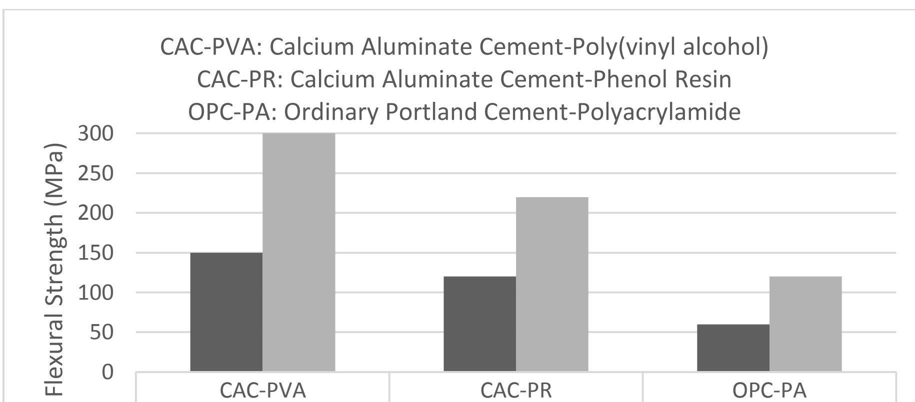
Concrete, mainly made with aggregates, cement and water, is the most consumed man-made material in the world. In addition to main ingredients, many additives are used in the production of concrete for different purposes. Notably, various types of polymers are used in concrete and mortar production to enhance the fresh and hardened state properties. The first usage of polymers in concrete dates back to 1924 (Ohama 1995). Polymer modification of cementitious materials has been witnessed to the innovation of polymer-modified materials with the improvement in polymer technology, and many different cement-polymer composites were produced since then.

Macro-Defect Free (MDF) cements are one example of a very broad field of cement-polymer composites, and had been developed and patented by Birchall *et al.* (1981, 1983) at Imperial College. The MDF cement can be prepared by using cement, polymer and water. 80-90% of this composite consists of cement by weight, while 10-15% is water and 1-7% is polymer (Ekincioglu 2009). Many researches had been conducted about MDF cements in last 30 years. In this study, a brief review of MDF cements is given. The main materials used, production processes, properties and limitations are summarized in detail. Also, some promising attempts to improve the durability properties are mentioned.

2 MDF CEMENT PRODUCTION PROCESSES

2.1 Materials

Different cement and polymer combinations have been used for the production of MDF cements. Calcium aluminate cement (CAC) (Russell 1991, Ekincioglu 2009) and poly(vinyl alcohol) (PVA) (Birchall 1983, Santos 1999, Ekincioglu *et al.* 2012a) are the most widely utilized materials for the production of MDF cements. Besides CAC, Portland cements and slag cements were also used (Sinclair and Groves 1984, Poon and Groves 1988, Titchell 1991, Poon *et al.* 1998, Santos *et al.* 1999) in productions. Polyacrylamide (Sinclair and Groves 1985, Poon and Groves 1988, Ohama 1993, Poon 1998), cellulosic products (Eden and Bailey 1984, Drabik *et al.* 1994, Drabik *et al.* 1999, Drabik *et al.* 2001, Mojumdar 2001) and alcohol soluble polymers such as phenol resin precursors (Hasegawa *et al.* 1995, Pushpalal *et al.* 1997, Walberer and McHugh 1998, Pushpalal *et al.* 1999) were proposed as polymers for the productions of MDF cement. The approximate flexural strength of most typical MDF cement combinations can be seen in Figure 1.



	CAC-PVA	CAC-PR	OPC-PA
Min	150	120	60
Max	300	220	120

Figure 1. Approximate flexural strength of different MDF cement combinations.

2.2 Production Methods

Birchall *et al.*'s (1981, 1983) production method by applying high shear was generally accepted for as the standard MDF cement production procedure. This process was optimized by Russell (1991) and later Ekincioglu (2009). Another production method, Banbury type mixer for high shearing, was introduced by Tan (1992). Basic steps followed in the production and testing of MDF cements by Ekincioglu (2009) can be seen in Figure 2.

Figure 2. Basic steps to produce and test MDF cements (Ekincioglu 2009).

3 PROPERTIES OF MDF CEMENTS

3.1 Mechanical Properties

Cement-based materials are known with their high compressive strength, but low tensile strength. On the other hand, MDF cements have superior mechanical properties both in compression and tension. However, they can be produced with various cement and polymer types, and their properties largely depend on the used materials. Comparison of some general properties of OPC, CAC-PVA and CAPR MDFs are shown in Table 1. As can be seen in Table 1, flexural strengths of MDF cements are 20-30 times higher than those of conventional (plain) cement pastes and nearly equal to that of an ordinary steel.

Table 1. Typical properties of OPC and MDF cement composites (Ekincioglu 2009).

Property	**OPC**	**CAC-PVA MDF***	**CAPR MDF****
Flexural Strength, MPa	5-10	150-300	120-200
Compressive Strength, MPa	40-60	380	300
Young's Modulus, GPa	20-30	40-50	32-45
Density, g/cm^3	2,3	2,5	2.2-2.3

*Polymer was PVA and the cement was alumina cement (Russell 1991).
**Polymer was phenol resin and the cement was alumina cement (Pushpalal *et al.* 1999).

The high strengths of MDF composites are obtained by both the eliminating of macropores in the composite during processing and also the crosslinking formed between cement and polymer. Studies (Rodger *et al.* 1984, 1985, Popoola *et al.* 1991) showed that crosslinking reactions between polymer chains and metal ions generated during the hydration reaction of cement are responsible for achieving such high strengths. On the other hand, MDF cements have serious durability problems. High strength losses are observed when they are exposed to water.

3.2 Durability Properties

The water sensitivity of MDF cements limits the usage of them in commercial applications. Therefore, many researchers have focused on this issue. Several different additives are used in MDF cement productions to prevent this problem. Some of the used additives are; alkali metal silicates (Lynn and Durey 1992), cross-linking chemicals (Desai 1992, Liutkus and Kovac 1988, Lewis and Boyer 1995), gypsum (Brown 1996), $CaCl_2$ and $ZnCl_2$ (Poon 1998), silica fume (Santos *et al.* 1999), activated carbon (Chowdhury 2004a, Chowdhury 2004b), epoxy resin (Ekincioglu *et al.* 2011) and TiO_2 (Ekincioglu *et al.* 2012b). All these studies provided a better understanding of MDF cements, although none of them ultimately reduced the moisture sensitivity.

MDF cements are mostly produced with alumina cements and poly(vinyl alcohols), and the effects of the type of these most common ingredients were also investigated recently by Ekincioglu (2009). In a first study, MDF cements were produced with seven different types of poly(vinyl alcohol-co-vinyl acetate) (PVA) copolymers with various hydrolysis degrees (between 79.6% and 99.1%) and their effects on the mechanical properties were investigated. All specimens prepared were adversely affected by moisture. However, the lowest strength losses were obtained with the least hydrolysis degree PVA (79,6 mole%). Increasing the degree of hydrolysis of PVAs increased the strength loss of MDF specimens which were stored in water. MDF cements could not be produced with fully hydrolyzed PVA or carboxylated PVA. In the second part of the study, the effect of Al_2O_3 content of alumina cements on the moisture sensitivity was investigated. Decreases in strength after 28 days water storage for w/c ratios between 0.09 and 0.19 shown in Figure 3. It seems that there is a minimum strength loss between 49% and 70% alumina contents of cement. Optimum Al_2O_3 content for the lowest strength loss was found approximately 58%.

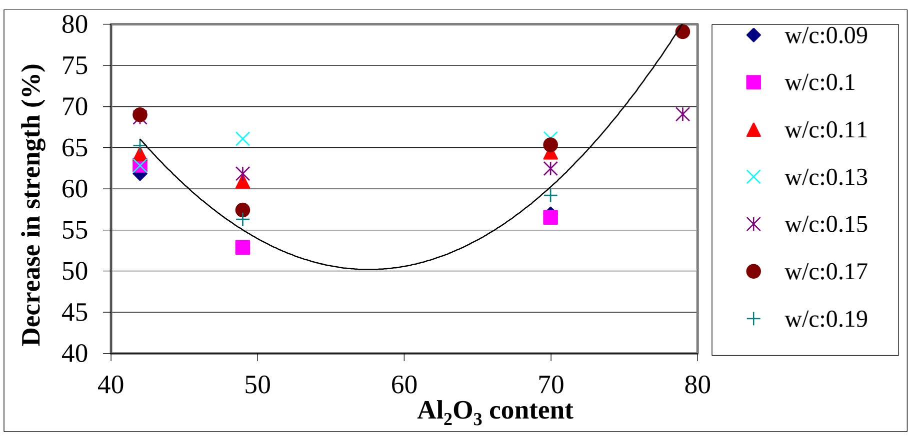


Figure 3. Strength loss versus Al_2O_3 content in cement for 28 days water storage.

4 CONCLUSIONS

MDF cements are cement-polymer composites and show superior mechanical properties. Special production techniques by using calendering are necessary to obtain high mechanical strengths. However, it is a brittle material, and especially the durability problems in water have limited its usage in any commercial application. Research activities about MDF cements have also declined in recent years due to durability problems. Many different additives, such as the addition of epoxy resin or TiO_2, were proposed to overcome the water sensitivity of MDF cements. Although some of them are promising, none of the proposed solutions completely solved this problem. A better understanding of crosslinking between the polymer and cement may allow us to produce water-resistant MDF cements. One area, which has not been sufficiently researched, is that coating MDF cements with a protective layer. MDF cements have superior properties and deserve further studies.

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