VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

BRNO UNIVERSITY OF TECHNOLOGY

FAKULTA CHEMICKÁ
ÚSTAV CHEMIE MATERIÁLŮ

FACULTY OF CHEMISTRY
INSTITUTE OF MATERIALS SCIENCE

MDF COMPOSITES AC-PVAL WITH INCREASED MOISTURE RESISTANCE

DIPLOMOVÁ PRÁCE
MASTER'S THESIS

AUTOR PRÁCE Bc. MARTIN REPKA
AUTHOR

BRNO 2010

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
BRNO UNIVERSITY OF TECHNOLOGY

FAKULTA CHEMICKÁ
ÚSTAV CHEMIE MATERIÁLŮ

FACULTY OF CHEMISTRY
INSTITUTE OF MATERIALS SCIENCE

MDF COMPOSITES AC-PVAL WITH INCREASED MOISTURE RESISTANCE

MDF KOMPOZITY AC-PVAL SE ZVÝŠENOU ODOLNOSTÍ PROTI VLHKOSTI

DIPLOMOVÁ PRÁCE
MASTER'S THESIS

AUTOR PRÁCE AUTHOR	Bc. MARTIN REPKA
VEDOUCÍ PRÁCE SUPERVISOR	Ing. FRANTIŠEK ŠOUKAL, Ph.D.

BRNO 2010

Brno University of Technology
Faculty of Chemistry
Purkyňova 464/118, 61200 Brno 12

Master's thesis Assignment

Number of master's thesis: **FCH-DIP0411/2009** Academic year: **2009/2010**
Institute: Institute of Materials Science
Student: **Bc. Martin Repka**
Study programme: Chemistry, Technology and Properties of Materials (N2820)
Study field: Chemistry, Technology and Properties of Materials (2808T016)
Head of thesis: **Ing. František Šoukal, Ph.D.**
Supervisors: Ing. Jiří Másilko

Title of master's thesis:

MDF composites AC-PVAl with increased moisture resistance

Master's thesis assignment:

- literature review
- selection of organo-titanate binding agent and optimisation of conditions of PVAl cross-linking
- modification of PVAl by cross-linkable functional groups
- preparation of MDF composites and their characterisation

Deadline for master's thesis delivery: 14.5.2010

Master's thesis is necessary to deliver to a secreatry of institute in three copies and in an electronic way to a head of master's thesis. This assignment is enclosure of master's thesis.

Bc. Martin Repka
Student

Ing. František Šoukal, Ph.D.
Head of thesis

prof. RNDr. Josef Jančář, CSc.
Head of institute

In Brno, 1.12.2009

prof. Ing. Jaromír Havlica, DrSc.
Dean

ABSTRAKT

Polymerem impregnované cementové materiály představují zajímavou a perspektivní alternativu klasických portlandských cementových past. Hlavním zástupcem těchto materiálů jsou macrodefect-free (MDF) kompozity, složené z anorganického pojiva a organického polymeru. I přes řadu vynikajících mechanických vlastností je plné zavedení MDF kompozitů na trh omezené především z důvodu jejich relativně nízké odolnosti vůči vlhkosti. Jednou z možností jak zvýšit odolnost výsledného MDF vůči vlhkosti je „in situ“ síťování polymeru.

V této práci byla připravena počáteční série MDF kompozitů na bázi hlinitanového cementu a polyvinylalkoholu se třemi typy organo-titanátových síťovacích činidel (Tyzory). Efekt modifikace MDF kompozitů byl hodnocen na základě zkoušek pevnosti v tahu za ohybu po uložení materiálů v různých vlhkostních podmínkách.

ABSTRACT

Polymer-impregnated cement materials represent an interesting and promising alternative to conventional Portland cement pastes. Macrodefect-free (MDF) composites correspond to the well-known group of these materials, consisting of inorganic binder and organic polymer. Despite the identification of many potential applications and unusual mechanical properties, MDF cements have certain limitations and particularly loss of strength on exposure to moisture or humidity. One option to increase the moisture resistance is “in situ” reticulation of polymer.

This work contains results of initial sample series of MDF composites based on alumina cement and polyvinyl alcohol with three types of organo-titanate cross-linking agents (Tyzors). Effect of MDF composites modification was evaluated by testing of flexural strength of materials in various humidity conditions.

KLÍČOVÁ SLOVA

MDF, polyvinylalkohol, Tyzor, hlinitanový cement, vysoká pevnost, odolnost proti vlhkosti

KEYWORDS

MDF, polyvinyl alcohol, Tyzor, calcium aluminate cement, high strength, moisture resistance

Repka, M.: *MDF composites AC-PVAl with increased moisture resistance*. Brno: Brno University of Technology. Faculty of Cemistry. Institute of Materials Chemistry, 2009. 76 p. Diploma thesis. Supervizor Ing. František Šoukal, Ph.D.

DECLARATION

I declare that the diploma thesis has been worked out by myself and that all the quotations from the used literary sources are accurate and complete. The content of the diploma thesis is the property of the Faculty of Chemistry of Brno University of Technology and all commercial uses are allowed only if approved by both the supervisor and the dean of the Faculty of Chemistry, BUT.

…..……………...……………………

student's signature

Acknowledgement

I would like to sincerely thanks to Ing. František Šoukal, Ph.D and Mgr. Soňa Hermanová, Ph.D. for valuable advice and professional inspiration, Ing. Jiří Másilko for his help with the practical part and my family for their support throughout the study.

1 CONTENT

2 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[1].

Although cement is an old and apparently well known substance, in reality, the concrete chemistry is not well scrutinized. This fact is associated with some problems namely water factor. Typical coefficient of water in the concrete that is necessary to obtain a compromise between the fluidity of the mixture and additional porosity in the cured product is about 0.5 − 0.6 (the higher coefficient of water the greater fluidity and porosity). High porosity is inappropriate because it results in a 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, in many studies the approach to improve the mechanical properties of concrete and cement pastes (inclusion of ultra-fine particles, optimization of particle size distribution, etc.) has been investigated, as a main result only compressive strength was improved. Tensile strength remained approximately the same. Polymer-impregnated materials, especially macrodefect-free cements (MDF) achieved a breakthrough in this area. These materials are characterized by extremely low porosity, which has a significant impact on strength.

Since the beginning of their development in the 1980s the MDF cements have been the subject of a variety of systematic research and recently review articles have reported their superior mechanical properties. However, even 26 years since they were first patented[2], the commercial potential has been very limited. The change of the mechanical properties when the MDF material is exposed to humidity represents the main restricting factor. To understand the relationship between the structure and properties of MDF, many investigations were focused on understanding the microstructure of MDF composites. Lewis et al.[3] suggested the hypothesis that the moisture sensitivity problem is related in fact to the polymer matrix. That is, the regions containing polymer (i.e., the bulk and interphase regions) are sensitive to water. Desai[4] reported an organotitanate crosslinking agent (Tyzor TE; DuPont de Nemours) has an ability to improve the moisture resistance of MDF cement. These crosslinking agents represent a group of various tetraalkyl titanates and titanate chelates utilized as aqueous (supplies as water solutions) and nonaqueous (as a solution in alcohol) solutions. These titanium chelates are compatible with relative high pH environments generated during MDF composite preparation and furthermore well utilized for cross-linking of polyvinyl alcohol-acetate copolymer (PVAA) in other applications[5].

In this contribution, the manufacturing process of MDF composite consisting of calcium aluminate cement and poly (vinyl alcohol-acetate) is described and the effect of the organotitanate crosslinking additives on processing and moisture sensitivity of MDF composite is discussed. The main objective of the study is to find out the suitable titanate chelate as a binding agent with the view of optimalization of PVAA cross-linking conditions and preparation of the final MDF material with enhanced properties.

3 THEORETICAL PART

3.1 Polymer-Modified Cement Mixes

The preparation of polymer-modified cement mixes consists of mixing together inorganic cement (mostly Portland cement or high alumina cement), water, and a dispersion of an organic polymer. When the concrete aggregates and possibly other components of formed mixture are includes a polymer-modified concrete or mortar mixes has obtained. In this case, the water ratio is rapidly limited compare to similar polymer-free mixes. Moreover, the addition of water may be omitted entirely. The reason comes with the polymeric dispersion supplies part or all of the water needed for hydration and for obtaining adequate rheology of the mix.

During the material mixing and subsequent hardening a three-dimensional polymeric network develops within the material from the polymer dispersion consists of small, separated droplets dispersed in the water phase. It can contain dispersing agents to stabilize the whole system. The polymeric system is intimately combined with the three-dimensional structure of the hardened cement paste. The possibility of polymer dispersion types which would combine with inorganic cements, as long as the polymeric materials are very limited. They have to sufficiently resistant to sustain the high-pH environment of the cement paste, for example.:

- Thermoplasts – polyvinyl acetate, polyvinyl chloride or polyacrylate;
- Thermosets – epoxides, polyesters, or polyurethanes;
- Elastomers – natural rubber latex or a butadiene-styrene copolymer.

A typical weight percentage of polymer additions is between 5% and 20%.

If the resinous materials of two components are employed, e. g. epoxy resins, it is necessary to mix the resin precursor with a curing agent to get the polymerization reaction under the control. The blended precursor/curing agent have only a limited time for storing after the mixing, and the viscosity is changing with time going during the polymerization reaction. It has been developed one component to reduce the drawback, epoxides as pot-life-free one-component part. Resultant products contain a curing agent. The reaction is carried out only for the normal temperature. Moreover, the mixture at the starting point has to be heated up to 80 °C to possibility of successful chain reaction. Ohama[6] suggested the possibility to initiate a slow polymerization reaction of the epoxy precursor by the catalytic action of alkalis present in the binder.

The addition of the polymeric dispersion usually improves the rheology of the fresh mix. It is very common to entrap at the same time the amount of air to the mix in the course of mixing is increased. An addition of defoamer, especially silicone type can be used to prevent this behaving.

Grosskurth[7] and subsequently Ollitrault-Fichet[8] confirmed that the initial rate of the cement hydration in the paste can adversely be affected by the presence of the polymeric dispersion and therefore can be explained by the formation of a diffusional barrier around the non-hydrated cement particles. Further, they suggested that the polymer acts as a retarder, first by suppressing the nucleation of the cement hydration products and thus increasing the induction time, and second by restraining the growth of these phases during the acceleration stage.

Grosskurth[7] also showed results that addition of polymeric dispersions significantly affects the physico-mechanical properties of the hardened material. Furthermore, all the properties depend on the existing temperature. At temperatures below the glass transition temperature the cement/polymer composite has the character of a brittle solid, without effect of the amount of polymer addition. On the other hand, material shows the significant increase of the fracture energy with increased temperatures above the glass transition temperature. The formed effect is particularly pronounced when an elastomer is employed as the polymeric component. Schulze[9] showed that the flexural strength increases with increasing polymer content in the mix in the constant water/cement ratio. The compressive strength is minimally changed, although can decline, owing to air entrapment.

3.2 Macrodefect-Free Cement

Firstly should be noticed that the term ‘macrodefect free (MDF) cement‘ is not perfectly correct and appropriate even among scientists in the research is very well-known and used. MDF cement is classified as a polymer-modified cementitious material, where the resulting matrix created on the basis of the chemical interaction between polymer and inorganic binder prepared by a special manufacturing process. The classification associates to cementitious material it will therefore continue to use the term rather MDF composites.

The 'MDF' signification, stands for 'Macrodefect-free' refers to the material’s structure, which is without relatively large voids or defects normally present in ordinary cement pastes. These pores in cement pastes are mainly caused by the entrapped air and/or inadequate mixing. Further, the signification is origin of the time when it was believed in the idea that the absence of macro defects is responsible for high strength[10].

3.2.1 MDF Composite Research

Macro-defect-free (MDF) cements were developed following work by the research group led by Birchall at ICI during the late 1970s and early 1980s[11]. The first promising materials were based on a combination of calcium aluminate cement with polyvinyl alcohol-acetate copolymer, which was subsequently patented. Material with maximum flexural strength consisted of 84 wt% calcium aluminate cement (Secar 71, Lafarge), 5 wt% polyvinyl alcohol-polyvinyl acetate co-polymer, saponification degree 79 % (Gohsenol KH-17s, Nippon Gohsel), 9.3 wt% deionized water and 0.6 wt% glycerol.

Further investigations confirmed outstanding properties consisted mainly of high flexural strength. It was associated with the theory about the polymer as a rheology modifier to eliminate macrodefects. It was believed the polymer does not contribute to material properties.

Following investigations in the late 1980s started to demonstrate this early theory is not fully correct. Several studies focused on effects associated with the removal of polymer by thermal degradation. As results were showing, after removal of the polymer by heating to 100 – 150 °C decreased tensile strength up to 10 % of the original value. It signaled the cement matrix should be composed of both the hydrated interphases, as well as the polymer itself.

Polymer in the system affects the hydration process but is influenced by hydration alone. The results of calorimetric measurements show hydration of aluminate cement Secar 71 is significantly retarded in the presence of polyvinyl alcohol. Hydration is significantly altered at higher concentrations of polyvinyl alcohol and the development of heat highlights at the beginning.

As explained by Fowkes, this behavior can be attributed to the relative intensities of the interactions between the components of the composite (see the section *3.5.1 Moisture Resistance*).

Modifications to the MDF manufacturing process and the selection of the polymer used have overcome many of these problems. The major obstacle to use MDF composites in many applications is the economics of manufacturing on a large scale and their overall commercial viability compared to existing materials.

The limitation of MDF materials stability made the subsequent investigations focused on understanding the microstructure of MDF composite and its relation to moisture transport and the degradation process. Turn should carry this knowledge for moisture resistance. Subsequently, acquired knowledge should have improved the moisture resistance of the material.

Popoola et al.[12] were the first, who observed an interphase region, containing both cement hydration products and polymer intimately mixed at the nanometer level, located at the interface between unreacted calcium aluminate cement grains and the polymer matrix in MDF cement (more in *3.3 Microstructure*).

Futher, they demonstrated on basis of in-situ environmental transmission electron microscopy (TEM) studies that the polymer and interphase regions absorbed moisture when exposed to humidity.

Lewis et al.[13] subsequently studied the percolation properties of the bulk polymer and interphase regions using the combined links of experiments and computer simulation involving the hard core/soft shell continuum percolation model. They determined that although both the bulk polymer and interphase regions form connected pathways through the three-dimensional MDF cement microstructure, the bulk polymer regions served as the main pathway for moisture transport. Their work ultimately confirmed earlier hypothesis that the polymer matrix is primarily responsible for the sensitivity of MDF materials to moisture because of that affinity polymer matrix to water.

This implies possible way to improve the moisture resistance of MDF composites, while those regions containing polymer (the bulk and interphase regions) are insensitive to water.

The Master Thesis from Desai[14] survey carried out several polymers (PVAA) cross-linking additives with emphasis on the ability to improve their resistance to moisture resulting MDF material. Results of their investigation showed an organotitanate crosslinking agent (Tyzor TETM; DuPont de Nemours) is a suitable additive. This commercial additive is compatible with the high pH environments generated during fabrication of MDF cement and is well known to cross-link PVAA. Chemical structure of tyzor TE and its reaction, see section *3.8.2 Organic Titanates*.

3.2.2 Components

In general, MDF composites are composed of ordinary Portland cement (OPC), high-alumina cements (HAC) or sulfate clinkers with water-soluble polymers (polyvinyl alcohol PVAA, polyacrylamide, etc.), some admixtures increasing their properties and finally by applying mechano-chemical processing techniques at very low water-cement ratios (0.08 – 0.20).

Further, small amounts of glycerol have been found to improve the processing, especially during the mixing.

The most critical factor in preparation of MDF composite is the components selection and their ratios. The main components of MDF composite are cement and particular impregnating polymer. Table below (*Table 1*) shows the used polymer/cement combinations for manufacturing of MDF in the past.

Table 1 Examples of polymer/cement combinations used in MDF manufacture

Polymer	**Hydraulic cement**	**w/c Ratio**	**Author [References]**	**Year**
BA/AN, starch, soluble Poly-P	OPC, SAFB, Al_2O_3 blends	0.2	Mojumdar[15]	2006
PVAA with 0.1 ratio of glycerol	CA (Secar 71)	0.1067	Lewis et al.[16]	1994
PBA, SACP, and poly-P	OPC, SAFB Al_2O_3 blends	0.08 – 0.2	Mojumdar[17]	2004
AAM – monomer and modifiers	OPC, SAC, Slag	0.195	Zhihong et al.[18]	2003
HPMC, poly-P (aq), poly-P(s)	SAFB, OPC 85:15	0.2	Drabik et al.[19]	2001
PVA, Novolac epoxies	CA	0.115 + heat treatment	Chandrashekhar[20]	1989
PVA, HPMC	OPC, CAC	–	Titchell[21]	1991
Phenol resin precursor and modifier	HAC	0.01	Pushpalal et al.[22]	1997

Research has shown that the most particularly suitable and most used cement/polymer combinations are:

- calcium aluminate cement in combination with a polyvinyl alcoholpolyvinyl acetate co-polymer, and
- Portland cement in combination with polyacrylamide.

The calcium aluminate cement used should preferably have a high incomplete hydrolysis of polyvinyl acetate. The selection of an appropriate product is critical. The simultaneous presence of hydroxy and acetyl groups within the polymer appears to be essential. It has been suggested, however, that both the strength and the water resistance of the resultant MDF cement will increase with decreasing degree of hydrolysis of the polymer[23] and with decreasing molecular weight[24]. The polymer droplets in the dispersion should be small enough to ensure rapid and effective distribution of the polymer within the MDF mix during processing.

Possibility of other polymers

In addition to polyvinyl alcohol/acetate and polyacrylamide, some other polymers have also been employed as the organic part of MDF composite, including polypropylene glycol[25] and hydroxypropyl-methyl cellulose[26]. As well as Portland and calcium aluminate cements, sulfoaluminate-ferrite-belite cement (in combination with hydroxypropyl-methyl cellulose) has also been employed as constituent of an MDF material[22].

3.2.3 Preparation of MDF Material

The following ratios of the individual constituents may be considered typical for MDF materials:

Table 2 Individual Components for MDF materials

inorganic cement	75-85 wt%
organic polymer	5-10 wt%
water	8-15 wt%
glycerine	0.3-0.6 wt%

The manufacture of MDF cement involves high shear mixing of selected polymers and hydraulic cements at low weight/concentration ratios typically between 0.08 and 0.20. Most research has used the preparation guidelines provided by Birchall[3] and later optimized by Russell[27]. Scheme on the *Fig. 1* illustrates the key stages involved in the MDF manufacturing process.

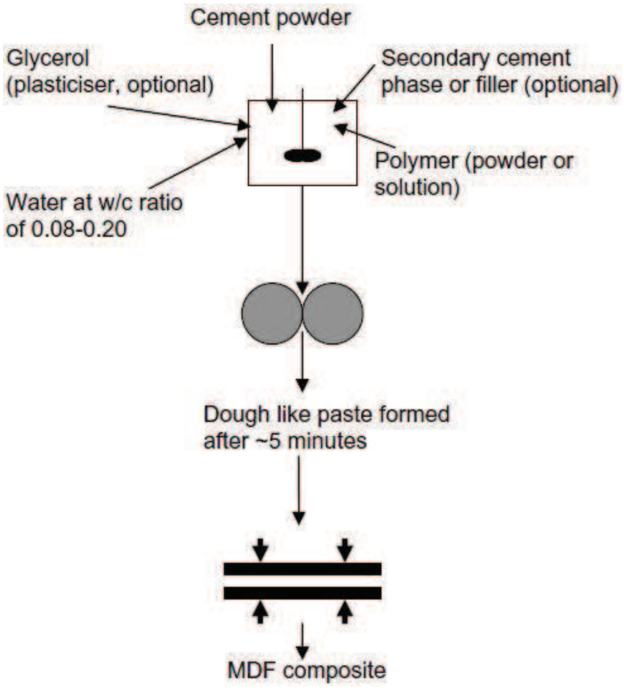


Fig. 1 Typical MDF manufacturing process[38]

- *Premixing*

The components are premixed in a conventional planetary mixer to get particular homogeneous mixture.

- *High-shear mixing*

Secondly the formed mixture undergoes to high-shear mixing usually obtained in a two-roll mill, a device commonly used in the plastics and rubber industry. The apparatus consists of two opposing rotating rolls. The gap between rolls can vary, particularly about 0.5 and 2 mm. Shear forces are generated in the material based on their different speed of rotation when the material is inserted into the gap. In this way shear rates exceeding 1000/s may be realized.

High-shear mixing is very important step during the MDF materials preparation. At the beginning, it was believed that high-shear mixing is used only to eliminate macro defects (large pores and air voids) from the paste, and the organic polymer acts as a processing aid to obtain and achieve it. This suggestion was based on the well-known confirmation about the flexural strength of porous mixture. Each porous material is a function of overall porosity and also the critical flaw size, which is characterized by the size of the largest pores present in cement pastes. Further development confirmed, that high-shear mixing, which helps to eliminate large pores, also induces chemical interactions between the polymer and the inorganic cement[28] during the mixing. Moreover, the surveys showed that the main effect of unusual mechanical strength of MDF materials is caused by mechanically induced chemical changes. Further, high-shear mixing determines to a large extent the final physical and mechanical properties of the resulting MDF material, in particular increased shear rate as well mixing time causes largely increase in strength (in a reasonable range). The other hand, increased rate of shear mixing brings the amount of generated heat by viscous damping. Subsequently, the increased temperature of the mixture can perform the material cured paste before the completion of processing. Moreover, the additional heat brings further consequences in form of exothermic chemical reactions in the material. A positive approach would have been a cooling of the rolls in the two-roll mill. It could lead to prolonged disposition of high-shear mixing, and thus positively affect the quality of produced MDF material. During high-shear mixing the mixture consistency is gradually changing. The material eventually reaches a rubbery consistency with viscoelastic properties.

- *Shape Forming*

Many different methods can be used to achieve the desired shape of the material. For example, calendering is one of the ways to produce sheets with a thickness of approximately between 0.5 and 2 mm. The resulting sheets can be further compaction of the other pressing between two plates with subsequent heating. Other processing methods might include extrusion and injection molding or pressing. However, these methods are used for demanding requirements on the shape of the product[6].

- *Curing*

Many studies have definite the different variable roles of polymer varying during the production process. Initially, the polymer acts as a rheological aid, significantly improves the workability of normally dry cement paste and reduces friction of particles during mixing and especially high shear-mixing process. Moreover, polymer also fills the space between the unreacted cement grains and allows them to join together in a tightly packed compact structure during compaction.

The functional groups of the polymer consequently chemically interact with the cement hydration products and the released ions of cement hydration. This further contributes to an increase in strength during curing procedure.

Many researchers in this field through differential thermal analysis (DTA) curves and infra-red (IR) spectrum of PVA and hydrated calcium aluminate cement (CAC) phase and PVA/CAC hydrated cement mixture of MDF material showed that the properties of polymers are completely without interaction with the hydration of cement phases .

3.3 Microstructure

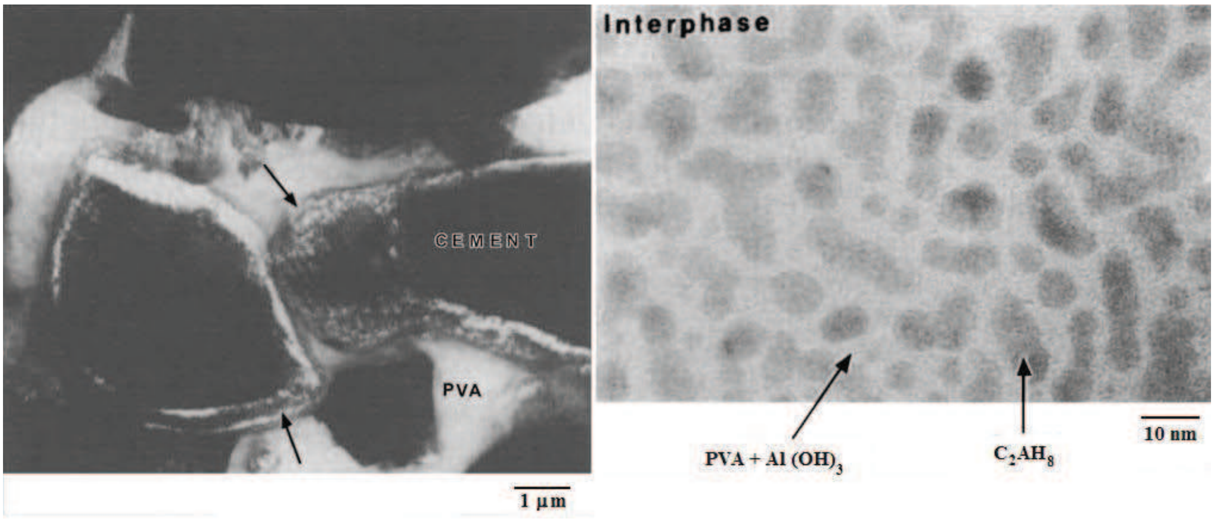
MDF cements consist of three regions, which were defined:

- unhydrated cement grains
- bulk polymer phase
- complex inter-phase region (hydrated cement particles and polymer chains)

Given the various limitations of MDF material was necessary detail to base research on the study and description of their microstructure. In 1990s the microstructure has been described as close packed unhydrated cement grains inside of a three dimensional PVA network (polymer matrix) with parts of hydrated cement coating on the surface of grains interacting with the bulk polymer by chemical cross-linkages.

The microstructure of the prepared MDF material is shown in *Fig. 2* acquired by the backscattered electron microcope. The *Fig. 2A* presents bright-field TEM image where the arrows indicate interphase region.

The absence of macro pores (>200 µm) and the intimate interaction between the polymer phase and the cement hydration products contribute to high strength. The degree of intimacy between polymer and hydrated cement is illustrated in *Fig. 2B*. It refers to interface region between the cement grain and PVA region[29].



A B

Fig. 2 Electron micrographs of MDF cement microstructure[25]

3.3.1 Unhydrated cement grains

The presence and significant volume of unhydrated cement grains has always been dissatisfied. The unhydrated cement grains has effect on the stability of the MDF composite during subsequent exposure to moisture. It refers to low w/c ratio and hence a stoichiometric deficit of water that prevents all the cement from fully hydrating.

A group around Desai[30] substituted up to 75 % of the original cement with inert Al_2O_3 and results had showed improved moisture resistance with decreasing unhydrated cement content. This research indicated that unhydrated cement behaves as a potential storage of moisture when exposed to high humidity. The locking of free moisture to newly hydrated cement phases maintains a positive gradient. It follows easier approach for new moisture. Hence, Donatello[26] suggested that a combination of solubilisation of the polymer phase and in situ cement hydration were responsible for loss of strength on exposure to moisture.

3.3.2 Bulk polymer phase

In case of MDF composites where the cementitious part is calcium aluminate cement, the bulk polymer phase presents complicating three dimensional cross-linked PVAA. Also this part of MDF composites contributes to the poor moisture resistance.

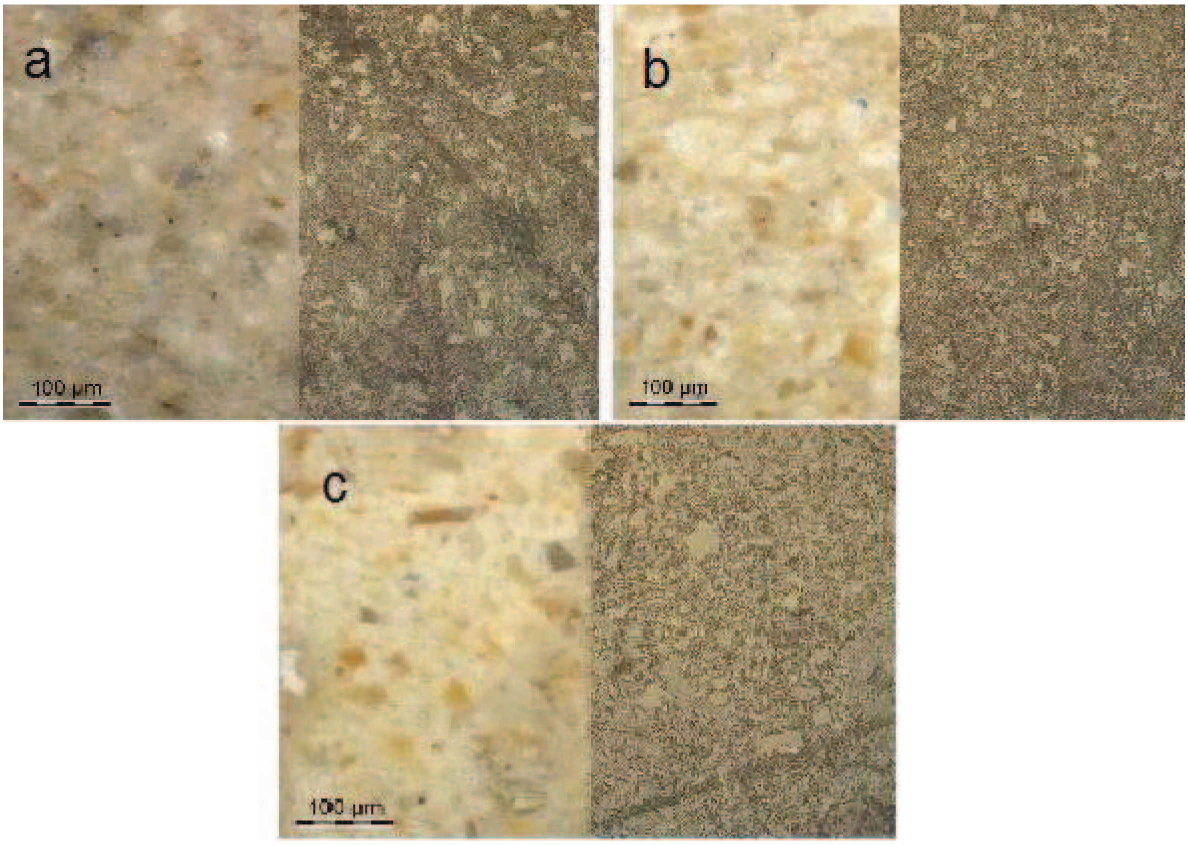


Fig. 3 MDF composite specimen stored at different conditions[27]

Másilko[31] studied the microstructure of MDF composites with 6 % polyvinyl alcohol cured at specific range of temperature and stored in different environment conditions (water, 100 % relative humidity, laboratory conditions) for 7 days on optical microscope Olympus BX 50U and examined the acquisition of two images in polarized and unpolarized light (see *Fig. 3*).

It has been noticed the polyvinyl alcohol is gradually turning up the complete disappearance of polyvinyl alcohol. It paint brightens the influence of clustering of the polyvinyl alcohol agglomerates. The reason is mentioned poor moisture resistance. The *Fig. 3a* present the specimen in laboratory conditions, while the *Fig. 3b* was stored in water and *Fig. 3c* in 100 % of relative humidity.

Observation has shown that the transport of moisture through the structure is mostly via the network of bulk polymer (PVAA) phase.

Moreover, Lewis et. al.[12] concluded this assumption when they used of a hard core-soft shell percolation model coupled with mercury intrusion porosimetry (MIP) analysis of MDF composite. Their result has shown that selective exclusion of bulk polymer phase leaving pores with diameter 30 nm approximately, whereas removing of the interphase region leaving pores around 5 nm. Therefore the water can pass readily through the bulk polymer phase.

Consequently, the mentioned increasing the cross-linking density of PVAA within the bulk polymer is a possible way to improve moisture resistance. The reason is reducing the diameter of pathways through the MDF composite.

3.3.3 Interphase region

Interphase region is a very complicated system that was subject to a number of different techniques to understand the chemical structure of this amorphous system.

A group around Connoti[32] publicized the polymer molecules are affected by interaction with inorganic atoms within 30 nm during the study by ^{13}C nuclear magnetic resonance (NMR) in combination with hydrogen relaxation time and the interaction of polymer phase with aluminium ions to an ester group and/or acetate ions has been further assumed. Popoola[33] did an observation of the organic–inorganic interface region with electron microscopy and confirmed it; polymer and hydrated cement phases were present on the surface of unhydrated cement grains.

The calcium and aluminium ions as a product of cement hydration were thought to have a main role in interaction and forming chemical links to dissociated alcohol and carboxylic groups formed from the PVA polymer. High pH environment occuring at the surface of hydrated cement grains, the ions Ca^{2+} and Al^{3+} forms particular hydroxides $Ca(OH)_2$ and $Al(OH)_4$. The suggestion of chemical behaving of MDF material during the preparation is in *3.4.1 Chemical reactions during MDF composite forming*.

3.3.4 Properties of MDF composites

MDF cements have significantly improved physical properties compared to normal hydraulic cement pastes. A comparison of some properties is given in *Fig. 3*.

This shows that although MDF cements and normal Portland cement (PC) pastes have similar densities, MDF cements present higher compressive and flexural strengths. MDF cements have almost double the Young's modulus of PC and the increased flexural strength. The improved strength was thought to be due to the removal of large pores with a lower overall porosity, and the strong chemical bonding between the polymer and the cement grains.

The chemistry and microstructure of the material had been studied previously, and it was demonstrated that there were significant amounts of Ca and Si in the polymer gel matrix. Metal ions were thought to cross-link with the polymer facilitating the bonding. However, it was reported that when soaking in water for a prolonged period, the material suffered a significant loss in strength and experienced large swelling and expansion. This was attributed to the instability of the polymer gel matrix in water. A previous study using transmission electron microscopy demonstrated that the water stability of the material was related to the chemical compositions of the polymer matrix.

Table 3 Comparison of Material properties

Material	Density (g/cm^3)	Flexural strength (MPa)	Youngs modulus (GPa)	Fracture energy (J/m^2)
OPC	2.3	5–10	20–25	20
MDF cement	2.3–2.5	>150	40–45	300–1000
Aluminium	2.7	150–400	70	1,00,000
Glass	2.5	70	70	10
Wood	1.0	100	10	10,000

The resultant physical properties of the polymer concrete are ultimately depend upon the chemical nature of the monomer used, degree of polymerization, the particle size of the aggregate, along with the degree of hardness it possesses.

Initiators, pigments and thixotropic agents were also added to improve the workability, setting characteristics and aesthetics of this material. The same application characteristics as with standard Portland cement concrete can be used for polymer-impregnated cement material.

Normally, good adhesion to the vast majority of substrates and a high degree of chemical resistance is achieved. Certainly, it depends on the type of used monomer pre-polymer. Further, very important physical property is the relative physical stability after the material's curing. This is principally due to the fact that the initial shaping process can require heat and pressure initiating specific chemical reactions during the curing process (describes in 3.6 Hardening and Strength Development of MDF Materials).

3.4 Hardening and Strength Development of MDF Materials

The hardening and strength development of MDF materials is the result of chemical reactions taking place in the material during processing and curing. These include both an interaction between the inorganic cement and the polymer, and cross-linking reactions within the polymer itself. Van der Waals forces may also be involved.

In the system comprising calcium aluminate cement and polyvinyl alcohol/acetate the cement hydration is limited, as the polymer slows down the hydration rate. Non-hydrated particles of the cement become constituents of the developed structure, held together by a polymeric-inorganic matrix. The phase C_2AH_8 is formed as the main hydration product of the cement.

In the system comprising Portland cement and polyacrylamide more hydrated material is formed, but again a significant part of the cement remains non-hydrated. The cement hydration products are similar to those formed in the absence of the polymer, but they exhibit a denser packing.

3.4.1 Chemical reactions during MDF composite forming

Because of the high pH of the liquid phase brought about by the hydration of the cement, the polymers also undergo chemical reactions. In the polyvinyl alcohol/acetate co-polymer a hydrolysis of the acetate groups takes place. The liberated acetate groups react with cations in the liquid phase, and in particular with Ca^{2+} ions and calcium acetate is precipitated; see the following reaction scheme in *Fig. 4*.

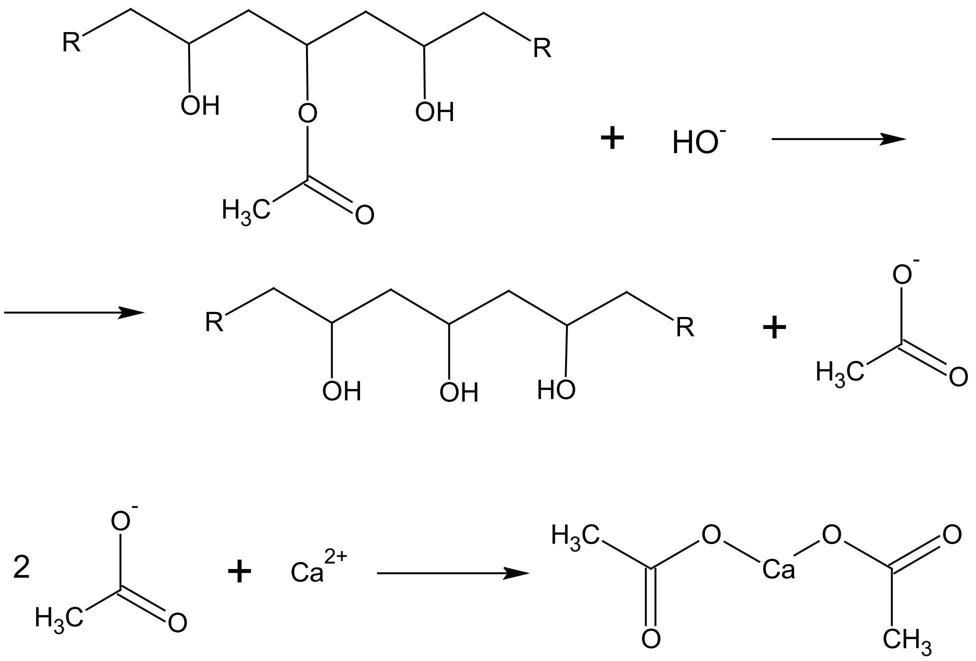


Fig. 4 Reaction mechanism of calcium acetate precipitation

In the case of polyacrylamide the amide groups undergo hydrolysis, and carboxy groups are formed instead (*Fig. 5*)

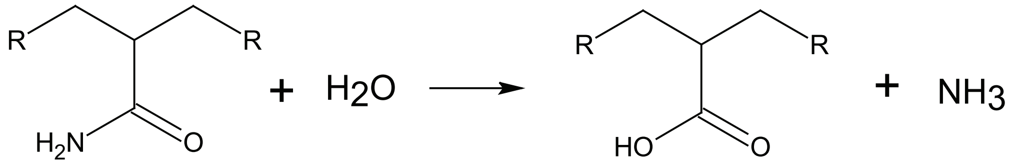


Fig. 5 Polyacrylamide hydrolysis

It is generally believed that the chemically modified polymer interacts with the cations liberated in the cement hydration, but the exact nature of this interaction is not obvious. It has been suggested that $(A1(OH)_4)$ ions released by the calcium aluminate cement cross-link the polyvinyl alcohol chain in the way structured in the figure *Fig. 6.*

However, this assumption was questioned by Desai et al.[30]. A similar cross-linking involving polyvinyl alcohol and Ca^{2+} ions is considered unlikely.

As to polyacrylamide, it has been postulated that after removal of the NH_2 group the following bonds may be formed, involved in cross-linking reaction.

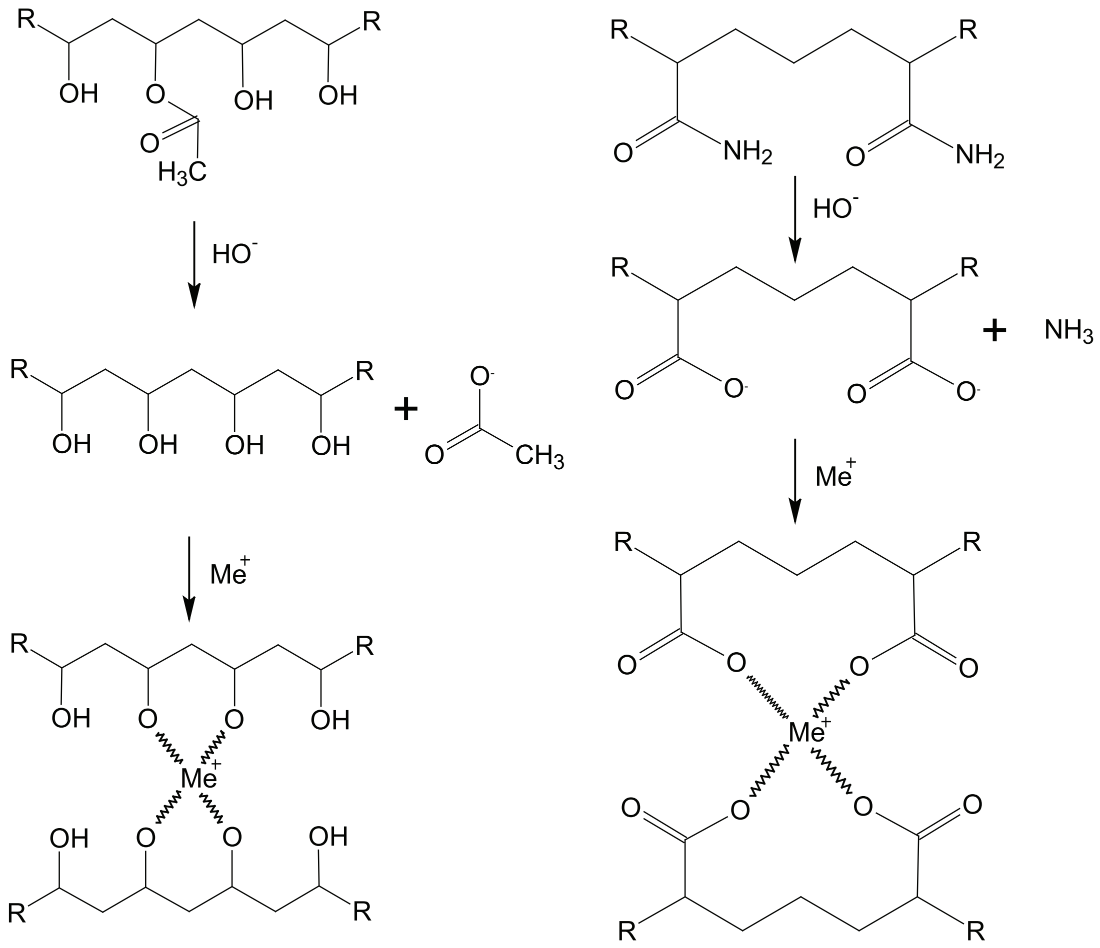


Fig. 6 Reaction of polyvinyl alcohol and polyacrylamide with the metal ions

3.5 Limitations of MDF composite technology

Important part of processional expansion is resolving limitations of MDF composite. These significant problems had been observed since they were patented in 1983 and includes:

1. Low moisture resistance,
2. Shrinkage,
3. Difficulties with processing on a commercial scale

3.5.1 Moisture Resistance

The limitation of changing the mechanical properties when MDF composites are exposed to moisture has been already reported many times. A lot of observations and research were lead to understand the process of moisture ingression and the forming chemical changes. It has been also widely reported and mentioned these chemical changes leading to a loss of compressive and flexural strength. A 55% loss in flexural strength was observed after 24 h immersion in water, although most of this was found to be reversible on drying at the temperature about 80 °C[34]. In the most common used CAC–PVA system of MDF material preparation the PVA polymer phase is associated with moisture ingress. Moisture enters via the polymer network during exposure the material of humidity, causing the polymer to swell. This has a significant and strong effect on the behavior of cross links in the polymer–cement interphase region respectively initiating in situ hydration reactions of unhydrated cement grains[29]. The rate of moisture uptake is thought to be diffusion controlled[35].

Chemically, the behavior can be attributed to the relative intensities of the interactions between the components of the composite. When the composite is almost anhydrous, the interactions between the polymer and the cement matrix are short range thanks to weak van der Waals forces. When molecules of water come into the contact with the polymer–cement interface, van der Waals attraction is more limited and therefore water and polymer interact by an acid–base association which is stronger than the original van der Waals force. Hence, the polymer interacts preferentially with water. This means, there is a competition between water molecules and cement matrix for the polymer[36].

To assure the appropriate rheological properties of the fresh paste, a water-soluble polymer is needed for the preparation of MDF material. In this sense, the presence of water will always reduce the polymer/cement matrix interaction. Many investigations have been done to limit the interaction dependence. The most common approaches are listed below.

1. *Reduction of polymer content*

In general, reduction of the water soluble polymer content in the MDF composite mixture is probably the simplest approach that can be used. The reason came from the idea the polymer concentration is lowered, the effective polymer-cement interface is also reduced and therefore the polymer does not have to react preferentially with water. The group around Drábik[22] pointed out the different investigation. The micro chemical aspects of the polymer/cement interface in the matrix are fundamentally important to the development of the mechanical properties formed composite. Typically, the polymer content varies from 5 to 20%, in relation to the cement weight. When the lower amount of polymer is used, the mechanical properties of the composite are negatively affected.

2. *Surface modification of polymer*

Another explored approach to eliminate the moisture effect which has showed very good results is the chemical modification of polymer surface. Santos[37] did a survey of the silica fume addition to decrease the acid resistance of MDF materials, suggesting that silica fume acts as inert filler. The method is not extensively used and widely reported because of the high costs involved.

3. *"In situ" reticulation of polymer*

Most discussed topics related to moisture limitation are the effort to control the process using a reticulation agent and form "In situ" reticulation of the polymer part. The aim is to make changes, especially in the cement-polymer interaction. Further, the extensive chemical study is needed to control the overall properties of the composite.

Group lead by Rodrigues and Joekes[32] were focusing their work on this approach. They suggested, the polymer reticulation is easier if the polymer is dissolved. They used aqueous solutions instead of the solid polymer, their reticulation agent was inert with respect to the normal cement properties (they used an inorganic, basic salt), partially hydrolyzed polyvinyl alcohol (PVA) as the water-soluble polymer and they used the sodium silicate solutions as the reticulation agent.

3.5.2 Shrinkage

The hydration reactions occur and form in a composite matrix during the MDF material curing. Many studies and surveys have been done to explore the possible mechanism. The ongoing reactions during curing and hydration are still the subject of research and it is very difficult to ascertain, especially when hydration is incomplete. The characteristic shrinkage during the curing occurs up to 10% volume (for the system CAC/polyvinyl alcohol). The shrinkage is probably caused by dehydration of the polymer when moisture is removed by reaction with unhydrated cement grains. Polymer is thus influences the hydration reaction that would normally have been carried out in pure cement parts.

The hydration reactions in PVAA–CAC systems are probably identical with the system involving only the CAC. The exception is the scope of the reaction:

$$CA + 10H \rightarrow CAH_{10} \qquad T < 15\ °C \tag{1}$$
$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \qquad 15\ °C < T < 30\ °C \tag{2}$$
$$3CA + 12H \rightarrow C_3AH_6 + 2AH_3 \qquad T > 30\ °C \tag{3}$$
$$2CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9H \tag{4}$$
$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \tag{5}$$

Cement chemistry use designation for clarity, the letters $C = CaO$, $A = Al_2O_3$, $H = H_2O$.

The reactions will thermodynamically proceed towards the products of *Eq. 5*. However the presence of PVAA inhibits the formation of the stable C_3AH_6 phase. The result is the formation of the intermediate hydration product CAH_{10} or C_2AH_8 during the curing process. These phases, complexes persist longer than it would for pure alumina cement. Eventually C_3AH_6 conversion will occur, but it is accompanied by approximately 10 % shrinkage during curing which is at a time when the stresses on the material can cause significant weakening. Ideally this shrinkage should occur during compaction or the formation of C_3AH_6 should be so rapid that the shrinkage is not noticeable.

3.5.3 Difficulties with processing on a commercial scale

Although MDF materials occupy a wide area of excellent mechanical properties there are many limitation with global processing on a commercial scale. In the first the assumption of financial costs of input materials compare to ordinary cement pasts. Alumina cement is for example ten times more expensive than traditional Portland cement. Moreover, other expensive additives (polymer, rheological additive) needed to produce the final MDF composite product associated also with costly manufacturing process.

Lastly, it is already mentioned changes of mechanical properties depending on humidity, which currently limits the production of larger scale.

On the other hand, it has been already explored how to produce coloured product from polymer-impregnated cement material without experiencing any chemical incompatibility with pigment and resin. It can be considered as very big advantage in commercial level as well as relatively fast manufacturing process and hardening time.

3.6 Procedure of Moisture Resistance Investigation

A common method of measuring MDF material moisture resistance is to place samples in a container with controlled relative humidity and measure the sample mass at regular intervals.

The outputs are dried samples weighed at regular intervals. Results of exposure show the reversible and irreversible extent of moisture absorption. The reversible changes in properties are generally attributed to polymer swelling whereas irreversible changes are linked with carbonation and the reaction of unhydrated cement[38].

Materials high in moisture resistance should exhibit a low mass increase under these test conditions. A noticeable feature of moisture attack is the formation of new $CaCO_3$ detectable by thermogravimetric TGA/DTA analysis in the temperature range 500 – 750 °C.

The following reaction shows the formation:

$$CaO + H_2O \rightarrow Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (6)$$

The effect of different cement phases on moisture resistance has been investigated. For example, using sulphoaluminate – ferrite – belite (SAFB) and Portland cement (PC) blends instead of CAC produced irreversible moisture absorption of 0.5 – 10% of initial weight.

Another survey leads to the changes of the polymer phase. PVAA with different degrees of hydrolysis and average molecular weights have been used as well as sodium polyphosphate (poly-P), hydroxypropylmethyl cellulose (HPMC) and butylacrylate/acrylonitrile (BA/AN). Using hydroxypropylmethyl cellulose started an interesting series of results and is still subject of research[39]. Titchell[40] studied another approach. They have been around to remove the moisture sensitive bulk polymer phase by heat treatment at 500 °C followed by incorporation of a heat resistant polymer into the structure. These materials showed good results with moisture resistance. CAC/PVAA cement heated to 500 °C before being partially rehydrated showed zero loss of strength after 48 hours immersion in water at 20 °C.

Chandrashekhar and his colleagues[41] studied the effect of cross-linking additives to cause the bulk polymer pathway to become narrower and less accessible and percolative to moisture has been investigated. The research has used an organotitanate linking agent (Tyzors) to increase cross-linking with polyvinyl alcohol. Unfortunately, the resulting cement paste had insufficient workability, respectively the mixture started to stiffening even before the manufacturing process thanks to extensive cross-linking. Results of the survey about the organotitanate linking agent addition to obtain the desired effect were very limited.

Using a monomer and activation agent instead of a polymer to occur the in situ polymerization during MDF cement hydration has been further part of investigation lead by Zhihong[42]. The in situ polymerization of acrylamide monomer (AAM) with a PC/sulphoaluminate and slag blend, the MDF cement formed showed no decrease in flexural strength after 4 months immersion in water. Reducing the quantity of unreacted cement in MDF composites by substituting cement content for inert fillers prior to pre-mixing had also been shown as a good result in moisture resistance improvement. Changing the curing conditions by either delayed drying during curing or prolonged curing in ambient water followed by oven curing have both been shown to improve moisture resistance.

There are several possible reasons theory. Firstly, the basic the basic compound formation or more stable cement hydration products. Second theory refers to a producing of possibly greater extent of hydrated cement phases.

3.7 High-Alumina Cement

To pursue the study of MDF materials based on calcium alumina cements, it is important firstly to understand the basics associated with this binder, respectively structure, properties and the hydration mechanisms.

High-alumina cement (HAC) consists primarily of calcium aluminates and achieves several outstanding properties, such as high early strength, excellent refractoriness, good resistance against certain chemical attacks, etc. Despite the applicability of these cements strongly affected, since even the slightest increase in temperature over the moisture can cause a permanent reduction in the strength of high-alumina cement pastes. The reduced strength is the result of the increased internal porosity of hardened high-alumina cement paste and the second reduction bonds due to spontaneous conversion of hexagonal crystals incurred during the hydration (mainly calcium aluminate hydrates) in more compact cubic structure.

3.7.1 Manufacture of HAC

Although the hydraulic properties of calcium aluminates have been recognized since about 1850, the first suitable method for the commercial manufacture of high-alumina cement was developed by Jules Bied and patented in 1908 in France. The commercial manufacture of such cements did not begin in the United States until 1924. Presently high-alumina cement is produced in many countries.

The raw materials customarily used for the manufacture of ordinary high-alumina cements are limestone and bauxite. The bauxite is ground with limestone, then the dry mixture is fed into a kiln where it is heated until it melts (fusion), which process takes place about 1600 °C. Then the molten clinker is cooled down, for instance by spreading water on it, and the granulated material is ground to cement fineness with or without the addition of a small amount of gypsum.

The clinker of high-alumina cement consists of a series of calcium aluminates, iron-containing compounds, beta-dicalcium silicate, and other, minor constituents. Considerably less is known about the compound composition of high-alumina cements than that of Portland cements. It is clear, however, that the monocalcium aluminate ($CaO.Al_20_3$) is by far the most important compound, since it is primarily responsible for the particular cementitious behavior found in this kind of cement. This compound is slow-setting but subsequently hardens with great rapidity. High-alumina cements that provide the highest early strength usually contain less than 5% silica[43].

3.7.2 Setting and hardening of HAC

Setting and hardening HAC is characterized by rapid increase in strength and development of a large quantity of heat. Further, fast hydrolysis and hydration of the main active phase occurs, as shown in simplified *equation 7*:

$$2\,(CaO.Al_2O_3) + 11\,H_2O = 2CaO.Al_2O_3.8H_2O + 2\,Al(OH)_3 \qquad (7)$$

The hydration of high-alumina cement produces again small crystals and gel. These consist mainly calciumaluminate hydrates; the most important product is $CaO.Al_2O_3.10H_2O$ (CAH_{10}). Simultaneously, the reaction product in the *Eq. 7* is formed with the CAH_{10} in a small amount. It occurs at lower temperatures (up to 20 °C). Then, the setting is becoming slower till 29 °C (insufficient hydration of CAH_{10}). CAH_{10} forms an amorphous structure around unhydrated cement grains.

The hydrates first form hexagonal crystals which, however, later tend to transform into the more stable $3CaO.Al_20_3.6H_20$ (C_3AH_6) of cubic form, particularly at temperatures higher than about 30 °C, when water is present. Firstly, amorphous products are formed during the transition, and consequently a stable compound C_3AH_6 taking part in the reaction. This is called conversion and is accompanied by loss of cement strength. It follows that a conversion of CAH_{10} and C_2AH_8 is primarily responsible for the reduction in the strength of HAC. The reaction scheme in the following reactions *Eq. 8* and *Eq. 9*:

$$3(CaO.Al_2O_3.10H_2O) \rightarrow 3CaO.Al_2O_3.6H_2O + 2(Al_2O_3.3H_2O) + 18H_2O \qquad (8)$$

$$3(2CaO.Al_2O_3.8H_2O) \rightarrow 2(3CaO.Al_2O_3.6H_2O) + Al_2O_3.3H_2O + 9H_2O \qquad (9)$$

It is also important that no free calcium hydroxide develops during hydration. It probably refers to lower pH value of high-alumina cement paste (approximately 10) compare to Portland cement paste.

3.7.3 Properties and Applications

Technically important properties of high-alumina cements, e. g. color, specific gravity, fineness, time of initial setting, total amount of hydration heat, storability, etc. has been confirmed to be similar to Portland cements. The workability, frost resistance, impermeability, creep, shrinkage properties, and thermal expansion of high-alumina cement concretes are also nearly the same.

The differences come with necessary water content. High-alumina cements require less water for normal consistency. Robson[44] determined the usual interval between initial and final settings in high-alumina cements is short (about 30 – 45 min.). Further, the sensitivity to the water-cement ratio during the final setting is reduced compare to classical cement pastes. Graf and his group[45] experimented the initial rate of heat development is high, around 9 cal/g.hr; and unsoundness does not occur in high-alumina cements.

Very important property of the high-alumina cements is the high resistivity to weak acid and sulfate compare to Portland cements. The reason is attributed to the absence of free calcium hydroxide in the hydrated high-alumina cement.

White alumina cements and the high-alumina cements with high content of calcium dialuminate, provide also superior properties in refractory bonding, and gives perfect suitability at high temperatures for prolonged service (in furnaces or kilns, up to 1600 °C).[46] Concrete from high-alumina cement (as well as Portland cement concrete) are loosing the strength during exposure to high temperatures. If the temperature is increased above about 700 °C, reactions begin to form ceramic bonds in the aggregates.

Other differences are in the creation of early strength development. Although many variations in the initial rate of high-alumina cement hardening, all of these cements are fast hardening. The low-silica cements can give with a 0.5 water-cement ratio (weight ratio) concrete strength of around 27 mPa at 6 hours storing. The early strength development of high-alumina cement (low-silica type) compared to Portland cements presents an example in *Fig. 7*.

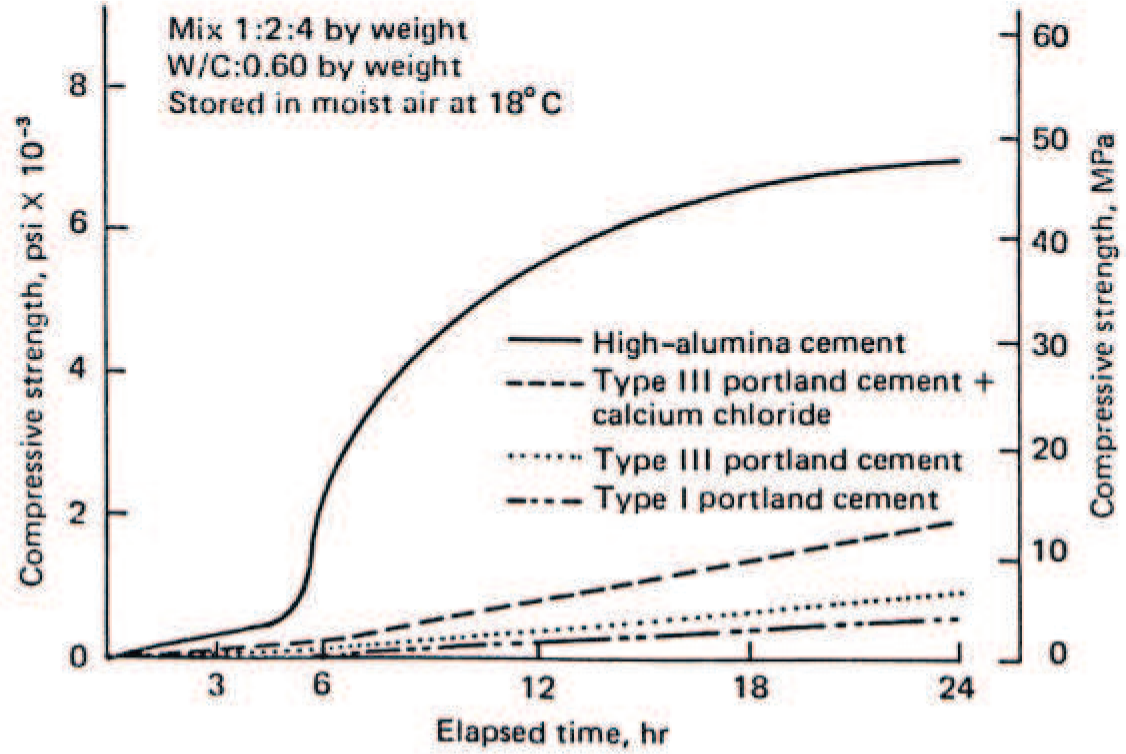


Fig. 7 Strength development of concretes made with a high-alumina cement and Portland cements.

The shapes of the concrete show the differences in strength dependent to time of storing. The strength of the Portland cement concrete is about half of the concrete after 90 days. The difference in strength developing ability of high-alumina cements positively increasing when the applied curing temperature is close to the freezing point.

Despite these important advantages, the structural applicability of high-alumina cements is very limited in commercial level and restricted. The reason is refers to higher temperature when the material of high-alumina cement is in contact with water. These conditions can cause a permanent strength reduction in high-alumina cement concrete. A typical example is given in *Fig. 8* where high-alumina cement mortar is cured in water with temperature 38 °C. The result shows the rapid decrease and reduction of compressive strength. The resulting diagram consequently confirmed that the weaker strength of concrete the loss of strength is further increase. The strength reduction is attributed to an increase in the internal porosity of the hardened paste of high-alumina cement. It is refers to the spontaneous conversion of hexagonal crystals of the calcium aluminate hydrates into the cubic form since the latter has a smaller volume[47]. Bolomey[48] in 1930 confirmed the conversion is occurred during the living time of the formed concrete when the material is applied to the higher temperature and humidity. Tabaler[43] added in 1962 the completely dry concrete is not subject to conversion. It still contains some mixing water in a free state; the conversion may easily take place.

The conversion takes place at a rate that depends on a number of factors, including the temperature, water-cement ratio, etc. The strength reduction of the concrete probably increases with the rate and water-cement ratio increase.

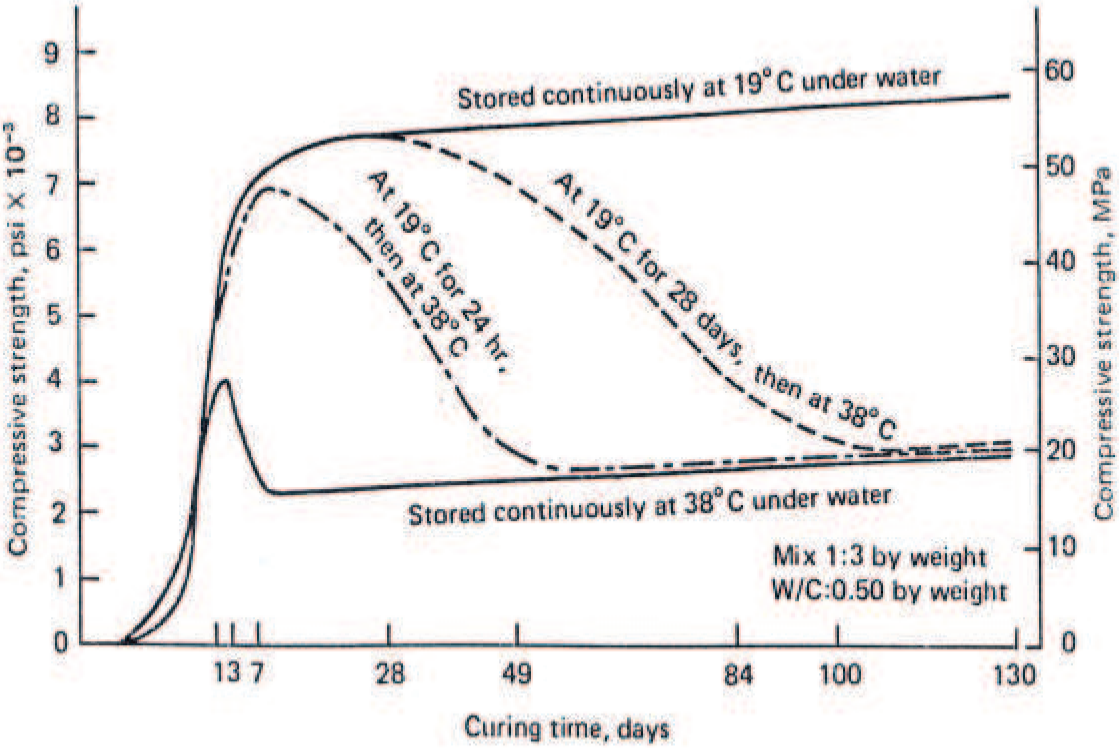


Fig. 8 Reduction in compressive strength of high-alumina cement mortar cured in water of 38°C.

3.8 Water Soluble Polymers

Water soluble polymers find applications in a number of fields of which the following may be worth mentioning: cosmetics, detergent, oral care, industrial water treatment, geothermal, wastewater treatment, water purification and reuse, pulp and paper production, sugar refining, and many more. Moreover, water soluble polymers play vital role in the oil industry, especially in enhanced oil recovery. Water soluble polymers are also used in agriculture and controlled release pharmaceutical applications. Therefore, a fundamental knowledge of solution properties of these polymers is essential for most industrial scientists.

Polyvinyl alcohol-acetate copolymer (PVAA) represents one of the most important water soluble polymers.

3.8.1 Polyvinyl alcohol

Poly (vinyl alcohol), respectively polyvinyl alcohol-acetate copolymer (PVAA), is a widely used hydrophilic synthetic polymer reactive with many kinds of functional groups due to a large number of hydroxyl groups[49]. PVAA has several unique features: dissolving in water over a wide range of temperatures, crystallizability, and capability of hydrogen bonding. The water solubility depends on its degree of hydrolysis, molecular weight, and tendency to hydrogen bond in aqueous solutions. As PVAA is produced by methanolysis of poly (vinyl acetate), a small amount of acetate groups is always present, depending on the production company. The characteristic Flory interaction parameter for the PVAA-water system has been determined by Peppas and Merrill[50] as a function of temperature and concentration.

PVAA has many applications, e. g. in the production of high-strength fibers, as a viscosity adjusting reagent in aqueous solutions, in formulating adhesives. Recently, the gelation capability of PVAA has been focused on by many researchers so as to understand the gelation mechanism.

Moreover, the coatings of polyvinyl alcohol improve strength and chemical resistance, as well as water resistance. It's also the main goal of the MDF cements preparation. Adding organic titanates to air dried varnishes that contain poly (vinyl alcohol) is one of the possibilities, how to get the coating.

Properties PVAA has excellent emulsification, film forming and adhesive proper- ties. Moreover, PVAA is water soluble but resistant to oil, grease and other solvents. It's very sensitive to moisture. The water, which is in this case a plasticizer, is reduces the tensile strength of PVAA, but increase the elongation and tear strength. PVAA is totally degradable material and semicrystallic due to small hydroxyl group. The decomposition of PVAA is above 200 °C (melting point is about 230 °C) with possibility of pyrolysis at high temperature.

Polyvinyl alcohol-acetate copolymer in semidilute aqueous solutions can form chemical or physical gels (by adding a cross-linking agent) due to hydrogen bonding and/or chemical reaction of hydroxy groups[49].

GL is a shortcut for Gohsenol, which is type of PVAA produced by Nippon with excellent water solubility, bonding strength, membrane forming properties and chemical stability and environmental friendly, which is very important property.

The production is similar to polyvinyl alcohol GL-05S. The main difference is in the viscosity of PVA. Polyvinyl alcohol GH-17S represents much higher value of viscosity than GL-05S. Other parameters are comparable. The proper parameters of this types of PVAA are described in the experimental part.

Gelation

Gelation is attributed to the copolymeric nature of the polymer, which is a result of incomplete hydrolysis of the basic polymer. Therefore, the stereoregularity also plays an important role: isotactic poly (vinyl alcohol) is dissolved easily in cold water, but syndiotactic poly (vinyl alcohol) does not dissolve even in boiling water. If the stereoregularity is not high, gels may be formed in aqueous solutions, where tiny crystallites act as multifunctional crosslinks.

Possible ways to form a cross-linked poly (vinyl alcohol) from solution:

- *In water*; gelation is accompanied by formation of helical structures which are formed by syndiotactic sequences in the poly (vinyl alcohol) molecules
- *In aqueous solution*, where PVAA gels are formed by cross-linking formation in terms of either hydrogen bonding followed by crystallization of PVAA chains or complexation with several kinds of inorganic ions such as cupric, borate[51], titanate[52], and vanadate ions[53];
- *In non-aqueous solutions*, where the process has to consist of organic solvents, e.g. ethylene glycol or dimethyl sulfoxide not necessarily mixed with water.

3.8.2 Organic Titanates

Organic titanates perform an important compounds have been using in a plenty of industrial application, e. g. as a Catalysts, surface modifying factor, a reagent used to create sol gels, ceramics, heterogeneous catalysts, last but not least to polymer cross-linking.

The cross-linking property of organic titanates improves viscosity control properties of solutions, apints and other coatings.

In preliminary research by Desai[4], several polymer (PVAA) cross-linking additives were surveyed with respect to their ability to improve the moisture resistance of MDF cement. Further, Lewis and Boyer showed that a significant improvement in both moisture absorption and resistance to strength degradation in a 100% relative humidity environment was achieved in the organotitanate-modified MDF cement materials[5]. At the end, in the case of polyvinyl alcohol, adding organic titanates to air-dried varnishes that contain PVAA gives coating improved strength and chemical resistance.

The TYZORs cross-link polymers through the active hydrogen of PVAA's hydroxyl group. Though the ROH is more volatile, the TYZOR do not undergo alcoholisms only. Equilibrium is moved to the right and converting ROH. This reaction is sometimes called ester interchange of a titanate, because the alkyl groups in an ester of Roth-titanic acid are intercharged (see *Fig. 9*).

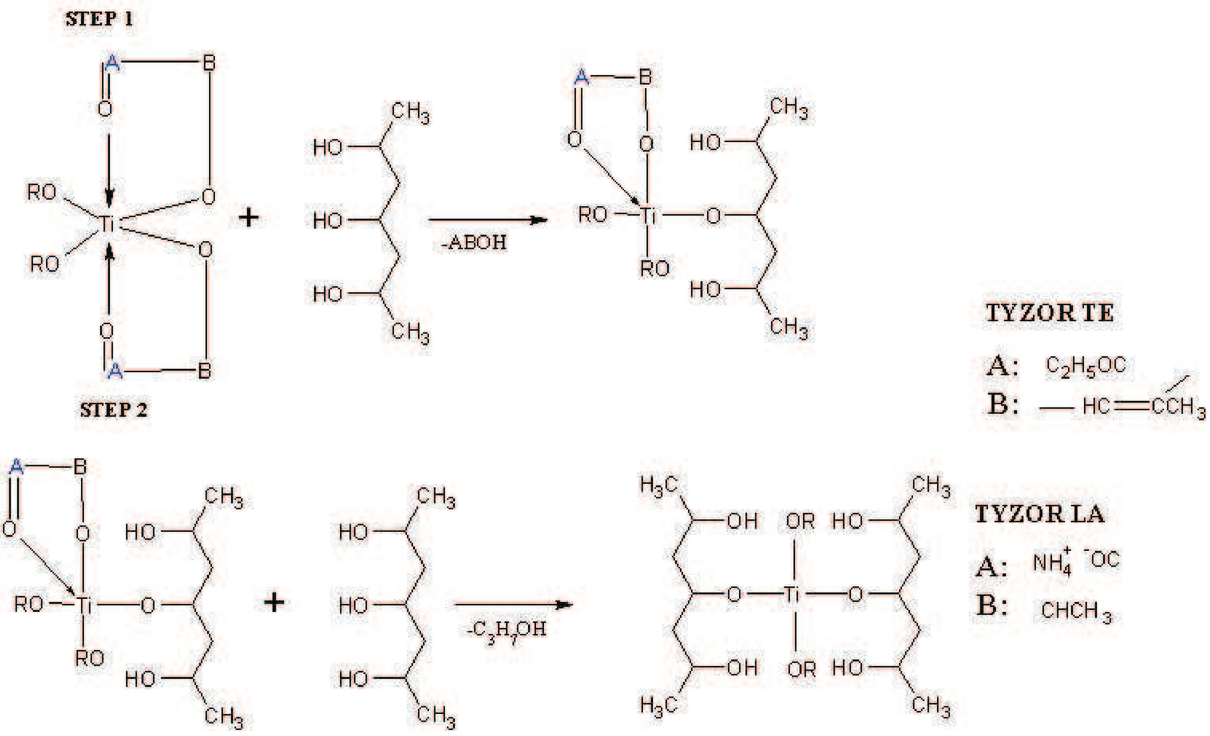


Fig. 9: Reaction sequence between Tyzor additive and fully hydrolyzed polyvinyl alcohol

Commercial organic titanates represent a company E. I. du Pont de Nemours and Company trademarked by Tyzor. The company supplies two general classes of these organic titanates:

tetraalkyl titanates, which can be represented by the general structure Ti(OR)$_4$, and titanate chelates. The chelates can be further subdivided into two groups:

- Nonaqueous, including products that are supplied as 100% active materials or as a solution in alcohol (main products with which to work in this work are in *Table 4*).
- Aqueous, including products that are supplied as water solutions (in *Table 5*).

Table 4 Grade selection chart for nonaqueous tyzors organic titanates used in the thesis

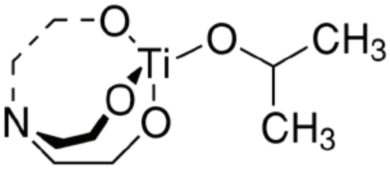
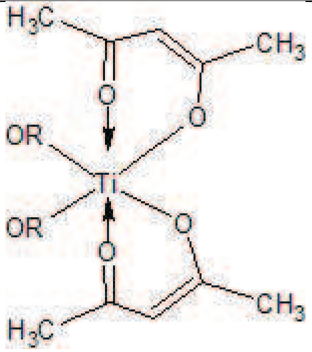
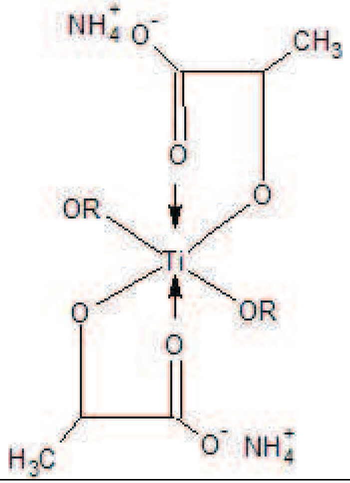
Nonaqueous system	**Tyzor TE** Triethanolamine titanate chelate	**Tyzor AA** Acetylacetonate titanate chelate
Structure		
Properties	Soluble in water (slow hydrolysis), 80 % active in alcohol, stable at lab temperature, pH = 2-5, more reactive at acidic conditions	75-100 % active in alcohol
Initiation of cross-linking	100-250°C	100-250°C
Application	Aqueous and non-aqueous formulations, Delayed cross-linking	Aqueous and non-aqueous formulations, Delayed cross-linking
reference	Lewis, Boyer et. al	Rohowetz, Neenah et. al

Table 5 Grade selection chart for nonaqueous tyzors organic titanates used in the thesis

Tyzor LA Lactic acid titanate chelate, ammonium salt				
Structure	*Properties*	*Initiation of cross-linking*	*Application*	*References*
	50 % active in water. Active at Most reactive of aqueous chelates	100-250°C pH 5-10	Aqueous formulations, Delayed cross-linking Esterification Catalyst	Shin, Exarhoz et. al

3.9 Other polymer impregnated cementitious materials

In fact, the introduction of polymers into cementitious materials in order to improve the bond adhesion, flexibility and workability of the resultant composite first occurred very earlier than polymer impregnated cementitious materials and MDF composites (1930s) where natural rubber was utilized. However, the main difficulty with using this naturally occurring polymer material was the inability to significantly modify the chemical structure and thus tailor the physical properties to those required for a particular application. Advances in polymer technology over several decades resulted in the manufacture of synthetic polymers with properties, which improved on those of the natural polymers available, i.e., polyvinyl acetate (PVA), styrene butadiene rubber (SBR), vinyl acrylics (VA), methyl methacrylate (MMA) and epoxy resins, etc.

The synthetic polymers were combined with inorganic cements by various preparation processes to yield materials with superior and unique properties. Important precondition for this application is a sufficient stability of the polymer in a high-pH environment which is typical for most cementitious systems.

The cementitious materials have been divided to three fundamentally different ways in which organic polymers may be combined with inorganic cements:

- The polymer can be employed to fill the pore space of the hardened cement paste and form the stronger material.
- A polymeric dispersion may be interblended with the fresh cement paste to yield a combined cementitious-polymeric system.
- A new material may be created in a chemical interaction between the polymer and constituents of the inorganic binder[6].

3.9.1 Calcium Aluminate Phenol Resin

Calcium Aluminate Phenol Resin, also called CAPR composite represents an alternative to classical MDF composites. Preparation of CAPR composite using similar processing method required for MDF cement manufacture. Although, the CAPR composite manufacture is considered sufficiently different to conventional MDF cements it is protected by a separate patent[54]. High alumina cement (also other hydraulic cement can be used) is mixed with a phenol resin precursor. Further, a modifier is used to control cross linking density and at the end the glycerol as a plasticiser is added. The manufacturing process is proposed without any addition of water. The cement part is hydrated by water given off the phenol precursor during the condensation polymerization reaction, respectively in situ polymerization. The process form CAPR composites with an effective w/c ratio close to value 0.01. A summary of this process is outlined in *Fig. 10*.

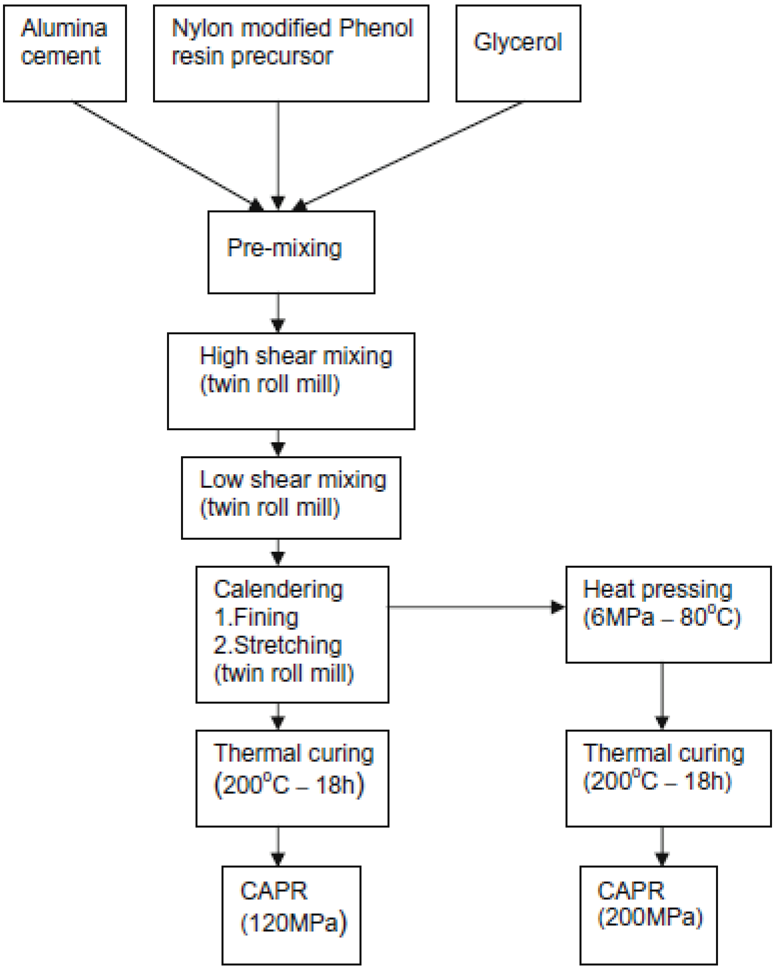


Fig. 10 CAPR manufacture process

Pushpalal and his colleagues[55] lead the survey about an ‘immunization procedure’ of the CAPR composites. The procedure consisted in immersion of CAPR composite in water at 20 °C for one year and the result showed only 0.82 % increase in mass and 0.12 % expansion and a loss in flexural strength of 9 %. The procedure has been developed for CAPR composites where the curing process in hot water has preference to heat curing in order to produce the stable phase C_3AH_6 instead of metastable CAH_{10} and alumina gel. Further, the 'immunized' samples showed particularly no loss in flexural strength after 1 year immersion in water at 20 °C.

Pushapal has also studied the behaving of interaction between the phenol and cement phases in CAPR composites. A cross-linking mechanism involved and started initially with calcium ions at the roll-milling stage and then aluminium ions during heat curing.

At the end, the fracture toughness of CAPR composites has been consequently reported. Crack propagation was found to initiate and occur through the phenol resin matrix, the cement particles were proposed to act as reinforcing particles. However, it has been confirmed that the limited particle lubrication during formation increasing the number of reinforcing cement particles in CAPR composites. It caused producing cements with inferior properties.

4 EXPERIMENTAL PART

Originally studied MDF composite samples without any special additives to improve the moisture sensitivity were prepared according to the procedure developed by Birchall et al.[2] and optimized by Russell. Novel, Tyzor modified MDF composite samples were prepared based on the developed progression and empirically deduced procedure. Different types of Tyzors were evaluated with respect to gelation of PVAA.

4.1 Chemicals

Calcium aluminate cement Secar 51

The calcium aluminates' cement used for investigation was selected based on several outstanding properties, such as high early strength and good resistance against certain chemical attacks.

The main prerequisite for the selection of the HAC was a high Al_2O_3 content. A product with the brand name Secar 51 by Lafarge, has been found to be particularly suitable, but other calcium aluminates' cements may also be used. Secar 51 produced by Lafarge company in France was represented the main compound of MDF composite.

Secar 51 is a fused hydraulic binder with a mineralogy focused on monocalcium aluminate to give strong hydraulic activity with an alumina content of approximately 50 %. The main components are calcium aluminates, which guarantee good refractoriness of the cement. Secar 51 is also particularly rich in monocalcium aluminate which imparts perfect properties to mortar and concretes. Secar 51 adheres to the following specifications shown in the *Table 6*.

Table 6 Chemical Properties of Calcium aluminate cement Secar 51[56]

Chemical Composition	*Usual Range*	*Specification Limit*
Al_2O_3	50.8 – 54.2	> 50.0
CaO	35.9 – 38.9	< 40.0
SiO_2	4,0 - 5,5	< 6.0
Fe_2O_3	1.0 – 2.2	< 2.5
MgO	< 1.0	-
TiO_2	< 4.0	-
$K_2O + Na_2O$	< 0.5	-
Fineness		
Blain specific surface (cm^2/g)	3750 – 4250	> 3700
Residue at 90 µm (%)	-	< 5.0
Setting time (min)		
Initial set	190 – 270	> 150
Final set	210 – 300	< 330
Mechanical Properties – Compressive Strength (MPa)		
Age: 6 h	20 – 55	> 15
Age: 24 h	55 – 85	> 50

Polyvinyl alcohol (PVAA)

Polyvinyl alcohol GL-05S and GH-17S were purchased from The Nippon Synthetic Chemical Industry Co. in Japan. The main chemical properties of polyvinyl alcohols are summarized in the *Table 7*.

Table 7 Properties of used polyvinyl alcohols

PVAA	GL 05S	GH 17S
Viscosity	5.0 mPa·s	29.1 mPa·s
Saponification degree	86.8 mol. %	87.6 mol. %
Volatiles	1.6 wt. %	3.7 wt. %
pH	6.0	5.7

Cross-linking additives

Three Tyzors, organotitanate cross-linking agents were used:

- *Tyzor TE* (Triethanolamine Titanate, supplied from E. I. du Pont de Nemours and Company)
- *Tyzor LA* (dihydroxy bis [2-hydroxypropanato (2-)-O1, O2]-, ammonium salt, E. I. du Pont de Nemours and Company)
- *Tyzor AA-75* (from E. I. du Pont de Nemours and Company was treated as follows to obtain a stable aqueous solution soluble in water. Tyzor AA-75 was added (10 weight parts) to methyl ethyl ketone (20 weight parts) and mildly stirred for 25 min. Then, distilled water (35 weight parts) was slowly added to maintain a clear solution).

Methyl ethyl ketone

(Methyl >99 %) was supplied by Fluka, Czech Republic.

Glycerol

(p. a.) was supplied by Lach-Ner, s. r. o., Neratovice.

Hydroxides

Aluminium hydroxide $Al(OH)_3$ produced by Penta-výroba a prodej čistých farmaceutických a speciálních chemikálií in Chrudim, Czech Republic and calcium hydroxide $Ca(OH)_2$ purchased from were used to experimental investigation of PVAA gelation.

Main properties of hydroxides are summarized in the *Table 8*.

Table 8 Properties of Aluminium and Calcium hydroxide

	Aluminium hydroxide	calcium hydroxide
Molecular Formula	$Al(OH)_3$	$Ca(OH)_2$
Purity	p. a.	p. a.
Molar Mass	78.00 g/mol	74.093 g/mol

4.2 Study of gelation behaviour of PVAA/Tyzor system

The gel point determination of PVAA GH-17s in water solution with presence of organotitanates (Tyzors) series at vial-scale and at conditions similar to that of real MDF process was carried out. The composition of used PVAA solutions was suggested according to Odler et al.[6] (see in *Table 9*).

Table 9 Batch composition of MDF cement samples[6]

Component	Composition		
	Weight (g)*	**wt %**	**vol %**
CAC cement	8.43	84.25	65.21
PVA	0.59	5.90	12.30
Glycerol	0.06	0.58	1.35
Deionized water	0.93	9.27	21.34

However, the cement part was eliminated in aqueous solutions, their pH was originally adjusted with $Ca(OH)_2$ (p. a.; Lach-Ner, s. r. o., Neratovice, Czech Republic) and $Al(OH)_3$ (p. a.; Penta, Chrudim, Czech Republic) to maintain the alkaline environment similar to that of MDF composite. The ratio of ions was in accordance with that of used alumina cement. The stock solution (1000 mL) was prepared by mixing the powders of 1.6 g of $Ca(OH)_2$ and 1.1 g of $Al(OH)_3$ (weight ratio of $3Ca^{2+}/2Al^{3+}$). After adding distilled water, the obtained suspension was stirred on shaking machine at lab temperature for 21 hours. The concentrations of aluminum and calcium ions at obtained aqueous solutions were determined by gravimetric analysis and chelatrometric titration. Although, the result did not show precisely the required weight ratio $3Ca^{2+}/2Al^{3+}$, the composition of stock solution was reproducible for gel point determination (the result was almost the same for both solutions).

The concentrations of aluminum and calcium ions in obtained aqueous solutions were determined by means of gravimetric analysis and chelatrometric titration respectively.

Concentration of Aluminum ions

A stock solution (100 mL) was introduced to a beaker (250 mL) and two drops of H_2O_2 peroxide and 2 g of NH_4Cl were added. Then, the solution was heated up to the boiling point. Next, NH_4OH was added in an excess upon stirring. Finally, the solution was cooled down to the lab temperature and formed crystals of alumina were filtrated off on a Buchner funnel and quantified gravimetrically.

Concentration of Calcium ions

Obtained filtrate from the previous procedure free of Al ions (50 mL) was pipeted to a clean, dry Erlenmeyer flask. Then, $pH = 12$ was adjusted by adding 2 M NaOH. Afterwards, 500mg of indicator (Murexid) was added and mixed thoroughly to obtain a pink solution. Finally, the solution was titrated with chelaton III to the violet end point. The volume of titrated chelaton III was 3.4; 3.5 and 3.4 mL.

Gel point determination

Gel point was determined by simple „tilted test tube method". Principally, the solution-gel transition was visually observed in a specific time and temperature range. The gel point of the polymer solution was defined as the point when the system stopped to flow.

Procedure

Polyvinyl alcohol GH-17s (0.59 g) was kept dissolving in 9.4 mL of the prepared solution for 24 hrs at lab temperature using a shaking machine. Then, suggested and calculated volume 1.35 ml of glycerol was added by pipette. Finally, Tyzor (1 – 5 wt %) was injected (see *Fig. 11*), the solution was thoroughly shaken by hand for 2 minutes. Then, obtained viscous mixture was visually observed for 48 hrs at lab temperature to record gelation time. The Tyzor percent was always based on the weight of the polymer during the MDF composite preparation. In this case, the percentage was measured based on the volume of vial scale.

Fig. 11 Gel point determination by tilted test tube method

4.3 The MDF Manufacturing Process

4.3.1 Material Composition

The basic composition of MDF composite was proposed according to literature[3] references (see *Table 9*) and to previous experimental experiences. Composition and volume of particular components forming new MDF composite was considered as the main effect on material's properties.

The aim was to examine the effect of organotitanate agent respectively Tyzor TE and LA added to the polymer content of the resulting MDF materials and its influence on final properties. Based on the results of the gelation determination and on theoretical aspects from safety lists of Tyzors, it was assessed that the maximum amount of added Tyzors to the mixture could conclude maximally 5% against the amount of polymer. It was tested also a higher weight percentage concentration of Tyzors. These mixtures have not been possible to mix and achieved the high shear effect. The high levels of added Tyzors had a negative impact in a high shear mixer caused by quickly stiffening.

The basic premise was good workability and suitable mixture amount during the preparation. An addition of further distilled water was necessary with increasing amount of Tyzor in the mixture to obtain the good workability with formed mixture paste. The resulting mixture compositions can be seen in the following *Table 10*.

Table 10: Final composition of MDF cement mixtures

Component	Weight [g]				
	Tyzor 0.1%	**Tyzor 0.2%**	**Tyzor 0.3%**	**Tyzor 0.4%**	**Tyzor 0.5%**
HAC	200	200	200	200	200
PVAA	10	10	10	10	10
	Volume [mL]				
Distilled water	34	35	36	37	38
Glycerol	3	3	3	3	3
Tyzor	0.1	0.2	0.3	0.4	0.5

4.3.2 Procedure

The procedure of MDF composite consisted by series of steps described in theoretical part properly. The first step was the premixing sufficiently.

Mixing

Beside the components ratio, the mixing of components is another important part of the MDF composite production. The components were mixed together sufficiently in order to achieve a mix as homogeneous as possible. In fact, the majority of failures and low flexural strength of the materials were often attributed to poor mixing of the individual components. Further, greater degree of mixing produces stronger polymer cross linking during cement hydration. Moreover, the cross-linking additive was added to achieve lower moisture sensitivity.

First of all, the components were premixed in a conventional planetary mixer properly. This was essential to achieve intimate contact between the polymer, water and cement. Polyvinyl alcohol GH-17S (used polymer) and calcium aluminate cement SECAR 51 had been mixing for a couple of minutes firstly. By that time the solution was prepared from exact volume of distilled water, glycerol (plasticizer) and Tyzor at the end. Formed solution was added to the mixture of polyvinyl alcohol and cement, then mixed again in a planetary mixer properly. High shear mixing was the final part of composite's pasta preparation.

High Shear Mixing

The MDF composite production has used a twin roll mill (see *Fig. 12*) to produce high shear mixing and this allows a satisfactory homogenous mix to form in less than 5 min because of the workability of the material. The mixing could be longer in case of MDF composite without Tyzor addition. One of two rolls was moveable to adjust the gap between the rolls that rotated counter to each other owing to a difference in their speeds of rotation. The gap was approximately 2 mm. Shear forces were generated in the material that is allowed to pass through the gap between the rolls. In this way shear rates exceeding 1000/s may be realized. Next parts of the twin roll mill were two copper spreaders to protect a layer of the composite mixture from getting ends of roll hence to keep an exact shape. Also, the over-supply of the mixture between gap lead to better high shear effect, more efficient mixing and homogeneous mixture.

Fig. 12 Two-roll mill for high-shear mixing

Compaction

After the MDF cement sheet was removed from the twin roll mill relatively low pressure compaction was required before the curing period. Pressures applied were typically around 7 MPa. As already mentioned in the introduction, compression of MDF composite's particles allows creating and maintaining a densely packed structure. This was beneficial in terms of moisture resistance. It has been achieved a reduction of the bulk polymer phase.

Specimen preparation

When the applied high-shear effect is finished the surface of the mixture paste starts to passivate immediately and quickly and therefore loses its cohesivity. Passivation is definitely caused the given lack of available water in the surface layer of formed material. It implies the consequence of impossible permeation of the surfaces these two cohesive phases.

The passivation complicates the material formation to the shape of a standard test sample (20x20x100 mm) to get a sufficiently homogeneous specimen. The result could perform a problem that inside of the fracture surface in the cured sample would then be possible to observe a few millimeters long cracks at the interface of the original layers of twin-roll mixer.

Therefore, a different type of test specimen for the measurement of mechanical properties has been suggested. The iron beam represented the standard dimensions (20x20x100 mm) was laid to the stable layer of cement material paste subsequently trimmed with a knife carefully. This method produced thin samples with thickness characterized by the gap between the cylinders of the twin-roll mixer. The resultant dimensions were 20x2x100 mm. Thus, the sufficiently homogeneous test glands specimens suitable for measuring mechanical properties were obtained.

Another possible way how to obtain a homogeneous specimen is through the extruder. This part was installed on the other side of the twin-roll mixer working place. It conclude approximately 75 cm long spiral, which is located in the stainless steel tube. At the end of the pipe flange is screwed where can be placed necessary jets. However, only the first part of the production samples has been used to the research and observations.

Curing and Storage

The already mentioned purpose of the experiment is to determine the influence of moisture on chemical-mechanical properties of MDF composites with different curing conditions, select the particular organotitanate cross-linked additives and optimize the conditions of PVAA cross-linking and characterized the sutitable composition. All the series produced samples were cured for one day at a selected temperature of laboratory temperature, 40, 80 or 110 °C. Subsequently were stored in polyethylene plastic bags for six days (144 hours). At the end, formed samples were divided into three groups. For the first group of samples were tested for flexural strength in humid climate. These specimens were placed to a container which simulate and maintain almost 100 % of relative humidity and stored in the atmosphere and conditions for a period of seven days (see *Fig. 13*).

Fig. 13 MDF specimens exposed to humidity

Second group of specimens was stored seven days in the distilled water. The container with the samples is in *Fig. 14*.

Fig. 14 MDF specimens exposed to distilled water

The final third group of the resulting specimens was placed to plastic bags and kept in the laboratory conditions for seven days.

It had to be prepared at least three of the same samples to measure the bending test to get and achieve a statistically sufficient and reproducible data. Based on the factor has been prepared four specimens for each of the observation.

4.4 Methods of Testing

4.4.1 Fatigue Bending Test

Fatigue bending test was a necessary factor for an observing and investigation of prepared specimens. Generally, the test gives important construction reference, especially for materials often applied to bend, e. g. supporting beams, self-supporting roof structure, sheathing material in construction, etc. Bending test also can determine the elasticity modulus E of material, which is not sufficiently precise to determine the tensile and pressure testing. Principally, the bending stress is distributed in the upper layers is tensile and toward the neutral axis is reduced and through the zero voltage across in the lower half of the section changes on pressure.

Three-point bend test was chosen and used for the investigation of prepared MDF material strength. The testing apparatus was ZWICK 010 (*Fig. 15*).

Produced MDF samples were cut asunder to half length with a diamond blade saw. The resulted specimen dimensions were approximately 20x2x50 mm. The dimension of MDF samples were not uniform, thus setting the test apparatus ZWICK 010 was optional according to tested specimen (see *Table 11*).

Table 11 Setting the test apparatus ZWICK 010

Settings	
Specimen Dimension	2x20x50 mm
Jaws	the three-point bending, load radius 5 mm edges supporting
Test speed	1 mm/min
Load cell	10 kN
Connector	10 kN
Pre-load Fv	5 N
Support separation "lv"	40 mm

Fig. 15 test apparatus ZWICK 010

4.4.2 Infrared Spectroscopy

Infrared spectroscopy is one of the most common spectroscopic techniques used for organic and inorganic characterization based on the interaction of infrared radiation (5000-200 cm^{-1}) with molecules of the observed substance. The absorbed energy increases the internal energy per molecule atoms in the molecule vibration and rotation of the molecule. Absorption bands of the experimental spectra identify the frequency of individual atomic groups present in the molecule, indicating also for its layout and its intensity inform concentration ratios of individual types of molecules in the measured sample. Infrared spectroscopy has its center of gravity in the structural analysis of molecules, a quantitative analysis of mixtures, such as ending the analytical separation of chromatographic methods, is also used in the study of equilibrium phenomena and reaction kinetics.

The results for prepared specimens were carried out using FT-IR analyzer Nicolet Impact 400 (*Fig. 16*) with the technique of pressing tablets from potassium bromide and analyte. The ratio for preparation was approximately 100.0 mg of KBr and 2.0 mg of the analyzed sample. Bromide and the samples were pre-spreads in a mortar and then mixed again. The procedure had been done several times to obtain higher homogeneity of the tablets.

Formed mixture was evenly pour into dies and was exposed to pressure 40 kPa for one minute and then 80 kPa on the hand brake. Final tablet was carefully removed from the mold and then placed in the holder for measuring the IR spectrometer.

Fig. 16 FT-IR analyzer Nicolet Impact 400

4.4.3 Scanning Electron Microscopy (SEM)

The scanning electron microscop has excellent usage in analyzing of surfaces. It is analogous to the reflected light microscope, although different radiation sources serve to produce the required illumination. The SEM uses electrons for image formation.

The electrons interact with the atoms of analyte and producing signals containing information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons, characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons.

The prepared samples of MDF composite were tested on the scanning electron microscope Tesla RS 340 used secondary electrons. Samples had to be adjusted because of a non-conductive structure. The dried samples of MDF composite with dimension of approximately 2 x 2 cm were electrically bonded to the aluminum pad and has sprinkled conductive layer of Au/Pd.

4.4.4 X-ray Diffraction

The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. It was the reason why the method was used in the MDF composite characterization.

The analysis was performed on the X-ray Powder diffractometer Siemens D-5005 (*Fig. 17*), where the X-ray was generated in a copper cathode ray tube and the monochromator was used in the range 5° to 60°. The diffractometer is normally used in reflection mode with either a position sensitive detector or a point detector. It is equipped with a high temperature stage allowing data to be recorded at temperatures above 1000 K and a low temperature stage for measurements down to 10 K.

In powder diffraction it is important to have a sample with a smooth plane surface. It was therefore grind the sample down to particles of about 0.002 mm to 0.005 mm cross section. The grinded sample was then pressed into a sample holder to reach smooth flat surface.

Fig. 17 X-ray Powder diffractometer Siemens D-5005

4.4.5 Confocal Microscopy

A confocal microscope creates sharp images of a specimen structure compare a conventional microscope. It is achieved by excluding most of the light from the specimen instead of microscope's focal plane. The image has less haze and better contrast than that of a conventional microscope and represents a thin cross-section of the specimen. Despite, allow observing more details and perform three-dimensional (3D) reconstructions of the tested specimen due to assembling series of thin slices taken along the vertical axis.

The observed MDF composite samples were acquired images of the cuts in a confocal microscope Olympus LEXT OLS 3000 (*Fig. 18*), confocal microscope for nondestructive interior observation. The technology features sub-micron imaging with outstanding resolution and accurate three-dimensional measurement capability. The magnification could have changed from 120x to 14 400x, ideal for the continued reduction in feature sizes. The other advantage was no expensive of sample preparation and possibility of fast measurement and observation tasks in high volume manufacturing applications without destruction.

Fig. 18 confocal microscope Olympus LEXT OLS 3000

4.4.6 Differential Thermal Analysis

Differential thermal analysis (or DTA) is an analytical method where the specimen part and an inert reference material are heated concurrently at a linear rate, each having its own temperature sensing and recording apparatus. The thermal-energy changes, either endothermic or exothermic, which occur in the course of heating, are plotted. The formed thermogram provides data on the occurred chemical and physical transformations, such as melting, sublimation, glass transitions, crystal transitions, and crystallization.

The measurement were proceeding on the SDT Q600 (*Fig. 19*) which provides simultaneous measurement of weight change (thermo gravimetric analysis, TGA) and differential heat flow (Differential scanning calorimetry, DSC) from ambient to 1500 °C. SDT technology features a dual beam thermobalance containing thermocouples that provide differential temperature measurements (DTA) within the dual ceramic beams and a purge gas system with digital mass flow control, gas switching capability and a separate gas inlet for the option to deliver reactive gas to the sample.

For analyzing samples that tend to lose weight during heating, it was not used the Argon atmosphere. The samples were measured with atmospheric air with heat flow integration. The DSC signal was also useful in providing higher temperature solid state phase and melting transitions where no weight loss occurs.

This was useful for the determination of polymeric part and moisture content.

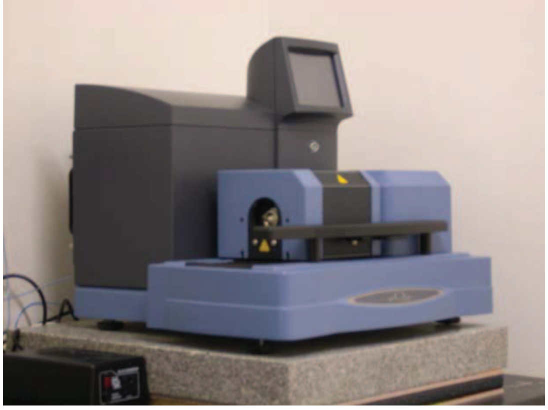


Fig. 19 DTA analyzer SDT Q600

5 RESULTS AND DISCUSSION

This work's purpose was to evaluate and select the particular organotitanate cross-linking additives and optimize the conditions of PVAA cross-linking. Further, to prepare MDF composite based on aluminate cement and PVAA to improve the mechanical properties and increase moisture resistance of formed MDF composite. A series of organotitanate compounds were examined as cross-linking additives with respect to mentioned moisture sensitivity of final macro-defect free composite. The experiments were carried out first to compare the effectiveness of the organotitanate cross-linking additives in conditions simulating real environment of MDF (pH, influence of rheological glycerol presentation, weight ratio of PVAA).

In the second stage the MDF composites were prepared with the proposed weight ratio of cross-linking additive/PVAA and consequently evaluated by three point bending test on Zwick 010.

5.1 Effect of Cross-linking Additives on PVAA Gelation Time

5.1.1 Vial-scale

The gel point was determined for the different types of Tyzors and polymers and also by blank test proposal with distilled water instead of cement part. The attempts were the examination with different weight percentage of Tyzors.

The tilted test tube methods were firstly experimented with polyvinyl alcohol GL-05S. Given that this polymer did not reach the required properties during the preparation of MDF composite, the results were not included in the evaluation.

The investigations have been proposed to continue with polyvinyl alcohol with higher viscosity – PVAA GL-17S.

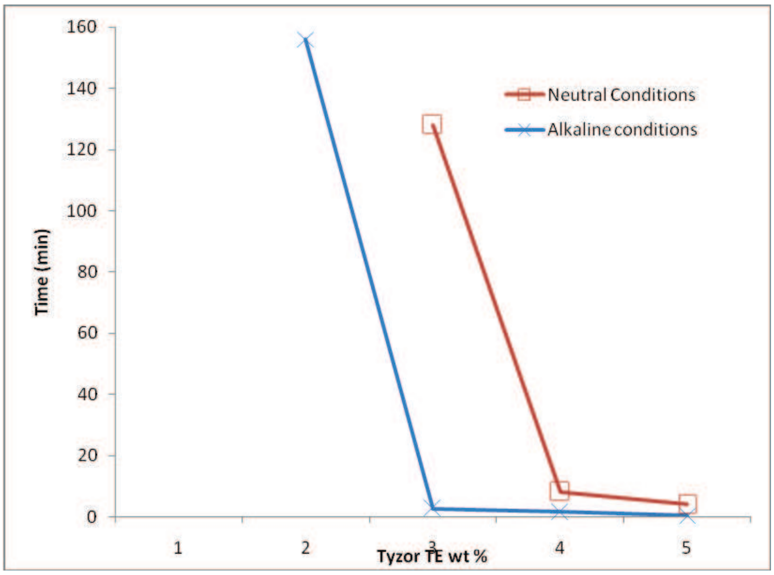


Fig. 20 Effect of Tyzor TE concentration on gelation of PVAA, initial pH = for alkaline environment, lab temperature

The determination of gel point has been done also with blank test. Solution representing cement part was substituted by distilled water.

Tyzor TE

The first series of experiments were proceeding with Tyzor TE as the crosslinked additive. The results of PVAA/Tyzor TE gelation behaviour are shown in Fig. 20. The gelation appeared faster with increasing Tyzor TE concentration. Interestingly, the same trend was observed when neutral conditions were maintained (blank tests).

Tyzor LA

Further, the gelation behaviour of PVAA/Tyzor LA was examined. Introducing of Tyzor LA (1-5 wt %) into the solution lead to polymer gelation immediately, hence the time dependence was not monitored. In the PVAA/Tyzor AA-75 the gel point has not been detected even after a several days. .

5.1.2 Effect of Temperature on Gelation Time

After 48 hours storing at room temperature, the test tubes were put to the oven and had been heating up to 40°C for 24 hours. The results of the experiments show the *Table 12*.

Further, same procedure had been repeated at higher temperature, especially 80 and 120°C. In this case, all of the Tyzors has similar behavior. Water was evaporated and then the formed xerogel was making a yellowish color as the result of high temperature (see *Fig. 21*).

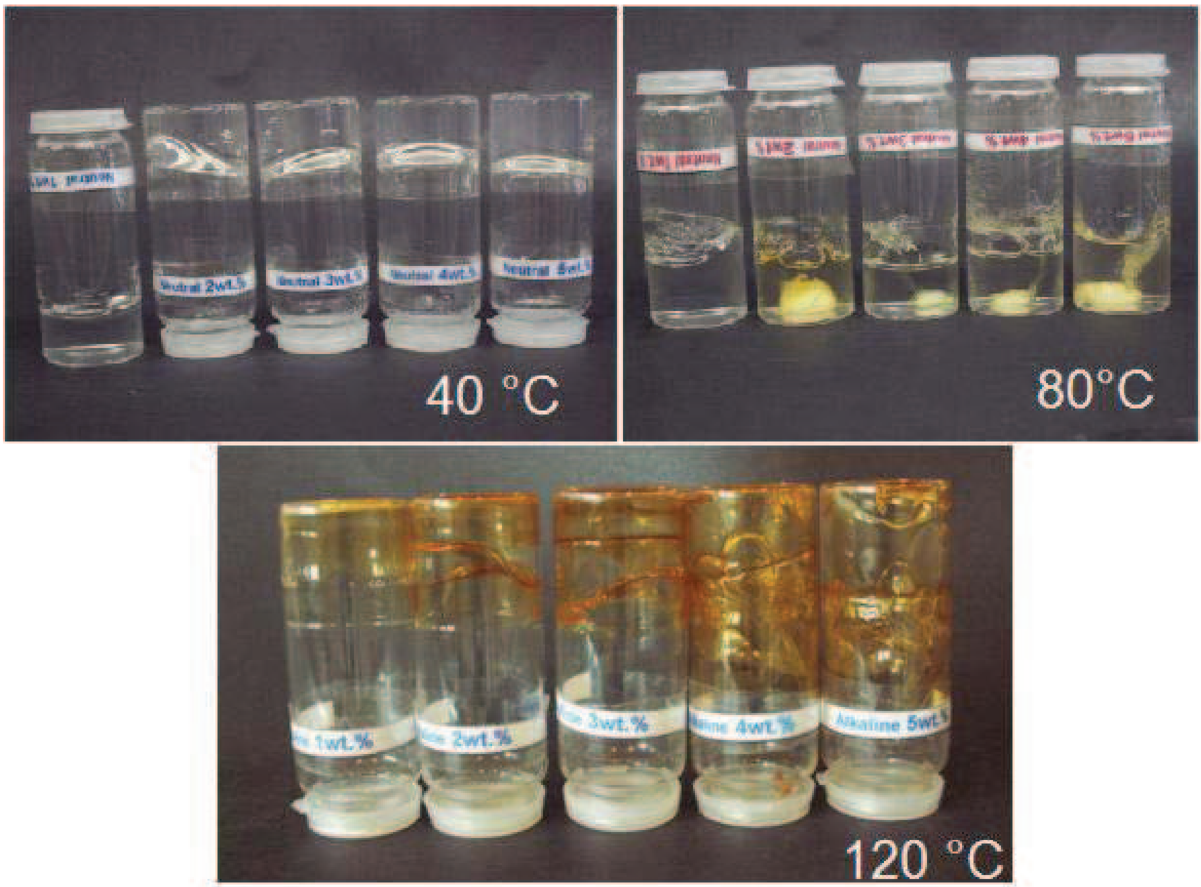


Fig. 21 Results of tilted test tube method at different temperature conditions

Table 12 Effect of crosslink additives in alkaline conditions

Tyzor TE		Gelation			Tyzor LA		Gelation		
wt. %	lab temperature	40 °C	80 °C	120 °C	wt. %	lab temperature	40 °C	80 °C	120 °C
1	x	x	x	Yellow gel	1	x	x	Yellowish gel	Yellow gel
2	x	x	x	Yellow gel	2	x	x	Yellowish gel	Yellow gel
3	60 s	White gel	Yellowish gel	Yellow gel	3	x	Gel	Yellowish gel	Yellow gel
4	35 s	White gel	Yellowish gel	Yellow gel	4	x	Gel	Yellowish gel	Yellow gel
5	5 s	White gel	Yellowish gel	Yellow gel	5	x	Gel	Yellowish gel	Yellow gel

Tyzor AA-75		Gelation		
wt. %	lab temperature	40 °C	80 °C	120 °C
1	x	x	Gel	Yellowish gel
2	x	x	Gel	Yellowish gel
3	x	x	Gel	Yellowish gel
4	x	x	Gel	Yellowish gel
5	x	x	Gel	Yellowish gel

Tab. 1 Effect of crosslink additives in neutral conditions

Tyzor TE		Gelation			Tyzor LA		Gelation		
wt. %	lab temperature	40 °C	80 °C	120 °C	wt. %	lab temperature	40 °C	80 °C	120 °C
1	x	Gel	Gel	Yellow gel	1	x	x	x	Yellow gel
2	x	x	Yellowish gel	Yellow gel	2	x	x	Gel	Yellow gel
3	x	x	Yellowish gel	Yellow gel	3	x	x	Gel	Yellow gel
4	134s	x	Yellowish gel	Yellow gel	4	x	Gel	Gel	Yellow gel
5	117 s	x	Yellowish gel	Yellow gel	5	x	Gel	Gel	Yellow gel

Tyzor AA-75	Gelation			
wt. %	lab temperature	40 °C	80 °C	120 °C
1	x	x	Gel	Yellowish gel
2	x	x	Gel	Yellowish gel
3	x	x	Gel	Yellowish gel
4	x	x	Gel	Yellowish gel
5	x	x	Gel	Yellowish gel

5.1.3 Effect of Polymer Content on Gelation Time

Another test was executed to determine the gel point as a function of time with crescentic weight percentage of polyvinyl alcohol. The weight percentages of PVAl were 5.9%, 10.9%, 15.9%, 20.9%, 25.9%, 35.9% and 45.9%. Last two concentrations were very high. Formed solutions were oversaturated resulting in irreproducibility of results.

5.1.4 Effect of plasticizer on Gelation Time

Finally the effect of glycerol as a rheological agent, plasticizer improving the processing mixture, was proved. Obtained results confirmed no impact of the glycerol used on cross-linking process in a vial scale. The results were reached the same values for the different weight percentage of added glycerol. The content of added glycerol to the vials were in a range of 0 – 5 wt% and was measured with all types of Tyzors and again the gelation time was measured. It was confirmed the glycerol has no effect on gelation. It has been reached the similar gelation time results given in *Table 12.*

5.2 Effect of Cross-linking Additives on Properties of MDF Composites

5.2.1 Mechanical Properties

Fatigue Bending Test

Samples were tested in three-point bending test on apparatus ZWICK 010. Obtained data were imported to MS Excel and final results are shown on the following pictures. Radius of load and supporting the blades were 5 mm, test speed 1 mm/min, pre-load 5 N and support separation 40 mm.

In spite of the large number of different aspects and therefore the variables involved in the evaluated observation, individual results had to be divided into several graphs presenting the different conditions and component contents. The first part of results is given in *Table 13* where the specimens were cured in laboratory temperature.

Table 13 Results of three-point bending test for MDF specimens cured at laboratory temperature

	Flexural Strength (MPa)				
	Lab conditions	1 day exposure in Humidity	7 days exposure in Humidity	1 day exposure in dist. water	7 days exposure in dist. water
TE 0.10 ml	29,01	23,08	23,18	21,08	27,04
TE 0.15 ml	30,02	22,71	18,91	21,45	20,26
TE 0.25 ml	31,01	24,38	29,21	22,03	20,48
TE 0.50 ml	34,94	26,44	31,43	20,09	18,47
LA 0.10 ml	29,55	24,36	29,43	25,35	22,83
LA 0.15 ml	24,03	23,17	23,18	21,15	23,21
LA 0.25 ml	23,72	21,72	23,02	20,91	20,66
LA 0.50 ml	24,89	22,79	25,37	20,50	20,77
AA 0.10 ml	23,05	23,08	23,18	21,08	27,04
AA 0.15 ml	30,02	22,71	18,91	21,45	20,26
AA 0.25 ml	31,01	24,38	29,21	22,03	20,48
AA 0.50 ml	34,94	26,44	31,43	20,09	18,47
without Tyzor	32,76	24,31	24,92	21,11	22,51

First, the examination of samples was subjected to conventional curing at room temperature and also the subsequent retention was proceeding in the laboratory conditions.

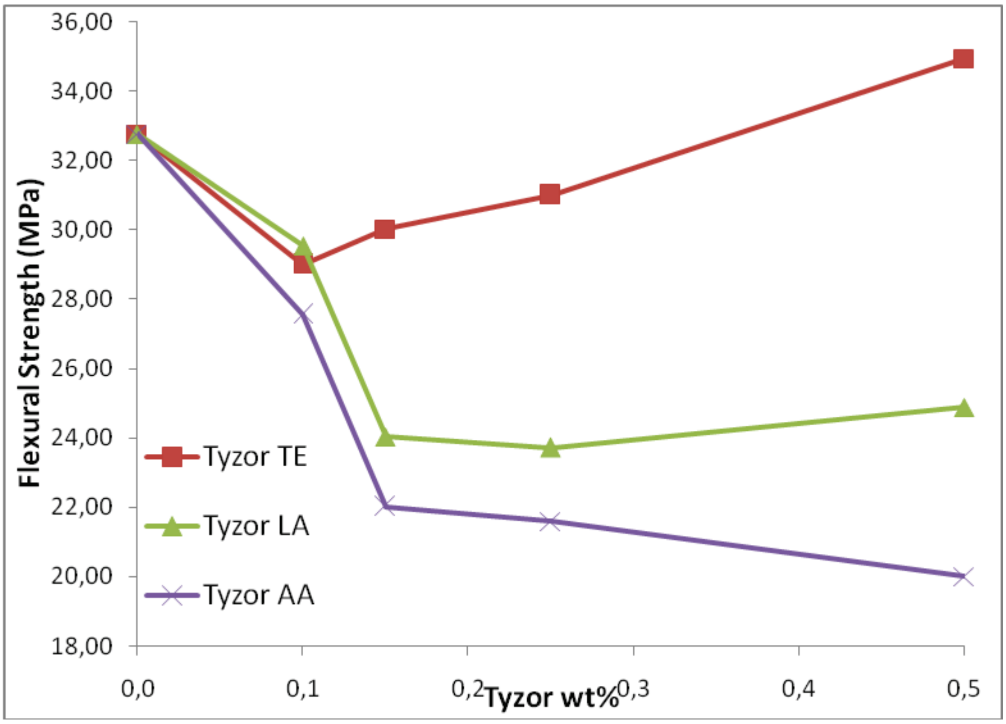


Fig. 22: Dependence of flexural strength of MDF composites on the volume of Tyzors

The final results of the flexural strength testing by three-point bending test on apparatus ZWICK 010 represent the diagram in *Fig. 22*.

The main aspect was to assess the impact of the actual dose of Tyzors on resulting mechanical properties, respectively on flexural strength. Tyzor selection and its content in the mixture was chosen according to the gel point determination, therefore Tyzor TE, Tyzor LA and Tyzor AA in the range 0 – 0.5 wt %. The results show the only Tyzor TE impressed strength increase namely at concentrations of 0.3 – 0.5 wt %. Reason is probably the easier forming of reactive hydroxyl titanium chelate from Tyzor TE as the result of reaction with water during the preparation. The hydroxyl titanium chelates form bonds with organic OH groups of PVAA and forms therefore the strong gels by crosslinking. Unhydrated calcium aluminate cement grains are closely packed with this three dimensional PVAA network. The improved forming of the strong gels can cause the increase of flexural strength.

The increase of flexural strength for Tyzor LA can be also noticed from the diagram. Although, the structurally lactic acid chelate ammonium salt provides also enough chelates to react with OH functional group, the reaction conducted in an elevated temperature. The curing of specimens was in laboratory conditions and therefore the increase of strength is lower compare to Tyzor TE.

Only final Tyzor AA showed no improvement in the strength, which has already been confirmed during the previous gel point determination of Tyzors.

Different conditions

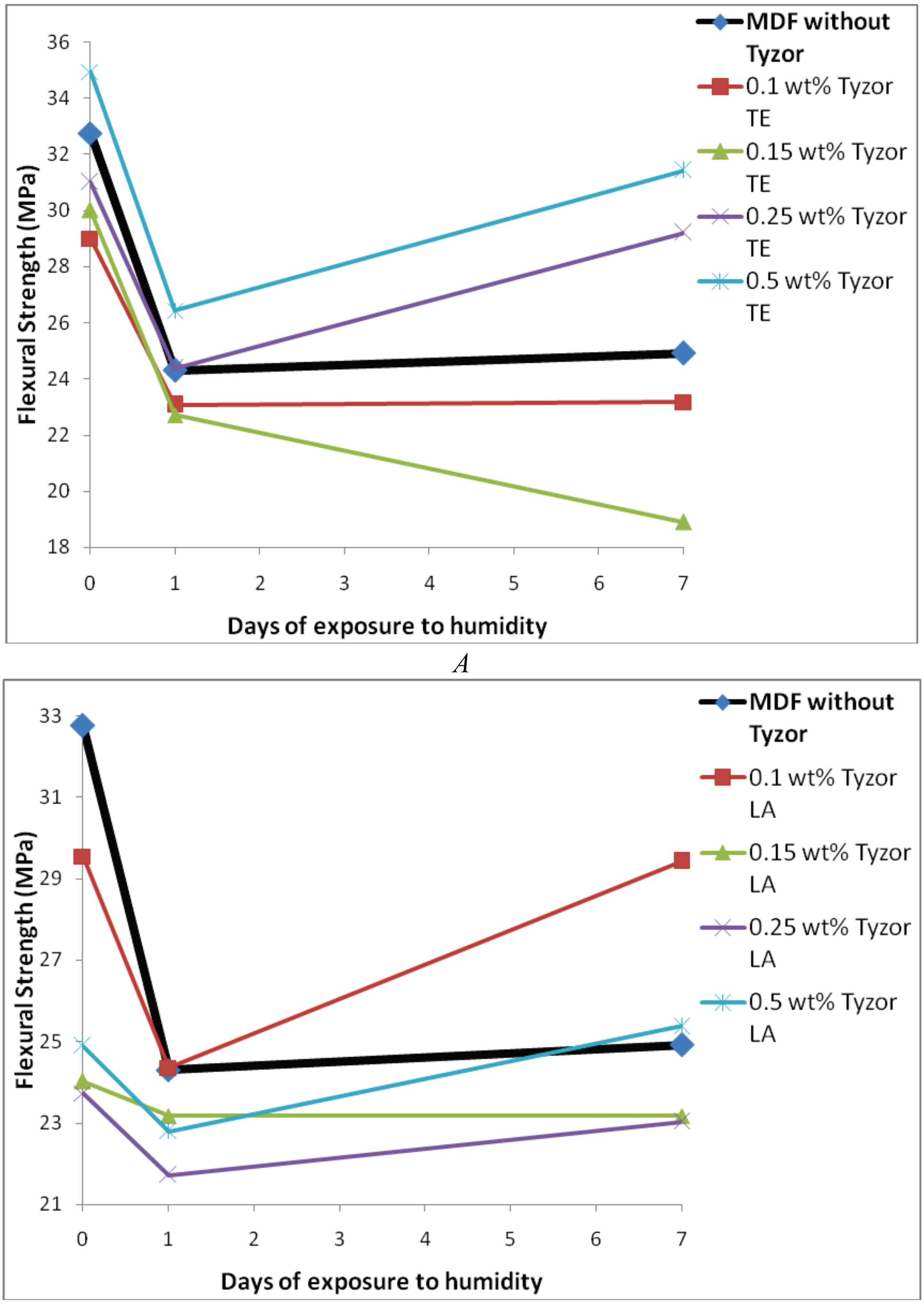
Another series of samples presents the observation of environmental influences on the mechanical properties of Tyzors modified MDF materials. The specimens were exposed to conditions with almost one hundred percent relative humidity. The aim was to measure the resistivity of MDF material to moisture by observation of formed changes in mechanical properties of the specimens. Flexural strength was measured for Tyzor LA (see *Fig. 23A*) and Tyzor TE (see *Fig. 23B*). The Tyzor AA was not measured on the basis of previous poor results (see previous *Fig. 22*).

Moreover, its workability in the final mixture paste was very limited. The rheological properties were reduced even after the addition of higher glycerol content as rheological agent.

The obtained values of the flexural strength are given also in *Table 13*. The *Fig. 23* shows a strength dependence plotted for specimens at different days of storage in the container with almost one hundred percent relative humidity. Results show the general decrease in flexural strength when the material is exposed to a contact with water. Relatively positive view of mechanical properties on moisture application achieved specimens prepared with 0.5 wt % of Tyzor TE. The specimen reached a similar strength (31.43 MPa) as in the beginning (34.93 MPa), even after seven days in a humid conditions. Similar behavior exhibited also specimen modified with 0.1 wt % of Tyzor LA.

Finally, a study was done for the samples immersed in distilled water for 7 days again to investigate the influence of Tyzor LA and TE. The resultant graphs are presented on Fig. 24. Tyzor TE modified MDF composite (*Fig. 24A*) and Tyzor LA (*Fig. 24B*) showed significant loss of strength when water was applied to the specimens.

Low w/c ratio during the MDF material preparation causes the stoichiometric deficit of water which prevents all the cement from full hydration. It implies the significant volume of unhydrated cement grains were can occurred which acts as a potential storage of moisturewater consumer and therefore can rapidly decrease the mechanical properties of the material because of volume changes.



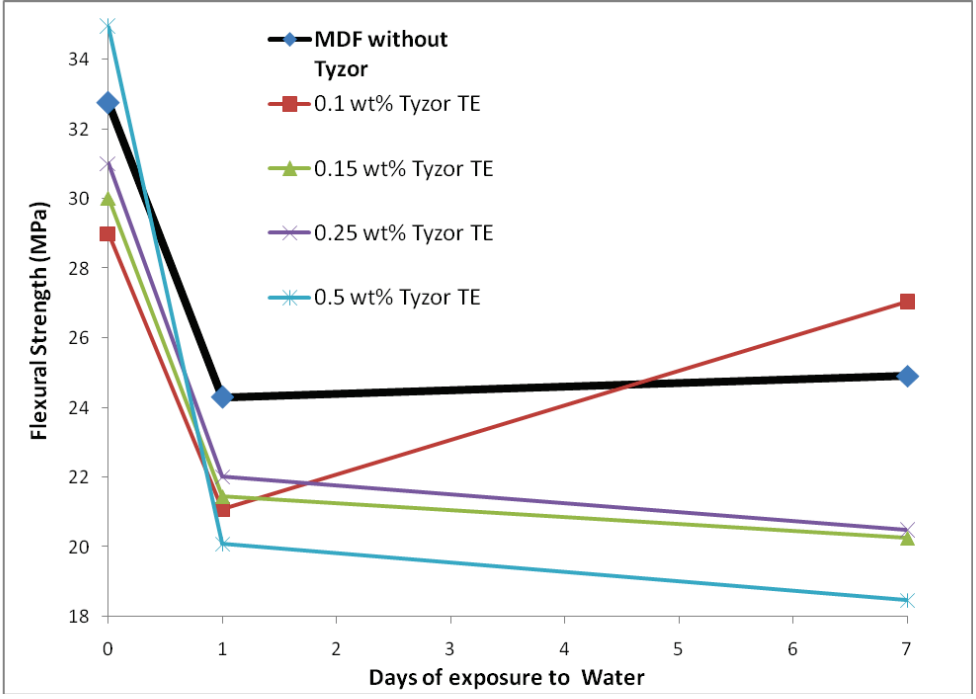
A

B

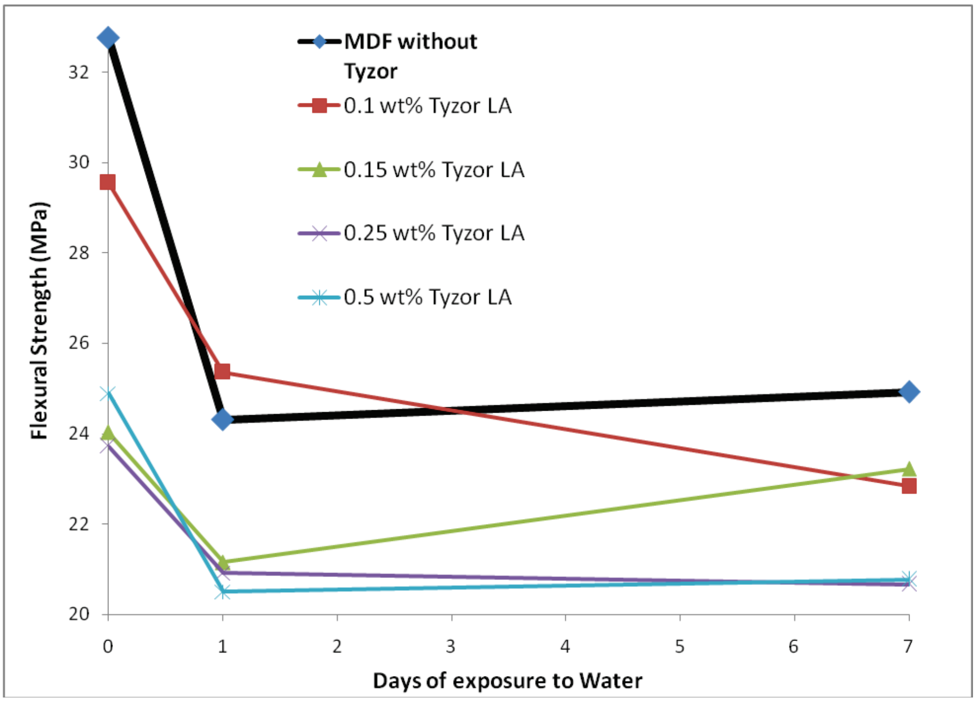
Fig. 23: Influence of humidity conditions on the strength of Tyzor TE (graph A) and Tyzor LA (graph B) modified MDF composites

The graph on *Fig. 25* shows an overall assessment of MDF specimens prepared with and without modification with particular Tyzors stored in individual circumstances and their influence to mechanical properties. The highest flexural strength reached a specimen modified by Tyzor TE with 0.5 wt% content. Even also mechanical properties were not changing and remained relatively stable when the material was exposed to container with 100 % relative humidity. Only after the application of distilled water and stored 7 days in this condition the strength decreased rapidly.

In general, all specimens exhibited similar mechanical properties and the influence of storage conditions has been especially fierce when the material was exposed to water. The decrease of flexural strength was obvious.



A



B

Fig. 24: Influence of water on the strength of Tyzor TE (graph A) and Tyzor LA (graph B) modified MDF specimens

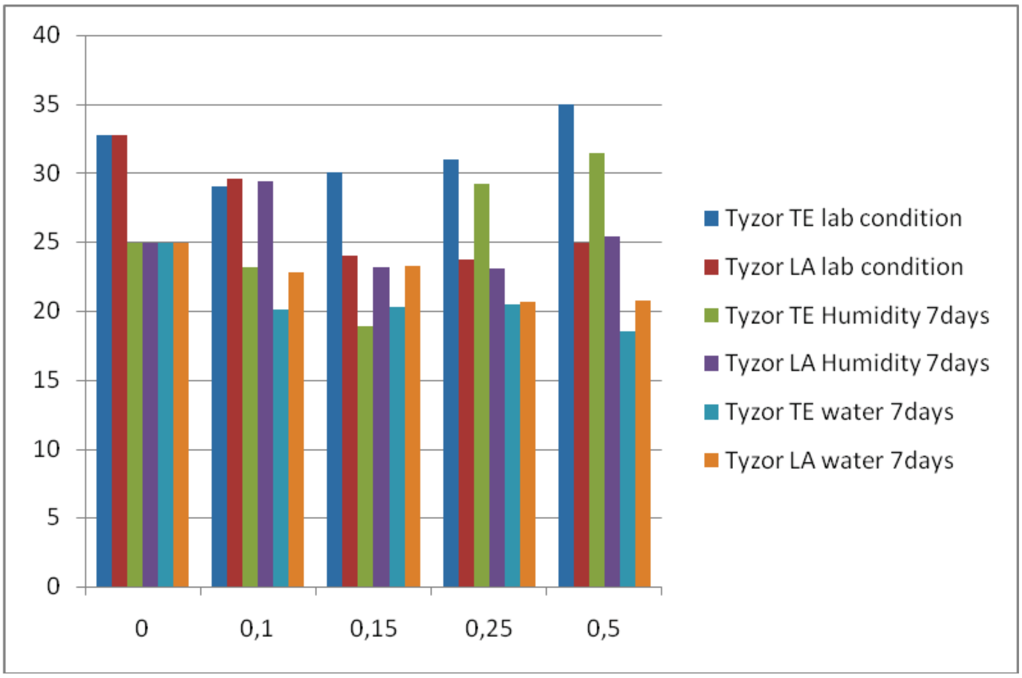


Fig. 25 Overall properties of Tyzors modified MDF specimens cured at laboratory temperature

Temperature effect

Subsequently samples of MDF composites specimens were exposed to elevated temperature during curing of manufactured specimens. The temperature range for the investigation was chosen similar to the gel point of PVAA determination from the previous part. Firstly, the specimens were cured at temperature of 40 °C for 24 hours and then stored at room conditions for 7 days. At the end, the specimens were again exposed to the different kind of environmental conditions. The same process followed for the temperature of curing 80 °C and 120 °C.

The first series of results are related to the dependence of flexural strength in bending, depending on Tyzors dosage and storage for the specimens hardened at 40 °C. The data represent the *Table 14* and the diagram on *Fig. 26*.

Table 14 Results of flexural strengths for Tyzor modified MDF specimens cured at 40 °C

	Flexural Strenght (MPa)		
	Lab conditions	7 days exposure in Humidity	7 days exposure in dist. water
TE 0.1 ml	54,28	26,85	23,59
TE 0.2 ml	60,35	28,46	20,02
TE 0.3 ml	61,00	24,84	19,26
TE 0.4 ml	65,32	25,28	18,06
TE 0.5 ml	60,40	20,51	18,32

LA 0.1 ml	40,00	24,72	23,53
LA 0.2 ml	39,88	23,32	24,68
LA 0.3 ml	35,00	23,40	20,46
LA 0.4 ml	29,89	21,64	21,02
LA 0.5 ml	20,82	15,45	20,30
without Tyzor	41,69	25,21	15,23

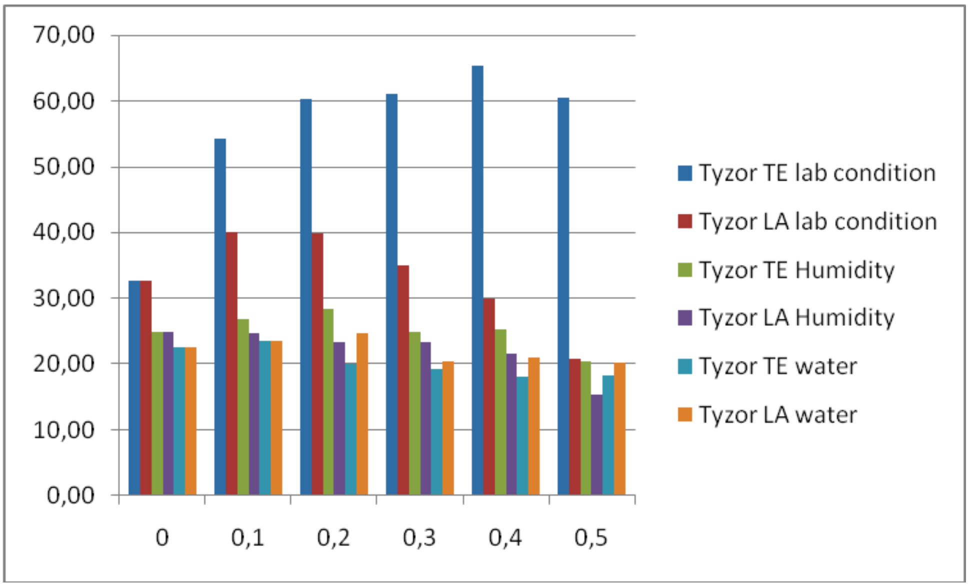


Fig. 26 Tyzor modified MDF specimens cured at 40 °C

For specimens cured at room temperature and at 40 °C, we see a decrease in strength depending on the storage conditions. With increasing intensity of exposure to water the flexural strength decreases relatively rapidly. The change of the properties had been expected. It can be noticed that the Tyzor TE modified MDF specimen in content of 0.4 wt% showed the best properties compared with other when the material was stored at laboratory conditions. On the other hand, the specimens prepared with this content were unfortunately loosing the excellent properties when the water condition was applied. The most stable in terms of change in mechanical properties with dependence on stored environment from Tyzor TE modified samples was specimen doped only 0.2 wt%. The same result was obtained paradoxically also with specimens where the modification of polymer was proceeded with Tyzor LA. This specimen moreover achieved the highest flexural strength from Tyzor LA modified MDF samples.

Generally, it is possible to observe a relatively large increase in strength for Tyzor modified MDF material for a temperature 40 °C. The reason leads to the theoretical prediction that higher temperature causes the higher production of titanium chelates responsible for the bonds forming with organic OH groups of PVAA and gels by crosslinking.

Another group of prepared MDF specimens were undergone the curing process at 80 °C. The results are shown in *Table 15* and graphically on *Fig. 27*. The higher temperature causes the rapid increase in strength for the samples of MDF composite modified by Tyzor LA. The reason could lead to reactivity of lactic acid chelate ammonium salt which is responsible for the crosslinking ability of this Tyzor. The reactivity is increasing with elevated temperature.

Table 15 Results of flexural strenghts for Tyzor modified MDF specimens cured at 80 °C.

	Flexural Strenght (MPa)		
	Lab conditions	7 days exposure in Humidity	7 days exposure in dist. water
TE 0.1 ml	31,05	21,13	18,77
TE 0.2 ml	49,34	27,42	17,58
TE 0.3 ml	30,62	27,11	24,33
TE 0.4 ml	28,68	20,05	22,36
TE 0.5 ml	39,64	18,64	18,20
LA 0.1 ml	78,71	36,78	33,36
LA 0.2 ml	62,68	48,80	41,15
LA 0.3 ml	51,58	30,72	25,04
LA 0.4 ml	47,77	29,69	27,77
LA 0.5 ml	46,09	22,81	10,64
without Tyzor	32,76	24,92	22,51

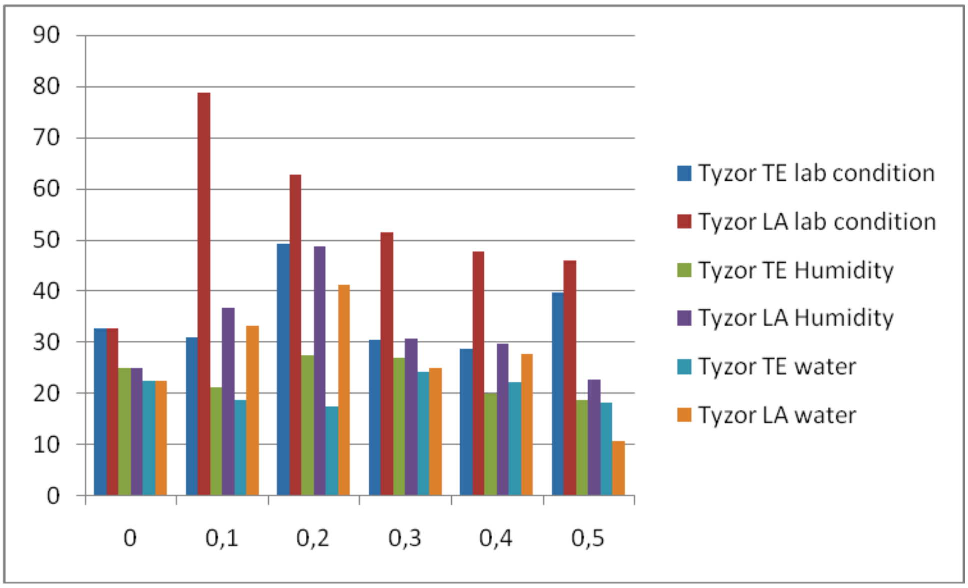


Fig. 27 Tyzor modified MDF specimens cured at 80 °C

The last tested group of MDF composite samples was cured therefore even at temperature 120 °C. Chosen temperature was later proved unreasonable, the strengths occurred were very low. The reason was inactive Tyzor activity at this temperature connected with partial PVAA degradation and the fact $(A1(OH)_4)$ ions released by the calcium aluminate cement are limited to cross-link the polyvinyl alcohol chain.

5.2.2 X-ray Diffraction Analysis

After application of mechanical strength tests for identifying characteristics of prepared specimens takes place the analysis of structure and microstructure. In the first instance the specimens were subjected to XRD analysis.

The analysis was performed on the X-ray Powder diffractometer Siemens D5005, where the X-ray was generated from the copper cathode X-ray tube with the secondary monochromator was used in the range from 5 to 60 °2Θ.

Firstly, the pure cement Secar 51 was characterized to get overview on structure of the main components. The resultant XRD spectrum represents the *Fig. 28.* It is obvious the presence of mainly monocalcium aluminate CA, gehlenite C_2AS, grossite CA_2, meyenite $C_{12}A_7$ and brownmillerite C_4AF.

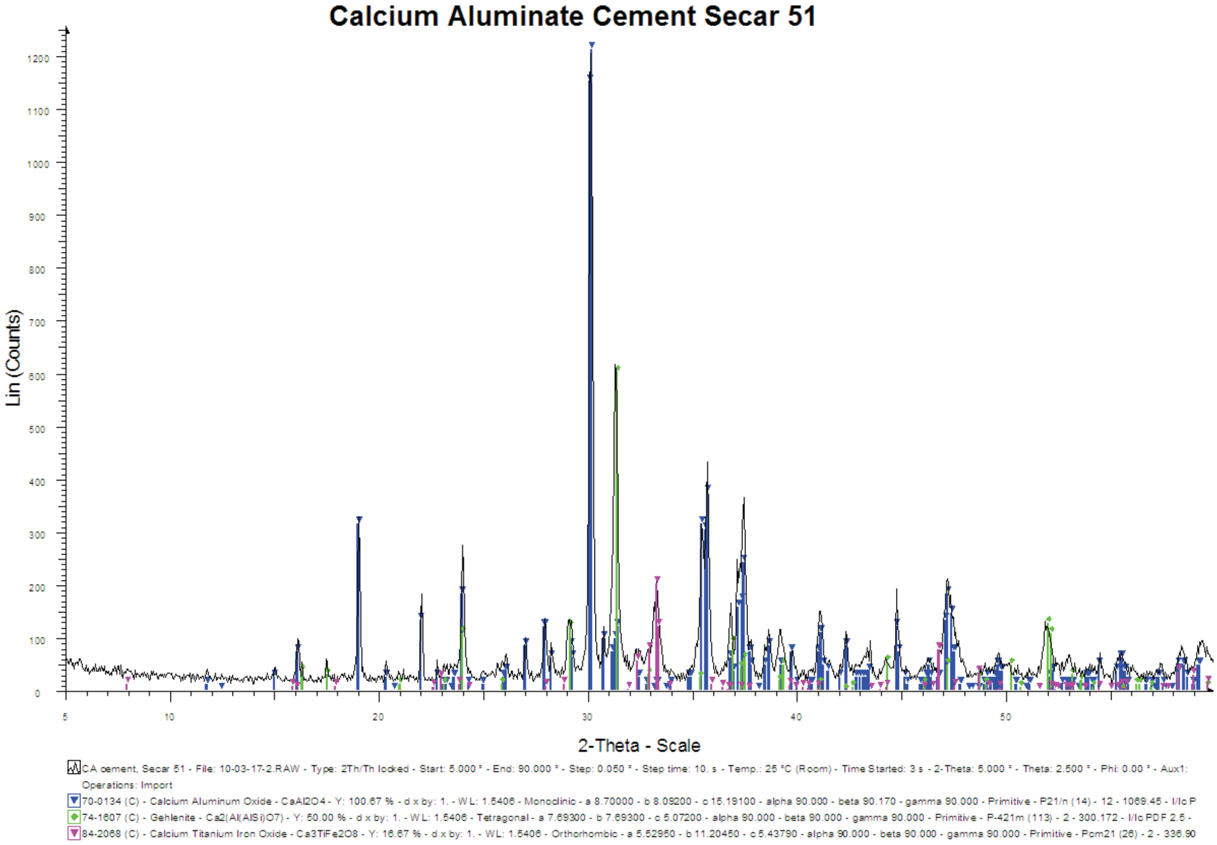


Fig. 28 XRD spectrum of calcium aluminate cement Secar 51

The spectrum on *Fig. 29* represents the sample of Tyzor LA modified MDF composite in a content of 0.2 wt%. The sample had been stored at laboratory conditions for 7 days. The XRD analysis revealed the presence of clinker minerals already identified in previous analysis of cement Secar 51, respectively calciumaluminates, gehlenite and Calcium Titanium Iron Oxides. The diffraction relative intensities indicate very high content of unhydrated cement grains. Further, the group of hydrates, namely gibbsite $Al(OH)_3$, hydrogarnet, and some hexagonal hydrates were detected in very low amount.

The similar results had been obtained with samples of Tyzor LA modified MDF composite stored 7 days at a container with almost 100 % relative humidity. Noticeable difference is in the intensity of very weak diffractions at range 5 – 9° (*Fig. 30*). The diffraction band is made up of a superposition of diffraction peaks of CAH_{10}, caldecahydrite, $C_3A_3H_{16}$ and C_4AH_{16}. The highest intensity of diffraction at this range was obtained with the sample stored in distilled water characterized by the XDR spectrum on *Fig. 31*. The reasonable fact leads to prediction of at least very low hydrated cement grains presence in a sample exposed to water.

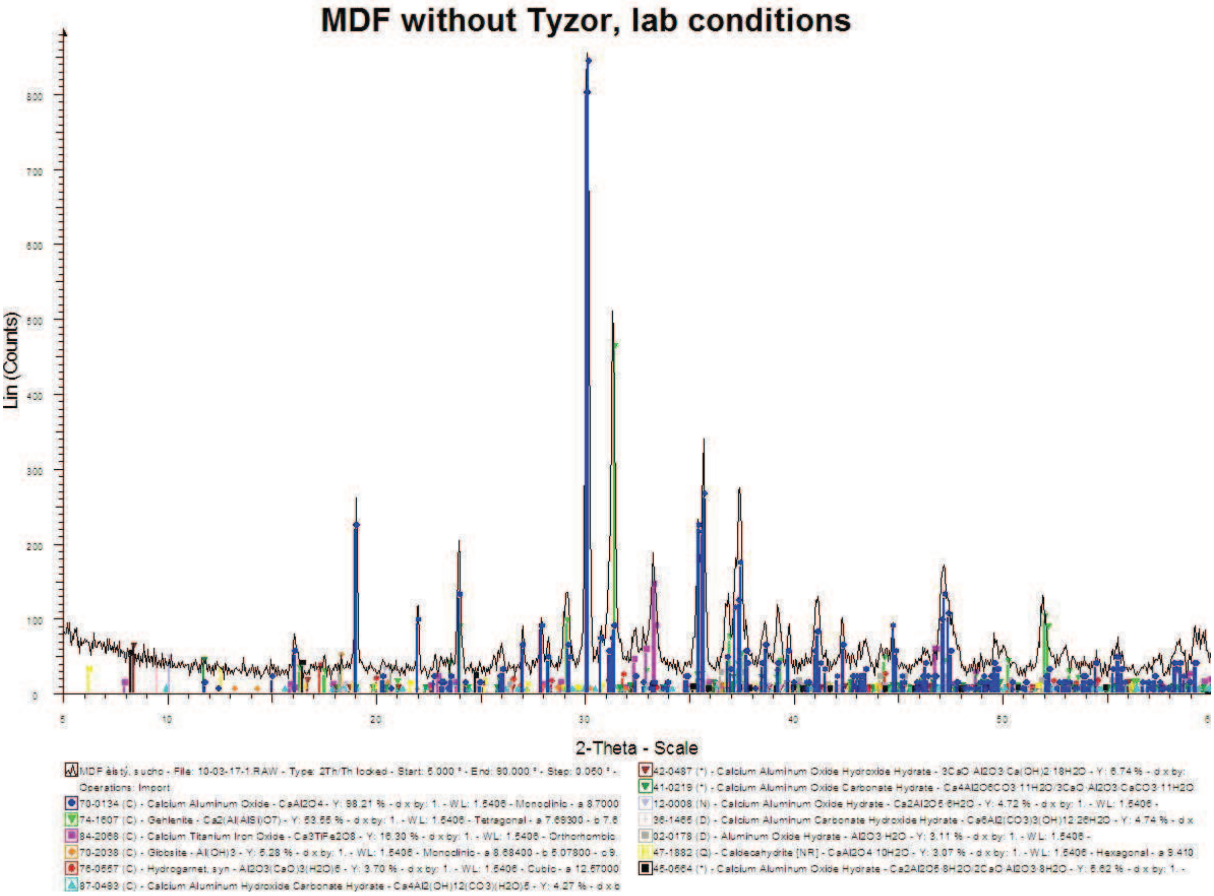


Fig. 29 XDR spectrum of MDF composite without Tyzor addition stored at laboratory conditions

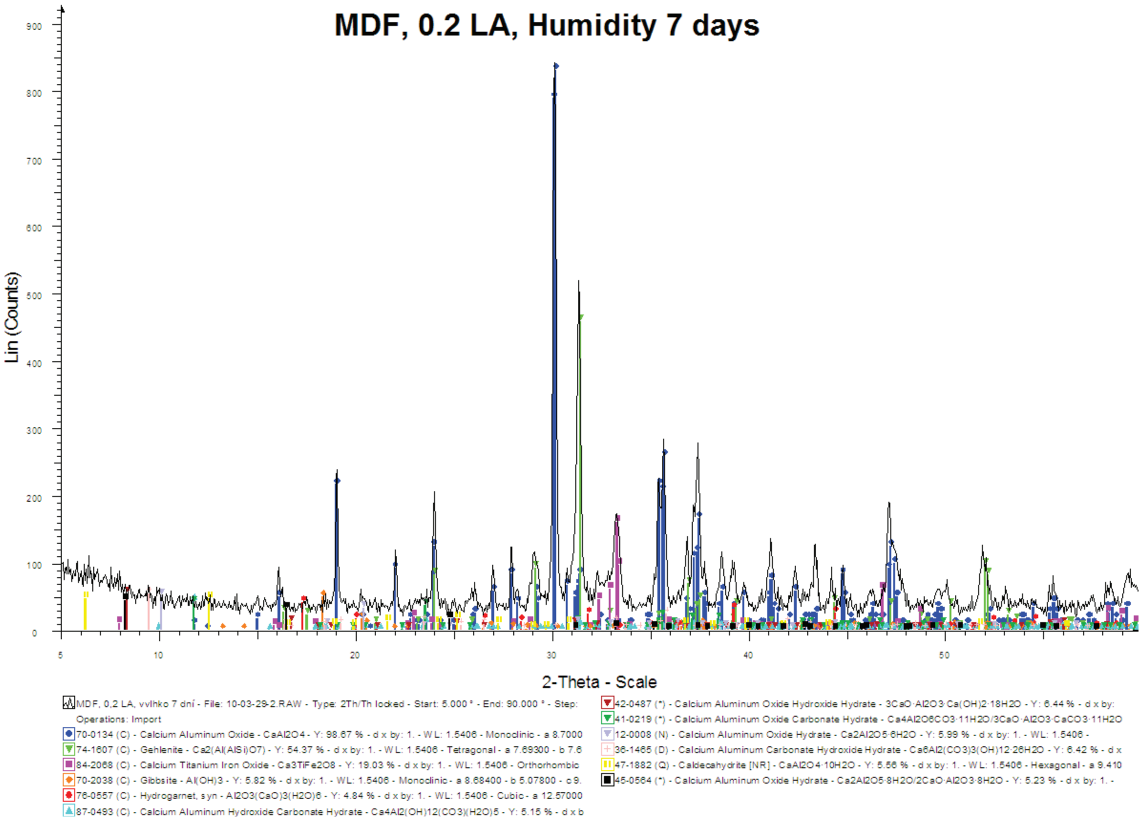


Fig. 30 XDR spectrum of MDF composite without Tyzor addition stored at a container with almost 100 % relative humidity

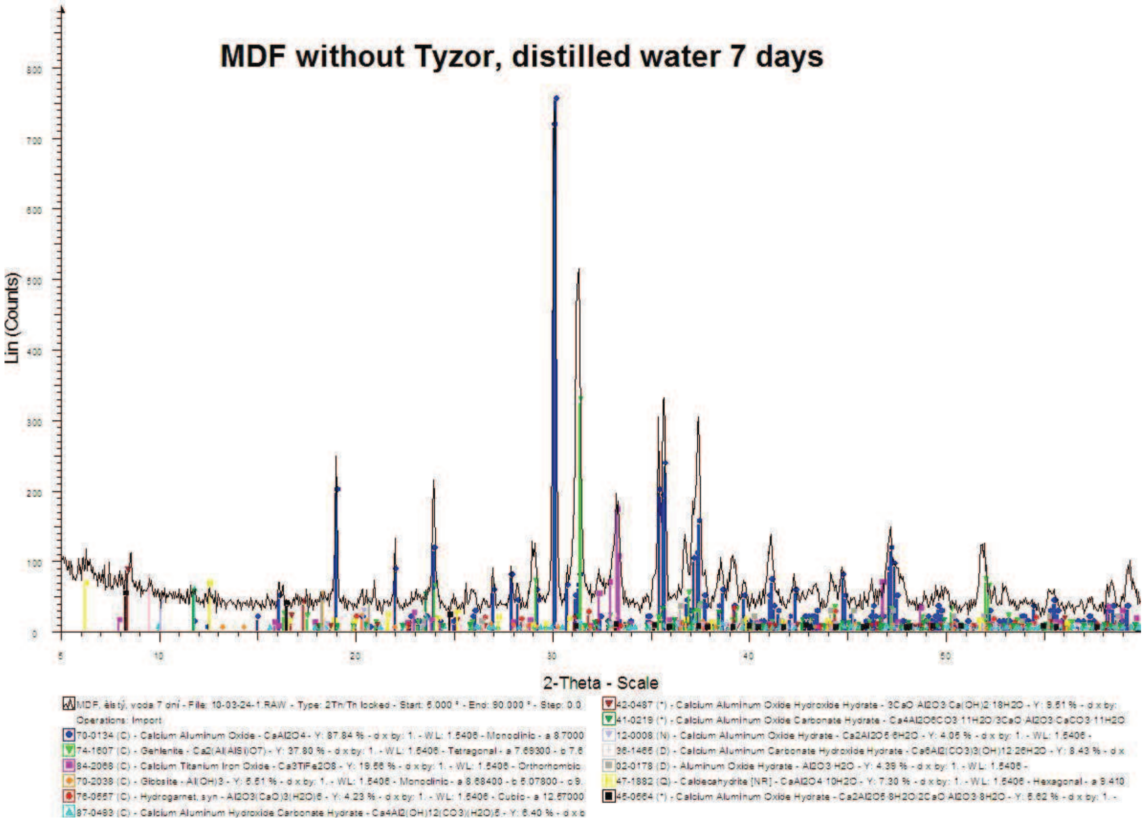


Fig. 31 XDR spectrum of MDF composite without Tyzor addition stored in distilled water

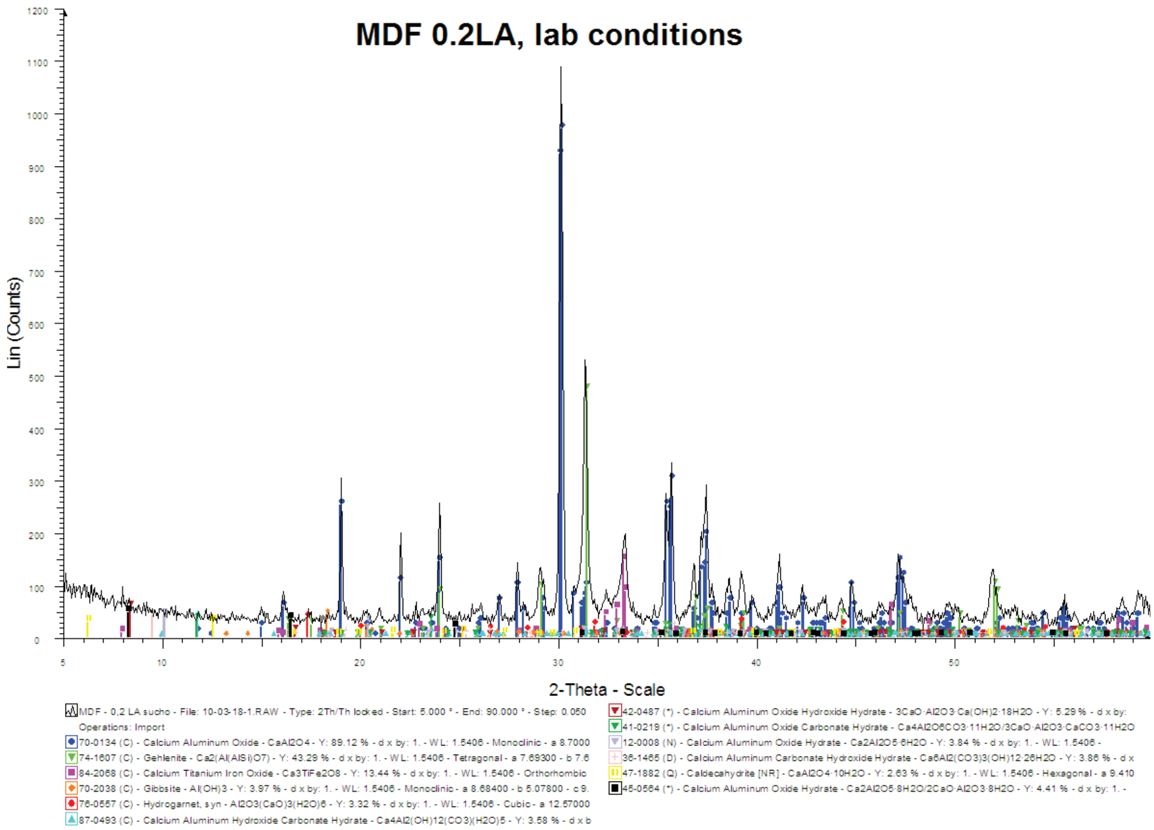


Fig. 32 XDR spectrum of Tyzor LA modified MDF composite stored at laboratory conditions

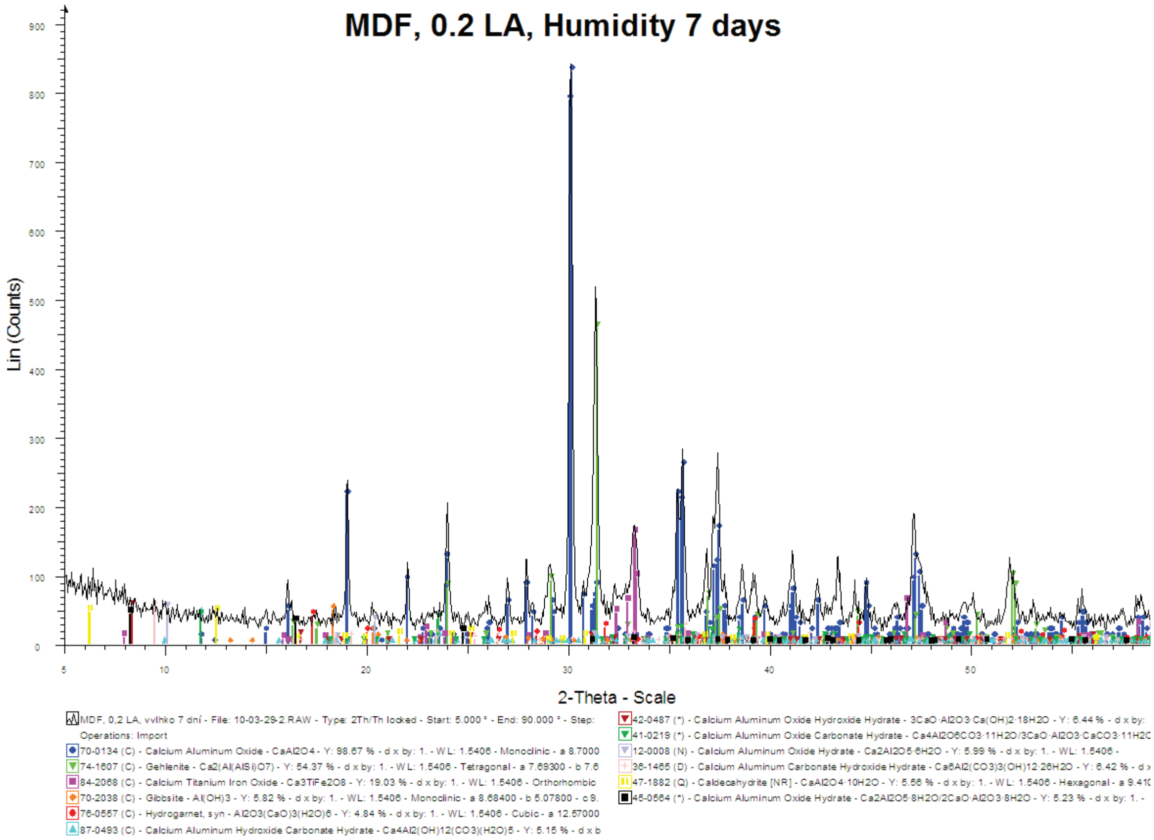


Fig. 33 XDR spectrum of Tyzor LA modified MDF composite stored at a container with almost 100 % relative humidity

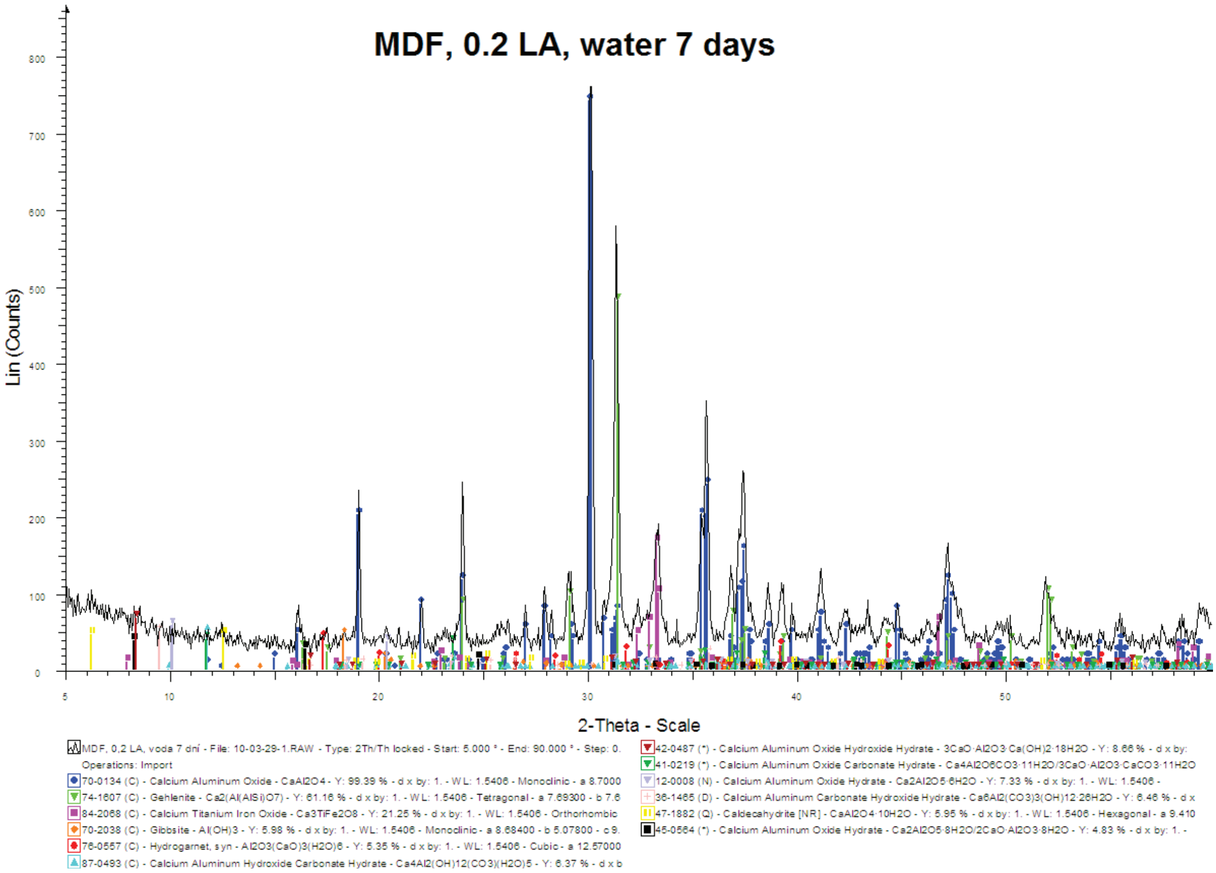


Fig. 34 XDR spectrum of Tyzor LA modified MDF composite stored in distilled water

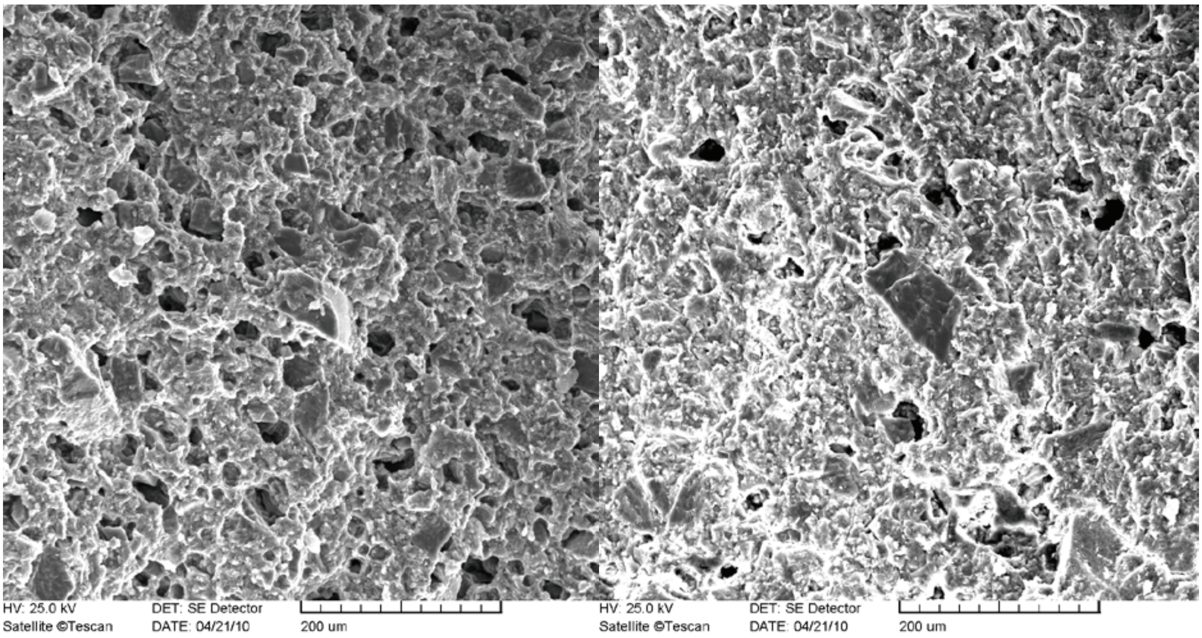
5.2.3 Microscopic Structure Observation

The most appropriate way to study structure in particular levels of MDF composite hydration is definitely scanning electron microscopy (SEM).

In order to obtain the best view of the MDF composite microstructure was performed microscopic analysis of fracture surfaces and also cuts. Cuts were prepared by grinding in a rotary grinder using a grinding wheel on the coarseness of P 400, P 600 and P 1200 then. These samples were also finally used for laser confocal microscopy to obtain and see the differences in cement grains in polymer matrix.

These samples were also finally used for laser confocal microscopy to obtain and see the differences in cement grains in polymer matrix.

The dried samples of two MDF composites were electrically bonded to the aluminum pad and has sprinkled conductive layer of Au/Pd. The prepared samples were subsequently inserted into the scanning electron microscope Tesla RS 340 and the result is on the *Fig. 35*, which demonstrates the effect providing with Tyzor addition in preparation of MDF composite on their fracture surfaces. The MDF composite without any addition of Tyzor is on the *Fig. 35A*. The sample was cured and stored in laboratory temperature. The *Fig. 35B* represents compared sample of MDF composite modified with 0.2 wt% Tyzor LA. The sample was kept for seven days in water and even after this time showed a surprising lower porosity than the MDF composite without any addition of Tyzor kept away from water. In the structure are evident unhydrated cement grains coated with polymer matrix.



A B

Fig. 35 SEM image of the MDF composite without any addition of Tyzor (part A) and modified by 0.2 wt% Tyzor LA (part B)

For more detailed overview of the cement grains diversity were acquired images of the cuts in a confocal microscope Olympus LEXT OLS 3000. The sample of MDF composite modified by 0.2 wt% of Tyzor LA exposed to distilled water for 7 days is on *Fig. 36* (magnification 14 400x).

The lower part is connected to imaging an illuminated aperture situated in a conjugate focal plane to the specimen respectively in reflection mode and the upper part by focusing a parallel laser beam. It is possible to observe the great diversity in content of particular grains. Right shows a homogeneous structure unhydrated cement grain made of primarily CA. The left part of image show already partially hydrated grain where the light spots represent gehlenite.

Comparison of porosity in the prepared samples at various storing conditions is shown in *Fig. 37*. The part *A* represents the sample of MDF composite without Tyzor addition stored at laboratory conditions. When the porosity and particular pores are compared with image *C*, which demonstrates the MDF composite with addition of 0.2 wt% Tyzor LA it is obvious the effect of Tyzor addition. Tyzor modified composite exhibit decrease in porosity and pore size. The images of parts *B* and *D* are connected the same samples exposed to distilled water for 7 days. The porosity is increasing rapidly causing dramatic decline in the mechanical properties what the result of bending test showed.

Despite an increase in porosity is evident from the results the Tyzors still have a relatively large effect on properties also when the material is exposed to water environment.

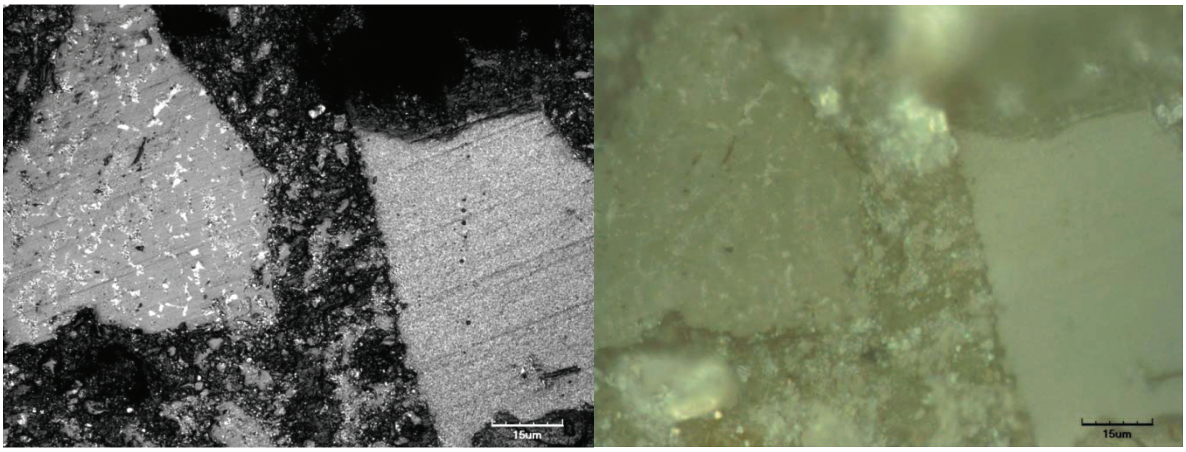
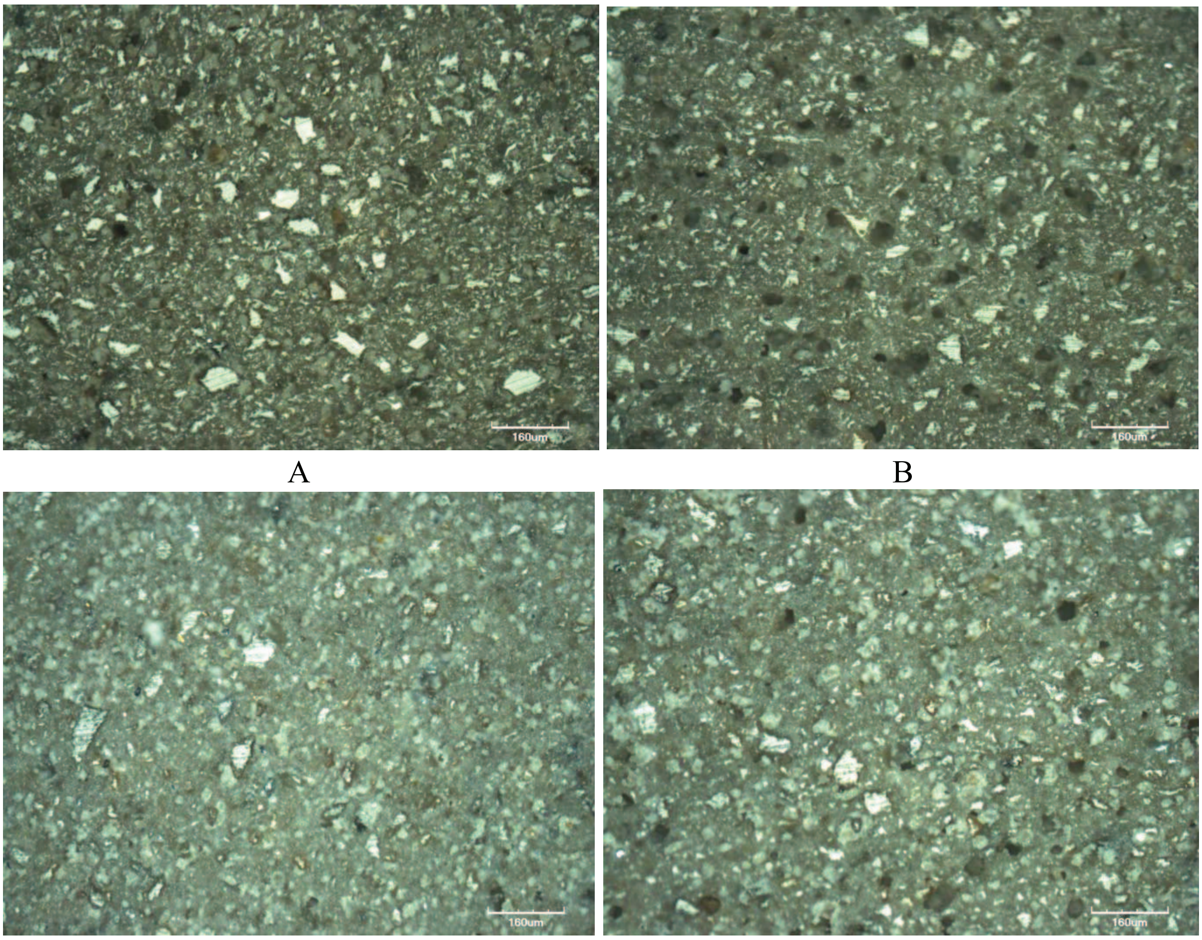


Fig. 36 Confocal microscopy of Tyzor LA modified MDF composite



A B

C D

Fig. 37 Confocal microscopy of MDF composite: without Tyzor addition stored at laboratory conditions (part A) and distilled water for 7 days (part B), MDF composite with addition of 0.2 wt% Tyzor LA also stored at laboratory conditions (part C) and distilled water for 7 days (part D)

The composition summarization for examination MDF composite samples was proceed by Differential Thermal Analysis and IR spectroscopy.

5.2.4 Differential Thermal Analysis with Effluent Gas Analysis

Thermal analysis techniques have been applied successfully to investigate the role of admixtures and additives in cement and therefore differential thermal analysis was chosen to better understand the structure of the prepared MDF composites. The following diagrams show the resultant DTA curves obtained on instrument SDT Q600 (TA Instruments) connected to FT-IR spectrometer iS10 (Thermo Nicolet) via heated capillary to analyze evolved gaseous products (EGA). The applied temperature increase was 10 °C/min under dried air atmosphere. Therefore each 10 min at EGA graphs represents 100 °C of temperature increase.

The initial weight decline at the TGA curves up to 200 °C represents the evaporation of residual water respectively unbounded water and partial dehydroxylation of PVAA takes place too. This process is characterized by endotherm at 100 °C at DTA curve. The weight loss up to 200 °C is connected only with water evaporation that can be seen at Fig. 35 – 37 where water vibration (4000 – 3500 cm^{-1}) and deformation (1800 – 1300 cm^{-1}) chracteristic absorption bands occur. The highest intensity of this effect (6.84 wt%) occurs in DTA analysis of MDF composite without Tyzor addition stored in distilled water for 7 days on *Fig. 39*. Oppositely the lowest intensity (had been obtained predictably for the sample stored in laboratory conditions without contact with the aquatic environment (*Fig. 38*) where weight loss reached only 4.79%. The results show the increase in this weight loss in contact with the aquatic environment. The weight loss was higher for Tyzor modified MDF composite, which could also be caused by additional swelling of copolymer PVAA.

The dehydration endotherm is followed with exothermic effect at temperature 220 °C with weight loss (see DTG curves double peak at 220 °C) that can be attributed to acetic acid and anhydride evolution as the products of the PVAA degradation. This is confirmed with EGA analysis where characteristic absorption bands of acetic acid, resp. anhydride (3000 – 2600, resp. 1750 and 1450 – 1350 cm^{-1}) takes place. It refers to elimination of existing unhydrolyzed parts (acetic functional groups) of PVAA copolymer. DTA curves confirmed the lowest content of acetate groups in MDF composites modified Tyzor LA (*Fig. 41* and *Fig. 42*). The reason probably leads to the cross-linking formation of PVAA by Tyzors.

Starting at 200 °C the progressive degradation of PVAA copolymer plays role. The degradation is attended by gradual polymer chain cracking and evolution of mainly carbon dioxide. This process can be seen from EGA at Fig. 35 – 37. Vibration and deformation absorption bands of CO_2 are localized at 2300 and 650 cm^{-1}. Also PVAA hydroxyl functional groups dehydroxylation continues within the degradation. This process is finalized at temperatures over 500 °C.

Further, weight loss at 260 °C that is well visible form DTG curve (Fig. 30 – 34) as a peak is attributed to formed calcium aluminate hydrates dehydroxylation. This process can be also well observed at EGA analysis (*Fig. 35, 36* and *37*) where water absorption bands (4000 – 3500 and 1800 – 1300 cm^{-1}) have a maximum at 26 min. This effect is the most expressive in case of samples stored in distilled water that leads to further hydration of cement grains and formation of hydration products confirmed with XRD.

Exo peak at 515 °C and following endo peak at 762 ° C are caused by a measurement error.

Further, weight loss at 648 °C is probably attributed to the $CaCO_3$ decarbonation originating from the dehydrated carbonate analogues of AFm and AFt phases detected with XRD. The general definitions of these phases are somewhat technical, but ettringite is an AFt phase because it contains three (t-tri) molecules of anhydrite when written as $C_3A.3CaSO_4.32H_2O$ and monosulfate is an AFm phase because it contains one (m-mono) molecule of anhydrite when written as $C_3A.CaSO_4.12H_2O$. Their carbonate analogues contain CO_3^{2-} ions instead of SO_4^{2-} tetrahedra.

The last weight loss with relatively high intensity and maximum at 890 °C refers to carbon (the residue of PVAA copolymer degradation) oxidation. This effect starts at 720 °C where the Boudouar thermodynamic equilibrium of CO_2, CO, C and O_2 lies.

Table 16 Weight loss percentage in DTA analysis

MDF Composite		**Unbounded Water loss**	**Bounded Water Loss**
without Tyzor	Lab conditions	4.79 %	11.31 %
	100 % relative humidity	5.53 %	11.82 %
	distilled water	6.84 %	14.58 %
0.2 wt% LA	100 % relative humidity	5.83 %	12.18 %
	distilled water	7.37 %	14.10 %

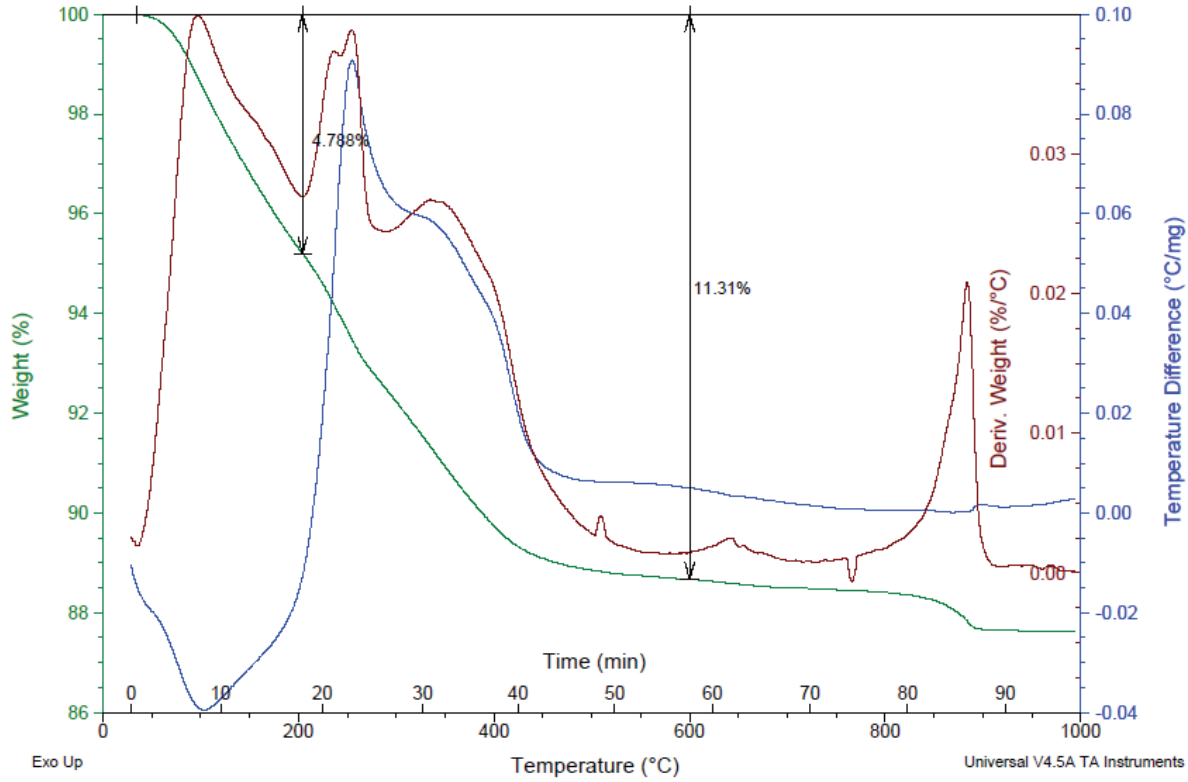


Fig. 38 DTA analysis of MDF composite without Tyzor addition stored at laboratory conditions

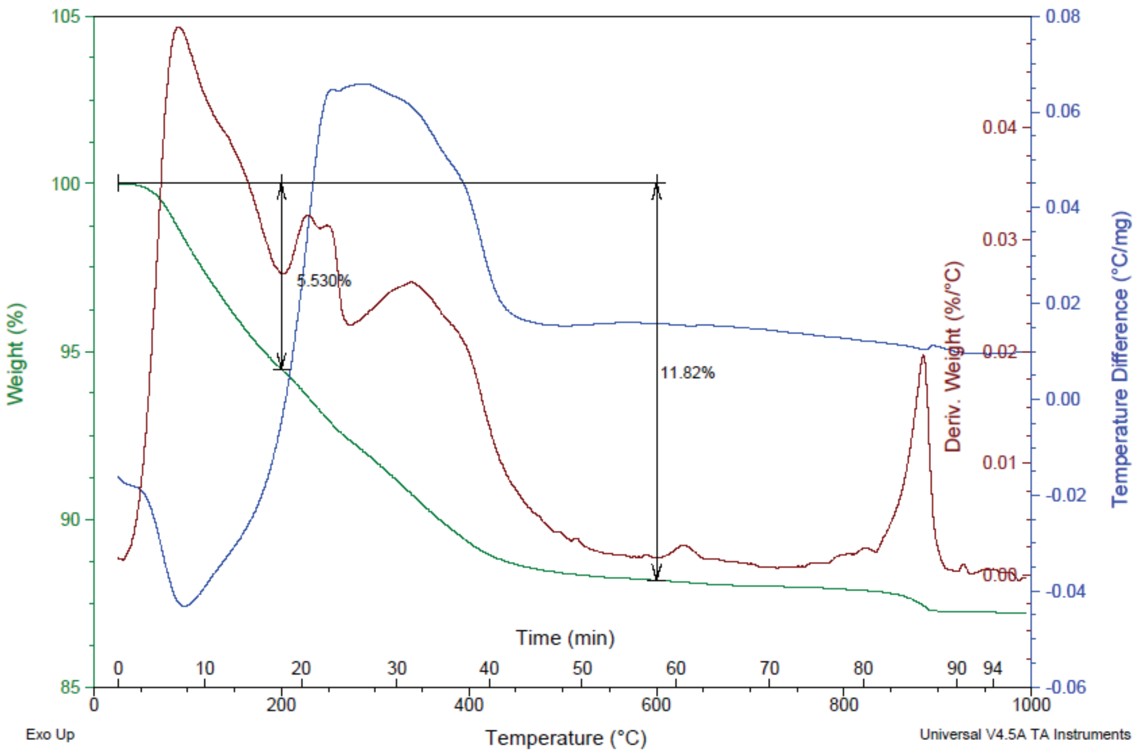


Fig. 39 DTA analysis of MDF composite without Tyzor addition stored at container with almost 100 % relative humidity for 7 days

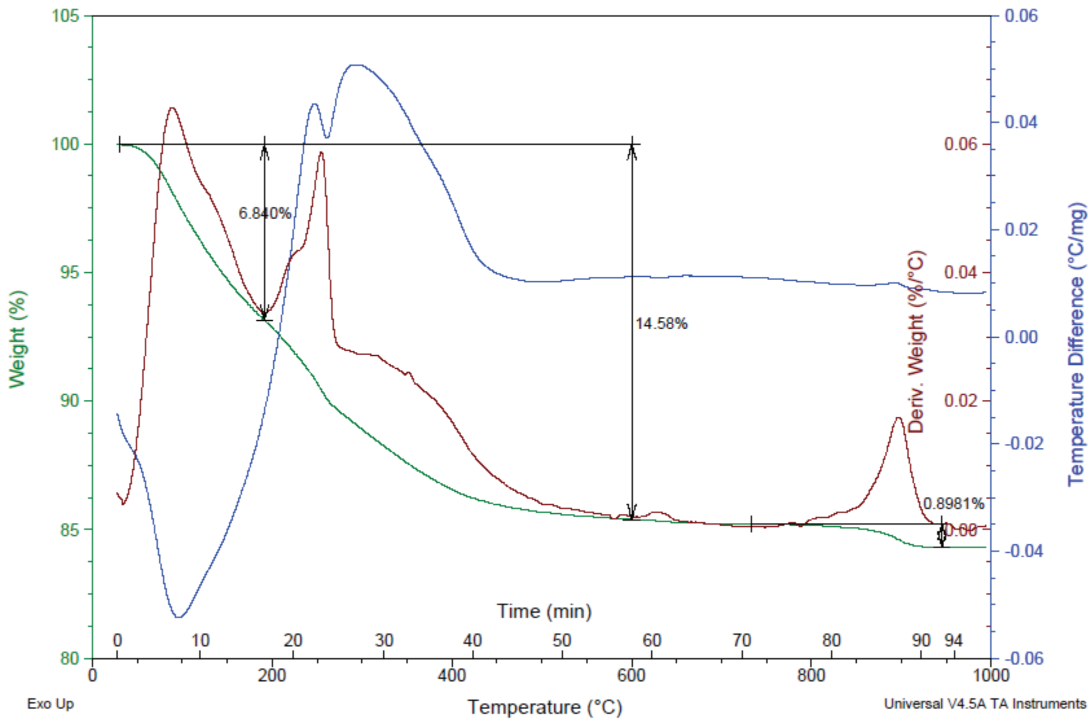


Fig. 40 DTA analysis of MDF composite without Tyzor addition stored at distilled water for 7 days

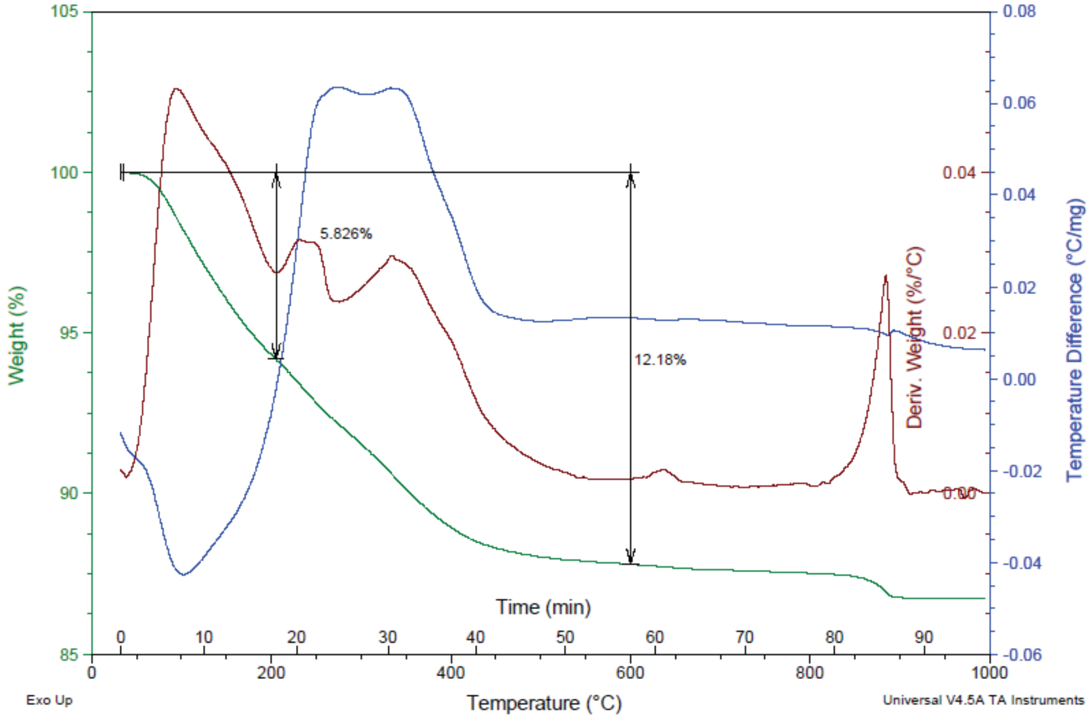


Fig. 41 DTA analysis of Tyzor LA modified MDF composite stored at container with almost 100 % relative humidity

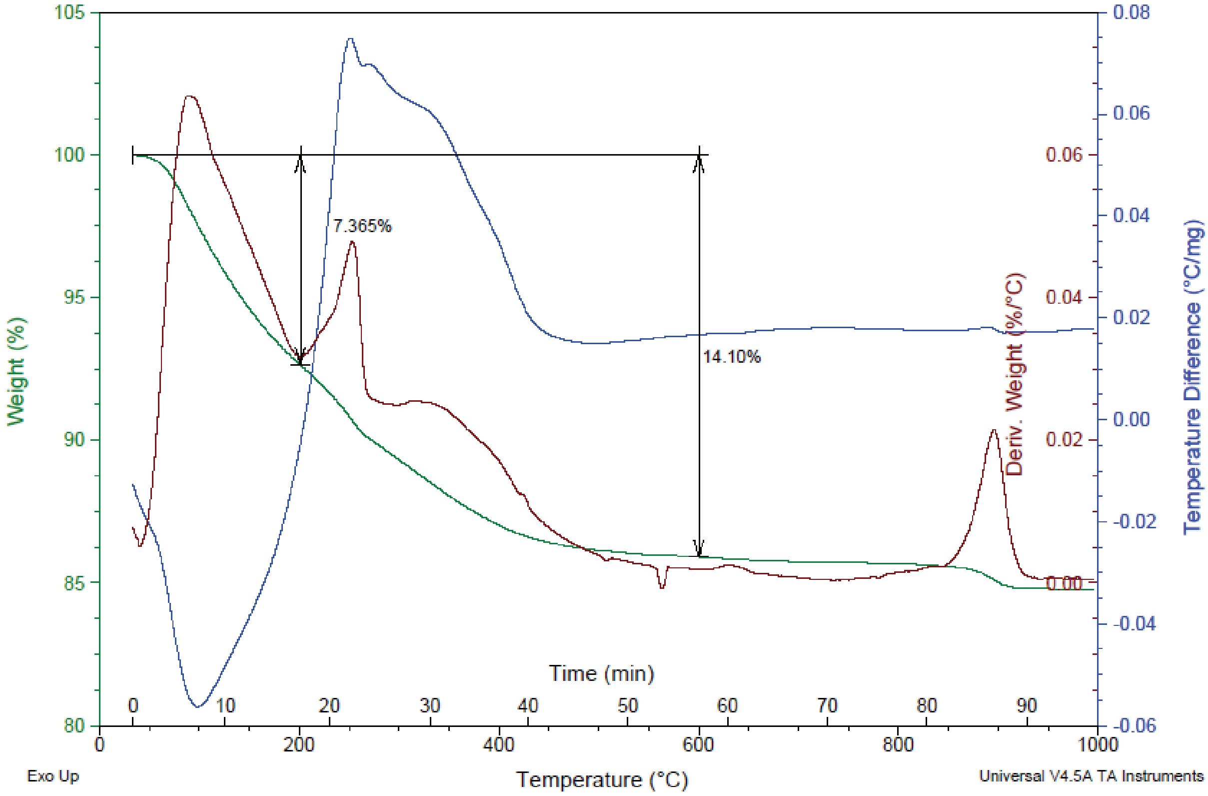


Fig. 42 DTA analysis of Tyzor LA modified MDF composite stored at distilled water

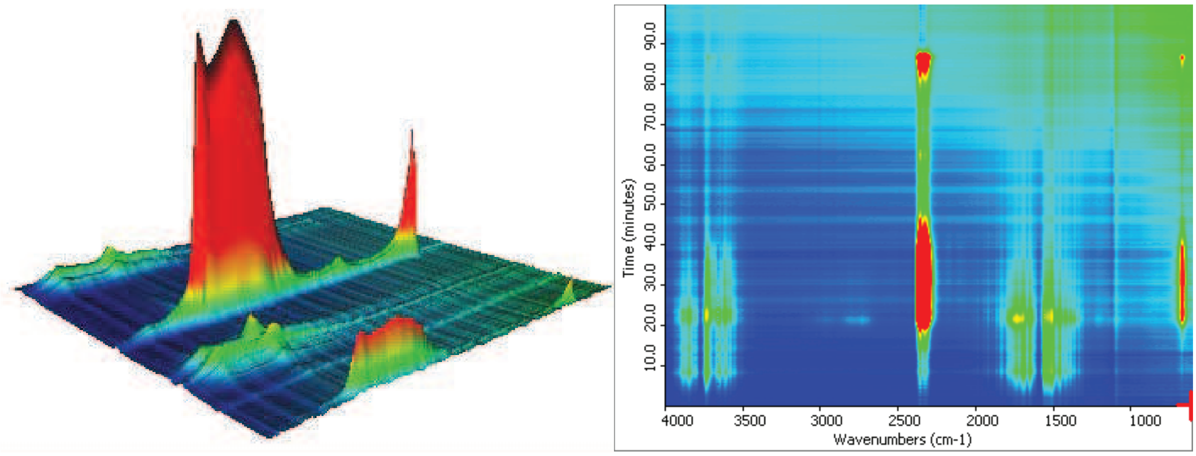


Fig. 43 EGA analysis of MDF composite stored at laboratory conditions

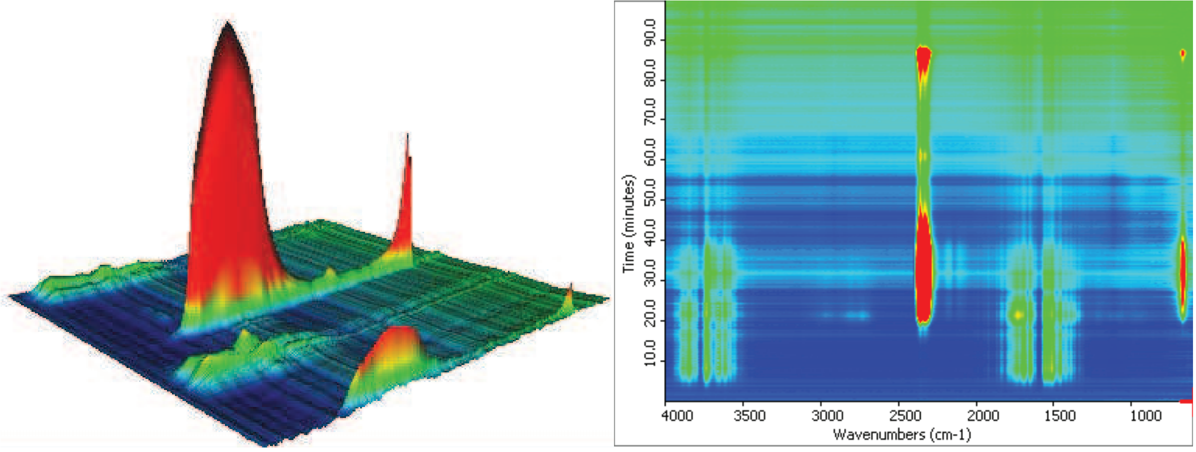


Fig. 44 EGA analysis of MDF composite stored at container with almost 100 % relative humidity

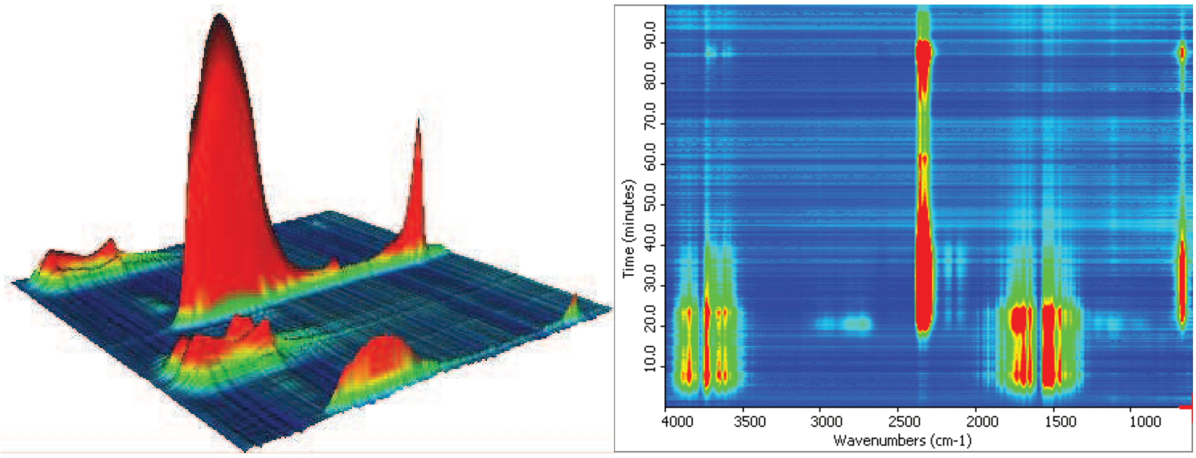


Fig. 45 EGA analysis of MDF composite stored at distilled water

5.2.5 FT-IR Spectroscopy

FT-IR spectroscopy is sophisticated method for observation of MDF composite microstructure in chemical point of view. This method enables study of organic as well as inorganic components present in samples. It can be supposed that modification of PVAA copolymer could be observed with it.

The spectrum at *Fig. 46* provides the FT-IR spectra of pure Tyzors LA and TE. Wide peaks in the range of wavenumber 2800 – 3200 cm^{-1} of relatively strong intensity can be observed. The first part of the peak at 3177 cm^{-1} (Tyzoru LA) and 3351 cm^{-1} (Tyzoru TE) corresponds to the H-chelate bridge and the second part at wavenumber 2910 – 2950 cm^{-1} to stretching vibration of asymmetric C-H bond, a fragment of ν(-CH2-). Peak is a moderate and has two peaks. Very small peak at wave number 1623 and 1651 belongs to N-substituted amides. The intensity is connected to concentration, which is 4 times higher in Tyzor LA. The structure of Tyzors is in section *3.8.2 Organic Titanates*.3.8.2

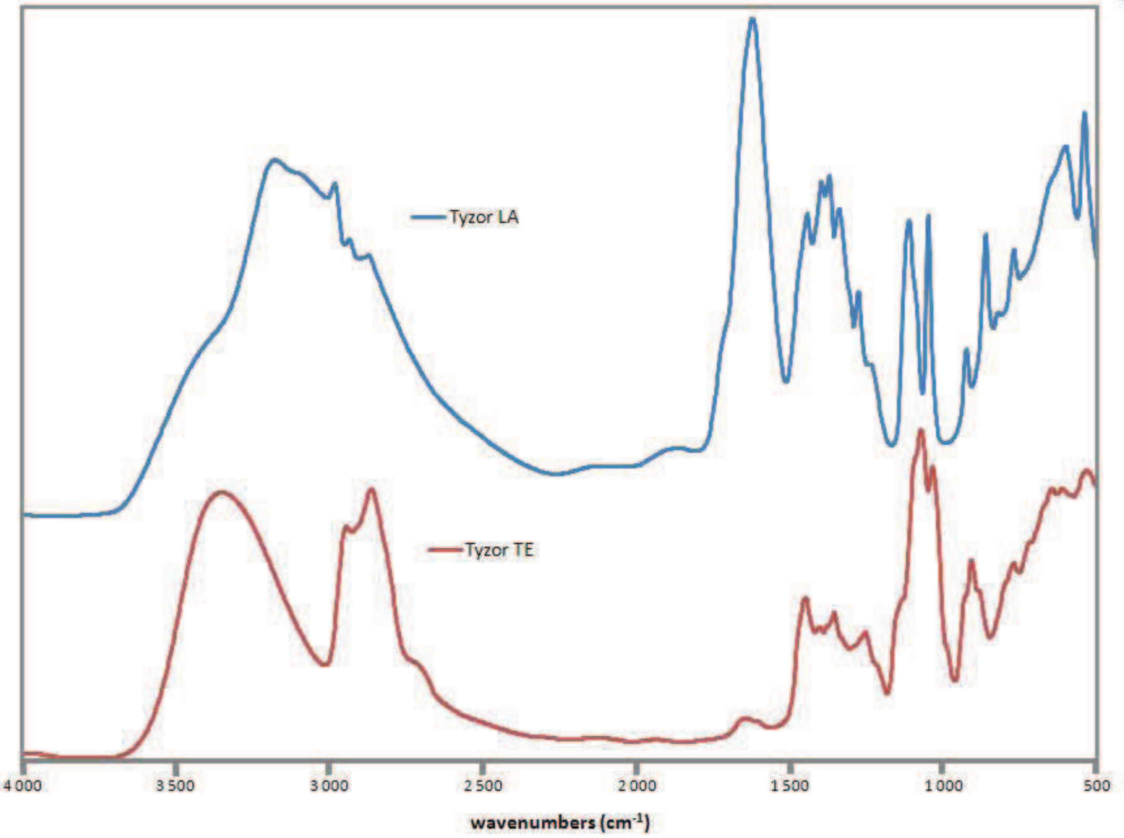


Fig. 46 FT- IR spectrum of Tyzor LA and TE

FT-IR spectrum on *Fig. 47* displays a model of MDF composites spectra with different type of environmental exposure and the addition of different amounts of Tyzor.

The result shows the high similarity of the samples. It corresponds mainly to a very broad absorption band at wavenumber 3200 - 3750 cm^{-1} differing only in intensity. Peaks in this area refers to stretching vibration O-H bonds in the molecule of polyvinyl. Peak is wide and strong due to the intermolecular and intramolecular hydrogen bonds with the maximum wavenumber 3421 cm^{-1}.

Two sharp maxima at 2923 and 2853 cm^{-1} are occurred in the absorption band, which is associated to the range 2910 – 2950 cm^{-1} and is the asymmetric stretching vibration of C-H bonds in the polymer chain PVAA. The intensity of this peak for the Tyzor modified MDF composite is lower. It predicts the presence of lower pure PVA aggregates content and therefore it is assumed the cross-linked polymer matrix formation.

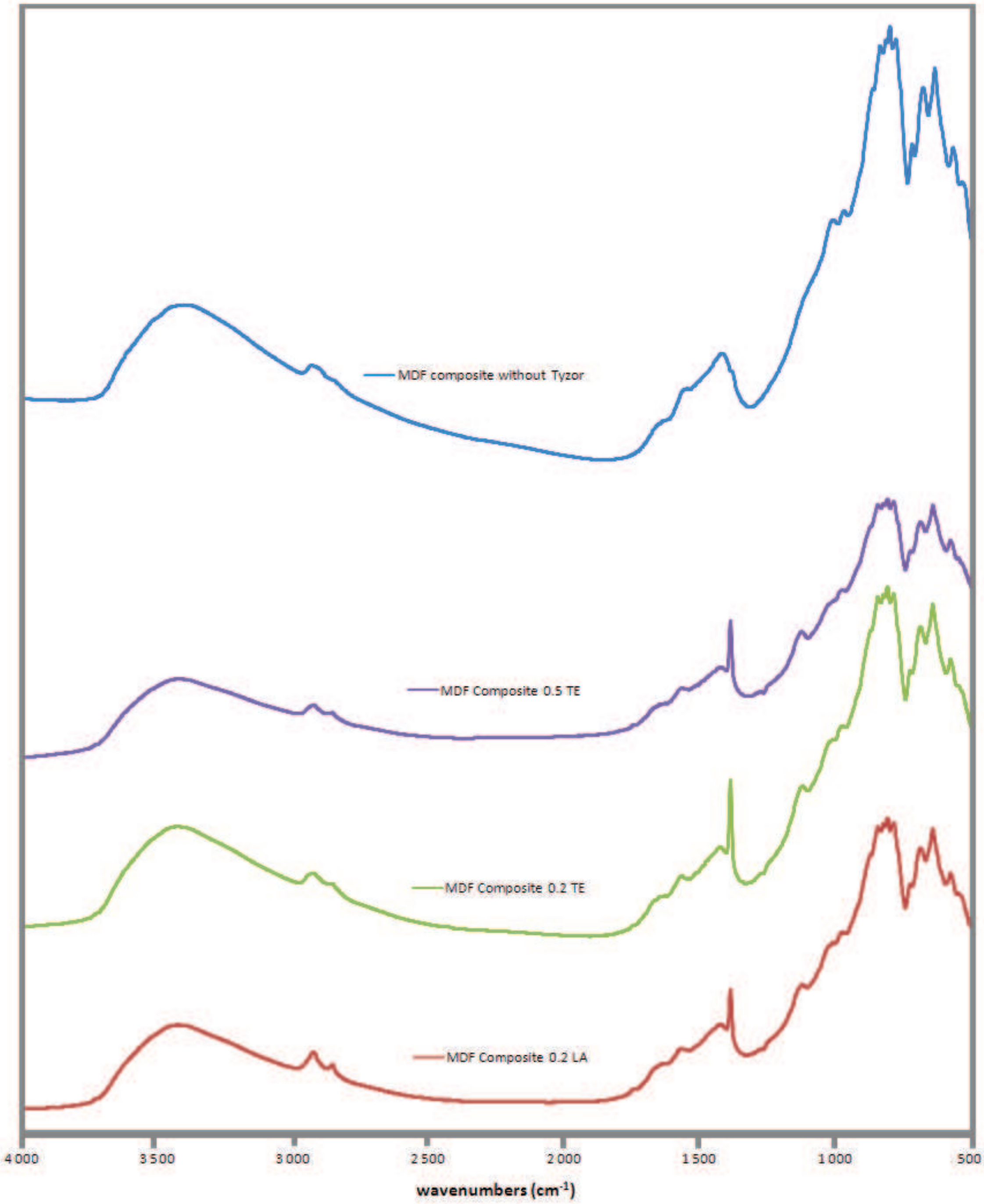


Fig. 47 FT-IR spectrum of MDF composite samples

The peaks within wavenumber range 1100 – 1750 cm^{-1} represents very important part with group of peaks 1559, 1418, 1384, 1272 and 1120 cm^{-1}. Due to the hydrolysis of acetate functional PVA groups there is a strong decrease in the intensity of the absorption band. The stretching vibration of C=O bonds of acetate functional groups at wavenumber 1740 cm^{-1} and also the overall decrease in the intensity of absorption bands at wavenumber 1020 – 1450 cm^{-1} vibrations also belongs to acetate functional groups. This decline is probably associated with the emergence of acetate salts, particularly calcium acetate, $Ca(CH_3COO)_2$, which was confirmed already in the DTA analysis. Establishment of acetate groups to metal cations leads to delocalization of the electron pair of the double bond C=O and the displacement of the absorption band of stretching vibrations of this bond.

The remainder of the spectrum in the absorption band 900 – 500 cm^{-1} is subject to inorganic phase of calcium aluminate cement which undergoes almost no hydration (*see chapter 5.2.2*) and therefore no changes of its absorption bands occurs.

6 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 on the purpose to increase the moisture resistance of these materials. The aim was associated to the evaluation and selection of particular organotitanate cross-linking additives, condition optimization of PVAA cross-linking and consequently preparation of MDF composite based on aluminate cement Secar 51 by Lafarge, France and polyvinyl alcohol GL-05S and GH-17S purchased from The Nippon Synthetic Chemical Insustry Co in Japan to improve the mechanical properties and therefore increase mentioned moisture resistance of formed MDF composite.

A series of organotitanate compounds namely Tyzor LA, Tyzor TE and Tyzor AA-75 from E. I. du Pont de Nemours and Company were examined as cross-linking additives with respect to mentioned moisture sensitivity of final macro-defect free composite. The experiments were carried out first to compare the effectiveness of the organotitanate cross-linking additives in conditions simulating real environment of MDF (pH, influence of rheological agent glycerol (p. a.) was supplied by Lach-Ner, s. r. o., Neratovice, weight ratio of PVAA). Simple tilted test tube method have been chosen to characterize the cross-linking properties of organotitanates.

The gelation appeared faster with increasing Tyzor TE and LA concentration. Beside Tyzor AA-75 have not form a gel even the concentration was higher and therefore it has not been subjected to further investigation. Interestingly, the same trend of gelation time was observed when neutral conditions were maintained.

Further investigation of gelation time was related to exposing of samples to elevated temperatures, especially 40, 80 and 120°C. In this case, all of the Tyzors had similar behavior. Water was evaporated and formed xerogel yellowed as the result of temperature 120°C.

The proposed weight ratios of cross-linking additive/PVAA were used for MDF composite specimens and evaluated by three point bending test on Zwick 010. Tyzor selection and the content in the mixture was chosen according to the gel point determination, therefore Tyzor TE, Tyzor LA and Tyzor AA in the range 0 – 0.5 wt % according to the polymer content.

The specimens were prepared on twin-roll mixer providing high-shear effect to get a higher compactness to avoid large pores and defects. The resulting specimens were then cured at temperatures of 40, 80 and 120 ° C and at laboratory temperature. Consequently, specimens were exposed to several different conditions. Part of the samples was stored in dry conditions at plastic bags, another in a container with almost one hundred relative humidity and the rest in distilled water each one for one and seven days. Subsequently, test samples were manufactured with dimensions 2x20x50 mm. At the end, the specimens were evaluated by testing tensile bending in 3-point bending test.

The results show the Tyzor TE impressed strength increase namely at concentrations of 0.3 – 0.5 wt % when the material was cured at laboratory condition. The increase of the flexural strength for Tyzor LA had been also noticed in these conditions. Only final Tyzor AA showed no improvement in the strength, which have already been confirmed during the gel point determination of Tyzors.

The effect had been proved also by microscopic structure observation where the porosity was much lower compared to MDF composite without Tyzor addition. Despite the perfect properties also Tyzor modified MDF composites exhibited significant loss of strength when water was applied to the specimens. The contact of specimens with water causes the increase in porosity (as the SEM images show) and then also the DTA analysis showed relatively large increases in weight loss attributed to the bound and unbound water.

Promising results came in high temperature assertion. Tyzor TE has been found suitable at curing temperature 40 °C where the flexural strength reached up to 65MPa – almost double increase compare to laboratory temperature. Application of higher temperatures, respectively 80 °C had negative influence on Tyzor TE, the strength was reduced back to 30MPa. On the other hand the opposite effect was observed for Tyzor LA. The curing of specimens at 80 °C showed even the highest strength of all samples at content of 0.1 wt% of the Tyzor LA respectively 78,71 MPa.

It was assumed the temperatures 40 °C is probably suitable to formation reactive hydroxyl titanium chelates from Tyzor TE to bonding with organic OH groups of PVAA and therefore produces strong gels by crosslinking and coating the cement grains. The effectivity of Tyzor LA is connected to the temperature of 80 °C where the structurally lactic acid chelate ammonium salt provides probably the highest concentration of chelates to react with OH functional group.

However, despite the Tyzors showed perfect ability of crosslinking especially in elevated curing temperature 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. The decrease in mechanical properties is still noticeable although the decline in elevated temperature of curing was lower.

MDF composite specimen prepared from 0.2 wt% addition of Tyzor LA exhibited the best results and very promising behaving when the material was exposed to water. The flexural strength 62.68 MPa obtained at dry laboratory conditions decreased to 48.80 MPa when the conditions with almost 100 % of relative humidity for 7 days was applied and to 41.15 MPa when the distilled water was used as the specimen environment.

Tyzor modified MDF composites exhibited the higher flexural strength and showed the improved moisture resistivity in the elevated curing temperature. It confirmed the “in situ” reticulation of polymer represent the possible way to decrease the effect of moisture on mechanical properties of these materials.

7 LIST OF SYMBOLS

AAM	Acrylamide monomer
BA/AN	Butylacrylate/acrylonitrile
CAC	Calcium aluminate cement
CA	Monocalcium aluminate cement
DTA	Differential thermal analysis
DSC	Differential scanning calorimetry
EGA	Evolved gaseous analysis
FT-IR	Infrared spectroscopy
HAC	High alumina cement
HPMC	Hydroxypropyl methylcellulose
MDF	Macro-defect free
MMA	Methyl methacrylate
OPC	Ordinary Portland cement
PBA	Poly(butyl acrylate)
PVA	Polyvinylalcohol
PVAA	Polyvinyl alcohol-acetate copolymer
Poly-P	Sodium polyphosphate
SACP	Styrene/acrylonitrile co-polymer
SAFB	Sulfoaluminate ferrite belite
SEM	Scanning electron microscopy
Tyzor TE	Triethanolamine titanate chelate
Tyzor LA	Lactic acid titanate chelate, ammonium salt
Tyzor AA	Acetylacetonate titanate chelate
VA	Vinyl acrylics
XRD	X-ray diffraction analysis

8 REFERENCES

[1.] Miller, M.: *Polymers in Cementations Materials.* **1st ed.** Shawberry: Rapra Technology Limited, 2005. 173p. ISBN: 1-85957-491-2

[2.] Birchall, J.D.; Howard, A.J.; Kendall, K.: *U.S. Patent 4,410,366*, 1983.

[3.] Lewis, J.A.; Boyer, M.A.; Bentz, D.P.: *J. Am. Ceram. Soc.* In press.

[4.] Desai, P.G., Young, J.F., and Wool, R.P. : *Cross-linking reactions in macro-defect free cement composites.* Materials Research Society Symposium Proceedings (1992), 245, 179-184.

[5.] Lewis, J.A.; Boyer, M.A.: *Effects of an organotitanate cross-linking additive on the processing and properties of macro-defect-free cement.* Advanced Cement Based Materials, 1995; 2: 2-7.

[6.] Ohama, V., Demura, K., and Endo, T.: *Strength properties of epoxy-modi-fied mortars without hardener.* Proceedings 9th ICCC, New Delhi, 1992; Vol. 5, pp. 512-511

[7.] Grosskurth, K. P.: *Morphology and long term behavior of polymer cement concrete.* Materials Research Society Symposium Proceedings, 1991179, 273-281.

[8.] Ollitrault-Fichet, R. et al.: *Microstructural aspects in a polymer-modified cement.* Cement and Concrete Research, 1998. 28; 1687-1693.

[9.] Schulze, J.: *Influence of water-cement ratio and cement content on the prop¬erties of polymer-modified mortars.* Cement and Concrete Research, 1999; 29, 909-915.

[10.] Odler, I.: *Special inorganic cement.* 1st ed. London: E & F.N. Spon, 2000. p. 226 - 247. ISBN: 0-419-22790-3

[11.] Birchall, J.D., Howard, A.J., and Kendall, K. : *Flexural strength and porosity of cement.* Nature, 1981; 289(29); 388-390.

[12.] Popoola, O. O.; Kriven, W.M.; Young, J.F.: *Microstructural and Microchemical Characterization of a Calcium Aluminate- Polymer Composite (MDF Cement).* J. Am. Ceram. Soc., 1991; 1928-1933.

[13.] Lewis, J. A., Kriven, W. M.: *Microstructure-Property Relationships in Macro-Defect-Free Cement.* MRS Bulletin, 1993. 18 (3); 72-77.

[14.] Desai, R. A.: *M.S. Thesis*, University of Illinois, 1990.

[15.] Mojumdar, S. C.; Mazanec, K.; Drabik, M.: *Macrodefect-free (MDF) cements–synthesis, thermal, chemical, SEM and magnetometric study and moisture resistance.* J. Therm. Anal. Calorim., 2006. 83. 135–9.

[16.] Lewis, J. A.; Boyer, M.; Bentz, D. P.: *Binder distribution in macro-defect-free cements: relation between percolative properties and moisture absorption kinetics.* J. Am. Ceram. Soc., 1994. 77(3). 711–6.

[17.] Mojumdar, S. C.: *Synthesis, moisture resistance, thermal, chemical and SEM analysis of macro-defect-free (MDF) cements.* J. Therm. Anal. Calorim., 2004. 78. 135–44.

[18.] Zhihong, W.; Yucui, H.; Yuan H.: *Research on increasing effect of solution polymerisation for cement-based composite.* Cem. Concr. Res., 2003. 33. 1655–8.

[19.] Drabik, M.; Mojumdar, S. C.; Galikova, L.: *Changes of thermal events of macrodefect-free (MDF) cements due to the deterioration in the moist atmosphere.* Cem. Concr. Res., 2001. 31. 743–7.

[20.] Chandrashekhar, G. V.; Shafer, M. W.: *Polymer impregnation of macro-defect- free cements*. J. Mater. Sci., 1989. 24. 3353–5.

[21.] Titchell, I.: *Environmental degradation of macrodefect-free cements – Part I. Mechanical properties investigation*. J. Mater. Sci., 1991. 26. 1199–204.

[22.] Pushpalal, G. K. D.; Kobayashi, T.; Hasegawa, M.: *High alumina cement–phenol resin composite: water resistivity and effect of post hydration of unreacted cement on durability*. Cem. Concr. Res., 1997. 27(9). 1393–405.

[23.] Branca, C.: *The influence of polyvinylalcohol on macro-defect free cement composites*. Materials Engineering, 1996. 7. 55-60.

[24.] Santos, R.S.: *Macro-defect free cements: influence of poly(vinyl alcohol), cement type and silica fume*. Cement and Concrete Research, 1999. 29. 747-751.

[25.] Hsu, K.C., and Juaang, Y.T. (1992) Preparations and characteristics of chemically bonded ceramics (in Chinese). Cailiao Kaksue 24, 231-239 [ref. CA 120/142248]

[26.] Drabik, M.: *Chemistry and porosity in modelled MDF cement materials, in Proceedings 9th ICCC*. New Delhi, Vol. 3, 1992. 386-392.

[27.] Russell, P. P.: *MS thesis*. University of Illinois; 1991.

[28.] Tan, L.S.: *Evolution of mechano-chemistry and microstructure of a calcium aluminate-polymer component. Part II. Mixing rate effect*. Journal of Materials Research, 1996. 11. 1739-1747.

[29.] Alfani, R.: *Effect of temperature on thermo-mechanical properties of macro-defect-free cement–polymer composite*. J Mater Sci 1999;34:5683–7.

[30.] Desai, P. G.; Lewis, J. A.; Bentz, D. P.: *Unreacted cement content in macro-defect-free composites: impact on processing-structure-property relations*. J. Mater. Science, 1994. 29. 6445–52.

[31.] Másilko, J.: *Zvyšování odolnosti MDF kompozitů proti působení vody*. Brno: Vysoké učení technické v Brně, Fakulta chemická, 2008. 79p.

[32.] Comotti, A., Simonutti, R., Sozzani, P.: *Morphology of the poly(vinyl alcohol)–poly(vinyl acetate) copolymer in macro-defect-free composites: a 13C magicangle–spinning nuclear magnetic resonance and ^{1}H spin-diffusion study*. J. Mater. Sci. 1997; 32: 4237–45.

[33.] Popoola, O. O., Kriven, W. M., Young, J. F: *High-resolution electron microscopy and microchemical characterisation of a polyvinyl alcohol acetate/calcium aluminate composite (macro-defect-free cement).* Ultramicroscopy 1991; 37 (1–4) : 318–25.

[34.] Harsh, S., Handoo, S. K., Ahluwalia, S. C.: *Investigations on moisture absorption and its effect on the performance of HAC based MDF cement*. In: Proceedings of the 10th international congress on the chemistry of cement, Gothenburg, Sweden; 1997

[35.] Delucchi, M., Cerisola, G.: *Influence of organic coatings on the stability of macrodefect-free cements exposed to water*. Construct Build Mater, 2001; 15:351–9.

[36.] Rodrigues, F. A., Joekes, I.: *Macro-Defect Free Cements: A New Approach.* Cement and Concrete Research, 1998. Vol. 28, No. 6, pp. 877–885,

[37.] R. S. Santosa, F. A. Rodriguesa, N. Segrea and I. Joekes: *Macro-defect free cements Influence of poly(vinyl alcohol), cement type, and silica fume*. Elsevier Science Ltd, 1999. Vol. 29, pp 747-751

[38.] Donatello, S.: *Recent developments in macro-defect-free (MDF) cements*, Constr. Build Mater, 2008.

[39.] Mojumdar, S. C., Mazanec, K., Drabik, M.: *Macro-defect-free (MDF) cements – synthesis, thermal, chemical, SEM and magnetometric study and moisture resistance*. J. Therm. Anal. Calorim. 2006; 83:135–9.

[40.] Titchell, I.: *Environmental degradation of macrodefect-free cements – Part I. Mechanical properties investigation*. J. Mater. Sci. 1991;26:1199–204.

[41.] Chandrashekhar, G. V., Shafer, M. W.: *Polymer impregnation of macro-defect-free cements*. J. Master. Sci. 1989; 24:3353–5.

[42.] Zhihong, W., Yucui, H., Yuan, H.: *Research on increasing effect of solution polymerisation for cement-based composite*. Chem. Concr. Res. 2003; 33:1655–8.

[43.] Popovics, S.: *Concrete Materials, Properties, Specifications and Testing*, 2nd ed. New Jersey: Noyes Publications, 1992. 661p. ISBN: O-81.55-1308-9

[44.] Robson, T. D.: *High-Alumina Cements and Concretes*, Contractors Record, London, John Wiley and Sons, New York, 1962.

[45.] Graf, O., Albrecht, W. and Schaffler, H.: *Die Eigenshaften des Betons*, 2nd ed., Springer Verlag, Berlin - Gottingen – Heidelberg, 1960.

[46.] Robson, T. D.: *Aluminous Cement and Refractory Castables, The Chemistry of Cements*, Acadecmic Press, London and New York, 1964. Vol. II, Chap. 12

[47.] Talaber, J.: *High-Alumina Cements*, A Principal Paper, VIth International Congress on the Chemistry of Cement, Moscow, 1974.

[48.] Bolomey, J.: *Fineness Modulus of Abrams and the Calculation of the Mixing Water of Concrete*, Materialprufungsanstalt, 1930.

[49.] Shibayama, M., Adachi, M., Ikkai, F., Kurokawa, H., Sakurai, S, Nomura, S.: *Gelation of Poly(viny alcohol)-Vanadate Aqueous Solutions*. Macromolecules, 1993. 26. 623-627.

[50.] Peppas, N. A. and Merrill, E. W.: *Determination of interaction parameter c1 for PVA and water in gels crosslinked from solutions*. Journal Polymer Science, 1976. 14-459.

[51.] Deuel, H., Neukom, A.: *Macromolecular Chemistry*. J. Materials Science, 1949. 3. 113.

[52.] Burkinshaw, S. M. and Kumar, N.: *A polyvinyl alcohol aftertreatment for nylon 6,6*. Elsevier, 2006. 1. 86-91.

[53.] Kawakami, H., Fujiwara, H., Kinoshita, Y.: *Complexation of Poly(vinyl alcohol)-Congo Red Aqueous Solutions*. Jpn Patent S47-40894, 1972.

[54.] Kobayashi, T., Pushpalal, G. K. D., Hasegawa, M.: *European Patents Office*, No. 0590948 A1; 1997.

[55.] Pushpalal, G. K. D., Kobayashi, T., Hasegawa M.: *High alumina cement–phenol resin composite: water resistivity and effect of post hydration of unreacted cement on durability*. Chem. Concr. Res., 1997; 27(9) : 1393–405.

[56.] SECAR®51, Product data sheet [online], [ref. 1. 2. 2010]. Available: < http://www.secar.net >.