IMPROVING THE WATER RESISTANCE OF MACRO-DEFECT-FREE CEMENTS

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ABSTRACT

Macro-defect-free (MDF) cements are perspective materials providing unique properties relative to traditional cement pastes with great potential to incoming constructional utilization. But it is known, that MDF cements exhibit sensitivity to water, with swelling and reduction of strength. This work is aimed at monitoring of an organic polymer effect on the moisture resistance of MDF materials and phase changes. The effects of three different organotitanate cross-linking agents on the properties and moisture sensitivity were investigated. The organotitanate-modified MDF cement samples exhibited improved moisture resistance as compared to the standard samples when exposed to 100 % relative humidity at 22°C. One way to eliminate the moisture sensitivity is chemical modification of the microstructure of the MDF cements, especially polymer matrix and the interphase. To increase the mechanical properties of MDF cements fibre reinforcements was used. Results show that fibre reinforcements have positive effects on the growth of these properties.

KEYWORDS:

Macro-defect-free; polyvinyl alcohol; moisture resistance; cross-linking; fibre reinforcements

INTRODUCTION

In a recent review published by The Concrete Society it was stated that cement and concrete should be regarded as one of the primary construction materials for use in the new millennium (Miller, 2005).

Although cement is an old and apparently well known substance, in reality, the concrete chemistry is not well scrutinized. The fact has led to some problems e.g. water factor. Typical coefficient of water in the concrete that is needed to obtain a compromise between the fluidity of the mixture and additional porosity in the cured product is about 0.3 to 0.45 (higher coefficient of water is greater fluidity and porosity). High porosity is inappropriate because it causes loss of strength and provides greater throughput aggressive agents (CO_2, H_2O, SO_2), which may cause deterioration of the concrete matrix properties, especially corrosion of reinforcements. Although, many studies found procedures to improve the mechanical properties of concrete and cement pastes (inclusion of ultra-fine particles, optimization of particle size distribution, etc.), it had been improved only compressive strength. Tensile strength remained approximately same. Breakthrough in this area experienced polymer-impregnated materials, especially macro-defect-free cements (MDF). These materials are characterized by extremely low porosity, which has a significant impact on strength.

Since the MDF cements were developed around 1980, have been the subject of several investigations and review articles due to their superior mechanical properties.

However, even 26 years since they were first patented (Birchall, 1983), the commercial potential has been very limited. The main factor for limitation is changing the mechanical properties when material is exposed to humidity.

Despite the fact many investigations focused firstly on understanding the microstructure of MDF composites. First important confirmation has been done by Lewis et al. (Lewis, 1995), who hypothesized the initiator of moisture sensitivity is the polymer matrix. It follows those regions containing polymer (i.e., the bulk and interphase regions) are insensitive to water. Desai (Desai, 1992) explored an organotitanate cross-linking agent (Tyzor TE; DuPont de Nemours) has an ability to improve the moisture resistance of MDF cement. Chemically, it is a group of various tetraalkyl titanates and titanate chelates subdivided to aqueous (supplies as water solutions) and nonaqueous (as a solution in alcohol) solutions. This commercial additives are compatible with the high pH environments (generated during MDF composite preparation) and furthermore well known for cross-linking of polyvinyl alcohol-acetate copolymer (PVAA) (Lewis, 1995).

The manufacturing process of MDF composite is described and mentioned effect of the organotitanate cross-linking additives on processing and moisture sensitivity of MDF composite, consists of calcium aluminate cement and polyvinyl alcohol/polyvinyl acetate co-polymer. Results will show the suitable Tyzor as an organotitanate binding agent to optimize the conditions of PVAA cross-linking and preparation of the final MDF material. Next there are the results of measurements of mechanical properties of MDF composites with the addition of various fibre reinforcements.

EXPERIMENT

Materials

Aluminate cement Secar 51 (Lafarge Aluminates) and polymer PVAA GH – 17s (purchased from The Nippon Synthetic Chemical Industry Co in Japan) for preparing the test specimens of MDF composites were used. Major phase of cement Secar 51 is $CaO.Al_2O_3$ complemented with $12CaO.7Al_2O_3$, $2CaO.Al_2O_3$ and $CaO.TiO_2$, with minimal Al_2O_3 content 50 %. The degree of hydrolysis of polymer PVAA GH – 17s is 87.6 % and viscosity of 4 % water solution is 29.1 mPa.s. To improve the hight-shear process a small amount of glycerol (Lach-Ner, s. r. o., Neratovice, Czech Republic) has also added. Overall, three types of Tyzors and three types of fibrous reinforcements were used (Table 1).

Table 1 – Types of the used Tyzors and reinforcements.

Organotitanate cross-linking agents	Fibre reinforcements
Tyzor TE – Triethanolamine Titanate (E. I. du Pont de Nemours and Company)	PVA fibres – KURALON A-8, 2.0 dtex x 4 mm
Tyzor LA – dihydroxy bis [2-hydroxypropanato (2-)-O1, O2]-, ammonium salt (E. I. du Pont)	Basalt fibres – Technobasalt (Ukraine)
Tyzor AA – 75 – (10 weight parts) to methyl ethyl ketone (20 weight parts), water (35 weight parts), (E. I. du Pont)	Wollastonite microfibres – Ankerpoort NV: The Mineral Company (Netherlands)

Mixing and samples preparation

First explored MDF composite samples without any special additives to improve the moisture sensitivity were fabricated using the process developed by Birchall et al. (Birchall, 1983) and optimized by Russell (Russell, 1991). Tyzor modified MDF composite samples were prepared based on the developed progression and experimentally procedure.

Composition and volume of particular components formed new MDF composite was considered as a main effect on material's properties. The basic assumption was proposed by literature (Odler, 2000) and experimentally consequently. The basic premise was good workability and suitable mixture amount during the preparation. With increasing weight representation of Tyzor was necessary to add weight proportion of water. The result can be seen in the following Table 2.

Table 2 – Final representation of the components in a mixture with Tyzors.

Component	Weight [g]				
	* Tyzor 1.0 wt. %	Tyzor 1.5 wt. %	Tyzor 2.5 wt. %	Tyzor 5.0 wt. %	Tyzor 10.0 wt. %
HAC	200	200	200	200	200
PVAA	10	10	10	10	10
Tyzor	0.1	0.15	0.25	0.5	1
	Volume [ml]				
Distilled water	34	35	36	37	41
Glycerol	2	2	2	2	2

* The weight percentages of Tyzors are relative to weight of PVAA.

Samples with the addition fibre reinforcement had a similar composition as samples with Tyzors. Amount of HAC was 200 g, PVAA 10 g, Glycerol 2 ml. Only the amount of fibre reinforcements and water was changed, as it is seen in Table 3.

Table 3 – The amount of fibre reinforcements and water.

Fiber reinforcements	* Weight [%]	Distilled water [ml]
Kuralon	0.5	35
	1	36
Wollastonite	1	33
	3	33
	5	35
Basalt	1	34
	2	34
	3	34

* The weight percentages of fibre reinforcements are relative to weight of HAC.

Finally, specimens were made from the resulting paste size 2x20x50 mm and cured at different temperatures and time intervals. At the end, specimens were kept at various conditions: in a laboratory conditions, water and almost one hundred percent relative humidity.

RESULTS AND DISSCUSION

Flexural strength

Samples were tested in three-point bending test on apparatus ZWICK 010. Radius of load and supporting the blades were 5 mm, test speed 1 mm/min, pre-load 5 N and support separation 40 mm. Results are shown in Figure 1, where is taken dependence of tensile bending MDF composites on the dose of Tyzors. Samples modified by Tyzor TE in the range from 1.0 to 1.5 wt. % exhibit an increase of strength in water storage, but the addition of more Tyzor the strength decreases. Optimal addition of Tyzors is ranging from 1.0 to 1.5 wt. %. Similar results have samples modified by Tyzor LA. So as to increase strength the modified MDF samples must be cured at higher temperature, as shown the results from gel point determination of PVAA in the presence of Tyzor LA. Samples with Tyzor AA-75 were not investigated because of poor strength results.

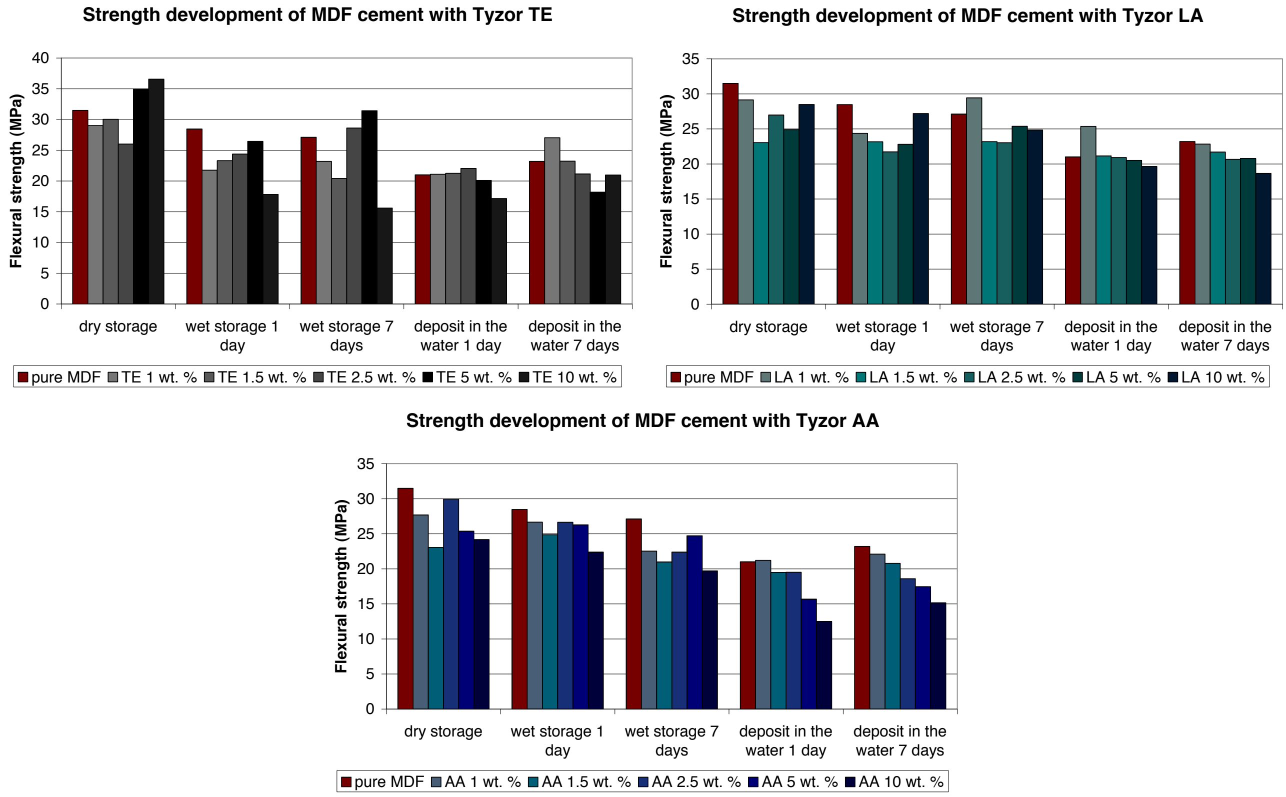

Figure 1 – Influence of water on the strength of Tyzor modified MDF samples.

Figure 2 demonstrates the flexural strength development of MDF cement with fibre reinforcement in different storage conditions. The obtained results show the best behavior in moisture and water achieved sample with 0.5 wt % of PVA fibres (Kuralon). Flexural strength of samples with wollastonite microfibres is not so hight. This may be due to poor investigation of these microfibres into the MDF matrix (Figure 3b). The addition of basalt fibres has not a significant influence on the strength of MDF matrix.

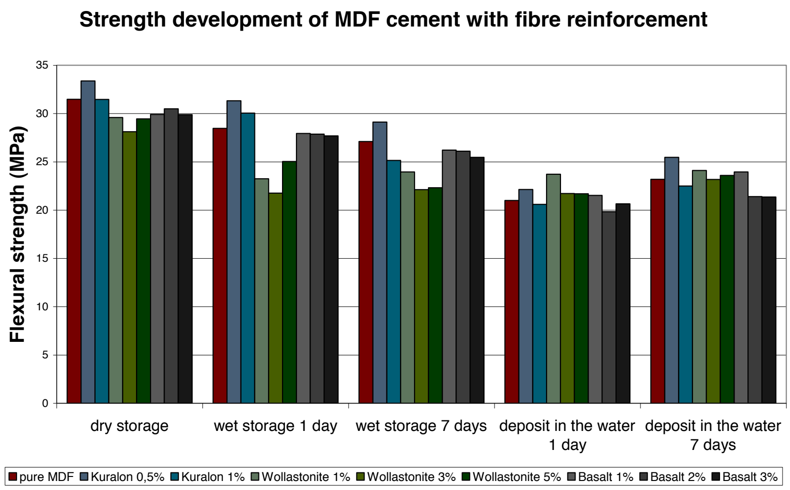

Figure 2 – Flexural strength of MDF composites with different amount of fibre reinforcements.

Microstructure analysis

Microstructure was observed by Scanning Electron Microscope (Tesla RS 340). Figure 3 shows SEM micrographs of fracture surfaces three MDF samples with different fibre reinforcements.

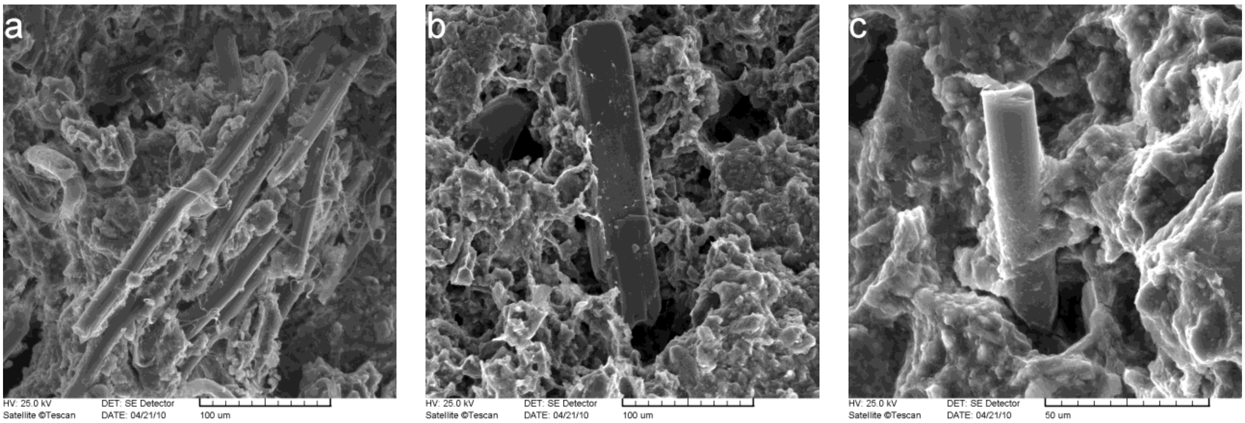

Figure 3 – SEM micrographs of MDF composites with fibre reinforcements: a) Kuralon 1 wt. %; b) wollastonite 3 wt. %; c) basalt 3 wt. %.

CONCLUSION

MDF composites have a great potential in wide range of technological applications, therefore it deserves further investigations to improve their resistance to moisture. The work focused on "In situ" reticulation of polymer. The aim leads to chemical modification of the polymeric region using organotitanate cross-linking agents, Tyzors. An initial series of MDF composites based on aluminate cement and polyvinyl alcohol with three types of Tyzors (Tyzor TE, LA and AA-75) was prepared with previous evaluation and investigation of Tyzors cross-linking properties. Effect of modification on MDF composites properties was further evaluated by testing flexural strength the deposit of materials in different humidity conditions.

The results show that the degradation of mechanical properties, respectively, flexural strength is significantly improved by using MDF composite modified by 1.0 wt % of Tyzor TE, but the samples with Tyzor LA have good results as well. However, despite the Tyzors TE or LA are promising cross-linking agent to minimize strong effect of moisture to mechanical properties, method and components are still not sufficient, as study of samples stored in water environment evidenced.

Effect of fibre reinforcements on the flexural strength of MDF composites has positive character, but the increase in strength with any fibres is less marked. Satisfying results have the PVA fibres (Kuralon), but there is a problem with sufficient dispersion of the fibres into the MDF matrix.

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