

# INFLUENCE OF THE SELF CROSSLINKABLE POLYMERS ON THE PROPERTIES OF THE MACRO DEFECT FREE (MDF) CEMENTS

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**Abstract:** *Macro-defect-free (MDF) cements are cement-polymer composites characterised by high tensile and flexural strength but serious durability problems were observed when these composite materials are in contact with water. In order to improve the water resistance, MDF cements were produced by addition of two types of self crosslinkable polymers. The aim of this study is to characterize the obtained MDF cements, by using contact angle measurements, FTIR spectroscopy and to correlate the results with the mechanical properties of the MDF cements in initial state and after their storage in water.*

**Key words:** *macro-defect-free (MDF), cement, self-crosslinkable polymer, poly(vinyl alcohol), water sensitivity.*

## 1. Introduction

Polymer addition in cement is one of the ways to improve the mechanical properties of ordinary cement pastes [1]. The researchers had attributed the high flexural strength as well as the name of these special cements to the elimination of the macro voids and pores from material structure during high shear mixing process, which is the most important step of the preparation process [3].

The interaction between polymer, cement grains and hydration products during setting and hardening, leads to a specific microstructure with higher mechanical properties [8]. This behaviour could be correlated to intimately blending of the polymer and cement particles during

the specific high shear processes followed by pressing the material at moderate temperature and pressure, and also to the polymer capacity to be crosslinked with the cement compounds.

The best results in terms of flexural strength for MDF cements were obtained when poly(vinyl alcohol) PVA copolymers, alumina cement and water were used for production [4].

In spite of its hydrophilicity, PVA has been used in MDF cements' preparation, due to its capacity to determine a dramatical increase in the mechanical properties of MDF cements and due to its ecological and economical benefits such as biodegradability, biocompatibility, non-toxicity and availability [5], [9], [10].

The main problem of MDF cements

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which limit their applications remains the decrease in mechanical resistance in humid atmosphere or in water. Some solutions proposed for solving this issue are: usage of a more hydrophobic polymer in the MDF production, of new methods of the PVA crosslinking, choosing the best vinyl alcohol-vinyl acetate ratio into the PVA copolymer, or blending of PVA with some acrylic, self-crosslinkable dispersion, changing the technology of MDF producing, aiming to obtain a suitable polymer repartition into the cement matrix. The aim of this paper is to improve the water resistance of MDF cements by adding two types of self crosslinkable polymer; to determine the decrease of the MDF surface hydrophilicity by inducing structural changes in the composition of the cement composites. Characterization of the obtained MDF has been done by using contact angle measurements and FTIR spectroscopy and these properties have been correlated to mechanical properties determined on the analysed MDF specimens.

## 2. Experimental Study and Results

### 2.1. Materials

One type of cement (Isidac 40) and two self-crosslinkable acrylic dispersions have been used: Steron K3-R and Steron K6, supplied by RomReRo Polymer Co. Rasnov, Romania. Small amounts of glycerol, PVA and water have been added in MDF recipe.

PVA KH 17, Gohsenol, Japan-Nippon Gohsei has hydrolysis degree of 79% and molecular weight around 110000.

In order to obtain composite samples, the PVA/cement and acrylic dispersion/cement ratios were maintained at 0.035. Small amounts of water (w/c ratio: 0.11) and glycerol (for workability) were added to the mixture. All the compounds were mixed in

a planetary mixer, and then, the mixture was passed through two roller mills which are turning on opposite directions at different speeds. The sheet - like product was pressed for 10 min at 80 °C and 5 MPa pressure and cured at 80 °C for 24 hours in a forced-air oven. MDF samples obtained were then coded by the name of the acrylic dispersion used at production, as K6 and K3R. In order to monitor the water action on mechanical and surface properties, half of the specimens were stored in a desiccator while the other half was stored in distilled water.

### 2.2. Testing

#### 2.2.1. Contact Angle Test and Evaluation

The contact angle analysis is widely used to test the wettability of a surface with different solvents as well as to determine the surface energy.

Contact angle ( $\theta$ ) tests were performed by using an OCA-20 Contact Angle System (Data Physics Instruments). The testing liquids, with known both polarity and surface tension, were ultra pure water and glycerol. A liquid drop was placed at three different points of one sample and the average values of measured contact angle have been used for data interpretation. At least five different dry specimens and washed specimens respectively, from every prepared series were used for this test. Dry specimens means the specimens stored in dry conditions (in desiccator) while the washed specimens are the samples stored in water. During tests, the volume of liquid drops was kept constant at about 5  $\mu$ L and the contact angle was measured immediately after droplet placing on the surface, at 21°C.

The surface energies of materials are connected to unsatisfied chemical bonds, dispersion and polar effects. Therefore, according to Fowkes, the surface energy

has two contributions: the polar ( $\gamma^p$ ) and the dispersive one ( $\gamma^d$ ) [2], [6] as equation (1) evidenced:

$$\gamma_s = \gamma_s^p + \gamma_s^d. \quad (1)$$

The surface energy ( $\gamma_s$ ) was calculated by using the method of Owens, Wendt, Rabel and Kaelble described by the equation (2):

$$\frac{1 + \cos \theta}{2} \cdot \frac{\gamma_l}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p} \cdot \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d}. \quad (2)$$

The letters “s” and “p” are referring to solid and liquid, respectively.

By plotting the left term of the equation

(2) versus  $\sqrt{\frac{\gamma_l^p}{\gamma_l^d}}$  the  $\gamma^p$  could be determined

as the slope of the line and  $\gamma_s^d$  as the intercept with y axis. Their sum is  $\gamma_s$ , the MDF surface energy.  $\gamma_l$  and its components are known values.

### 2.2.2. Biaxial Flexural Strength Test

Biaxial flexural strength tests were carried out on circular specimens with a diameter of 31.75 mm at 28<sup>th</sup> days of hydration. Biaxial flexural strengths of the specimens were measured according to ASTM F 394-78 (Reapproved 1996). An Instron model universal testing machine equipped with a 100 kN load cell was used

to test the specimens with a cross-head speed of 0.1 mm/min.

### 2.2.3. FTIR Spectroscopy Tests

The infrared spectra were collected in the range of wave number from 4000 to 650  $\text{cm}^{-1}$  using a Perkin-Elmer spectrophotometer. The FTIR spectra were normalized and major vibration bands were associated with chemical groups.

FTIR spectroscopy was used in order to monitor the structural changes that occur during immersion in water of MDF specimens.

## 3. Test Results and Discussion

Contact angle test results and the obtained surface energies are presented in Table 1.

Higher values of the initial contact angle of glycerol compared to those of water are obtained due the weaker interactions between cement surface and glycerol. Small differences between the obtained values of surface energies corresponding to both surface energies corresponding to both MDF studied series are due to the very close hydrophilicity indicated by the initial value of the contact angle (determined by water and glycerol, respectively) as it could be seen in Table 1. High value of the surface energy means a better surface wettability and thus, a high amount of hydrophilic components, not linked into the cement mass, could be released, lowering the mechanical properties.

The surface characteristics for both MDF series studied

Table 1

Sample	$\theta_{initial}$ with water degree	$\theta_{initial}$ with glycerol degree	$\gamma$ [mN/m]	$\gamma^d$ [mN/m]	$\gamma^p$ [mN/m]
K6	70.66	80.50	264.06	99.89	164.17
K3R	70.08	78.92	235.18	83.29	151.89

These results are in good agreement with those obtained by mechanical tests, as it is shown in Figure 1.

A correlation between contact angle and mechanical results could be established: same value of initial contact angle led to

similar mechanical properties in terms of biaxial flexural strength. The highest value of the surface energy obtained for the sample K6 is related to its better wetting and a decrease in strength about 52% by comparing to low surface energy and 49% decrease in strength for K3R series.

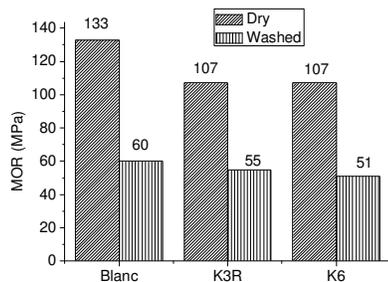


Fig. 1. Flexural strength results for MDF cements obtained by using K3R and K6 self crosslinkable polymers, in dry state and after washing

By comparing K3R and K6 samples with the blank it could be noted that the replacement of a part of the PVA, from the MDF composition, led to the decrease of mechanical resistance, but also to a smaller decrease of the loss of strength (Figure 1) after samples contact with water. It seems that self-crosslinking of the polymer is not enough to increase the MDF mechanical strength but helps to cements hydrophilic character decrease.

Figure 2 presents the FTIR spectra of MDF/K3R in dry state, after 28 days of immersion in water and PVA (KH 17) used at production.

Regarding PVA, the characteristic absorption bands could be assigned to the following vibration types:  $3300\text{ cm}^{-1}$  - stretching of the O-H bonds,  $2925\text{ cm}^{-1}$  - stretching C-H from alkyl group, the bands between  $1750\text{-}1720\text{ cm}^{-1}$  corresponds to the C=O and C-O bonds from acetate groups,  $1236\text{ cm}^{-1}$  - stretching of the C-C bond and the band from  $1141\text{ cm}^{-1}$  provide information

about cristalinity of the PVA [7].

The specific bands from the spectra of the K3R in dry and hydrated state were as follows: the strong band at  $3300\text{ cm}^{-1}$  is attributed to O-H stretching vibrations in its hydrates [11] and the other large absorption band from  $1409\text{ cm}^{-1}$  is assigned to carbonate group [11], [12]. An intense band at  $873\text{ cm}^{-1}$  is ascribed also to carbonate group vibrations. The intensity of this band could be correlated to the concentration of carbonate group. It could be noticed that for dry sample, this last band is not present, while for hydrated specimen, the band intensity is high being a measure of the carbonates deposits on the sample surface. The presence of this chemical group indicates that the MDF specimens, obtained by using acrylic dispersions are still sensitive to moisture.

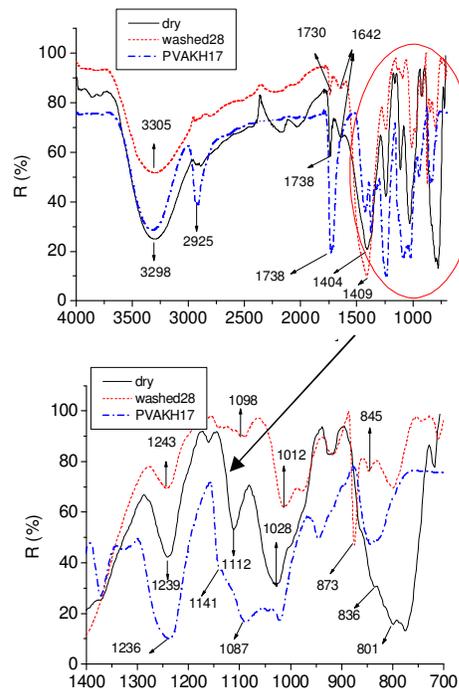


Fig. 2. FTIR spectra for MDF cements K3R in dry state, after 28 days of contact with water and PVA (KH 17)

The band at  $1730\text{ cm}^{-1}$  could be assigned to C=O and C-O bonds from acetate groups remained in PVA [7] as well as due to acrylic dispersion and at  $1642\text{ cm}^{-1}$  the band detected is probably due to the vibration of C-O-Al bonds.

Some superimposed bands are present in the region of  $700\text{--}900\text{ cm}^{-1}$  corresponding to Al-O bonds and C-C bonds in the dry samples.

The decrease of the band width and the shifting of the maximum from the  $760\text{ cm}^{-1}$  to  $845\text{ cm}^{-1}$ , for the wet samples by comparison to dry samples evidences the release of some components containing aluminum, and as consequence the material's instability to water.

The absorption band from  $1028\text{ cm}^{-1}$  and  $802\text{ cm}^{-1}$ , respectively, is probably due to the non-reacted compounds from cement such as:  $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ ;  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ;  $\text{Al}_2\text{O}_3$  and the band at  $1112\text{ cm}^{-1}$  could be assigned to the vibration of Al-O group [11].

Other small bands shift to higher wave numbers, such as  $3298\text{--}3305\text{ cm}^{-1}$ ;  $1640\text{--}1645\text{ cm}^{-1}$ ;  $1409\text{--}1412\text{ cm}^{-1}$ ;  $1239\text{--}1243\text{ cm}^{-1}$ ;  $1112\text{--}1098\text{ cm}^{-1}$  and  $1028\text{--}1012\text{ cm}^{-1}$  proved the MDF structural changes that occur during the hydration process.

#### 4. Conclusions

MDF cements based on PVA and acrylic self-crosslinkable dispersions have been obtained. The surface properties of the MDF series were evaluated both by contact angle measurements and FTIR spectroscopy and used to analyse the effect of water on the MDF specimens.

Moisture sensitivity is strongly influenced by surface morphology of the MDF cements and its hydrophilicity. Same degree of surface hydrophilicity led to similar mechanical properties while the higher surface energy means better wettability and lower

mechanical properties in terms of biaxial flexural strength.

By comparing the MDF obtained only with PVA with the MDF prepared by replacing a half of PVA with self-cross-linkable acrylic dispersions, the decrease of mechanical strength is with 5% lower, but the absolute value of the biaxial flexural strength of the MDF prepared only with PVA is higher by approximately 25%.

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#### References

1. Birchall, J.D., Howard, A.J., Kendall, K.: *Flexural Strength and Porosity of Cements*. In: *Nature* **289** (1981), p. 388-390.
2. Bismarck, A., Pfaffernoschke, M. Selimovic, M.: *Electrokinetic and Contact Angle Measurements of Grafted Carbon Fibers*. In: *Colloid Polym. Sci.*, **276** (1998), p. 1110-1116.
3. Drabik, M., Mojumdar, S.C., Galikova, L.: *Changes of Thermal Events of Macro Defect-Free (MDF) Cements Due To the Deterioration in the Moist Atmosphere*. In: *Cement and Concrete Research* **31** (2001) Nr. 1, p. 743-747.
4. Ekincioglu, O., Ozkul, M.H., Struble, L.J.: *Moisture Resistance of Macro Defect Free Cements Produced with Different Calcium Alumina Cements*. In: *Turkish Cem. Manufact. Assoc. 3<sup>th</sup> Int. Symp., Sustainability in Cement and Concrete, Istanbul Turkey, Vol. I* (2007), p. 421-429.
5. Finch, C.A.: *Polyvinyl Alcohol Properties and Applications*. New York. John Wiley & Sons Ltd., 1973.

6. French, R., Winey, K., Yang, M., Qiu, W.: *Optical Properties and Van der Waals-London Dispersion Interactions of Polystyrene Determined by Vacuum Ultraviolet Spectroscopy and Spectroscopy Ellipsometry*. In: Aust. J. Chem **60** (2007), p. 251-263.
7. Herman, M., Sadahira, C.M., Souza, A., Mansur, A.P.: *FTIR Spectroscopy Characterization of Poly(Vinyl Alcohol) Hydrogel with Different Hydrolysis Degree and Chemically Crosslinked with Glutaraldehyde*. In: Materials Science and Engineering (2007), doi:10.1016/j.msec.2007.10.088.
8. Morlat, R., Orange, G., Bomal, Y., Godard, P.: *Reinforcement of Hydrated Portland cement with High Molecular Mass-Soluble Polymers*. In: Mater. Sci. **42** (2007) Nr. 1, p. 4852-4869.
9. Paţachia, S., Ranja, M., Papancea, A., Valente, A.J.M., Friedrich, C., Varga, Şt., Florea, C., Idomir, M.: *Tailored PVA-based Matrices for Controlled Drugs Delivery*. In: Workshop on Nanoscience and Nanotechnology: MNT-JS, Gran Canaria, Spain (2007), p. 339-346.
10. Paţachia, S., Ranja, M.: *Effect of the Poly(vinyl alcohol) [PVA] Hydrogels Microstructure on Their Water Absorption*. In: Buletinul Institutului Politehnic din Iaşi, Vol. **LI** (LV), Fasc. 4 (2005), p. 183-190.
11. Sugama, T., Brothers, L.E., Weber, L.: *Calcium Aluminate Cements in Fly Ash/Calcium Aluminate Blend Phosphate Cement Systems: Their Role in Inhibiting Carbonation and Acid Corrosion at a Low Hydrothermal Temperature of 90 °C*. In: Journal of Materials Science **37** (2002), p. 3163-3173.
12. Trezza, M.A., Lavat, A.E.: *Analysis of the System  $3CaO \cdot Al_2O_3 - CaSO_4 \cdot 2H_2O - CaCO_3 - H_2O$  by FT-IR Spectroscopy*. In: Cement and Concrete Research **31** (2001), p. 869-872.