

CHEMICAL INTERACTIONS, OPEN POROSITY AND STRENGTH OF SOME MODELED MDF MATERIALS

MILAN DRABIK¹, LUBICA GALIKOVA¹, IVAN ODLER²¹ Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic² Institut für Nichtmetallische Werkstoffe, T U Clausthal, 3392 Clausthal-Zellerfeld, BRD

Received 3. 5. 1993

In addition to the study of "MDF processability" of various systems there is a strong need for the experimental evidence of the aspects of chemical hypothesis about the origin and properties of MDF materials. We have compared chemical interactions, open porosity and strength of the mixtures $C_4AF - C_4A_3S - \text{hpmc}$ (pva/ac) – poly-P to those of Secar-based mixtures, both after MDF procedure. Al and Fe environments are close to cross-links topical in interphase regions of clinker and polymeric parts of the aluminous MDF's (Secar-based). (Al,Fe)-O-CR cross-links conform to the minimization of the amount and dimensions of pores, as well as affect the evolution of strength during model MDF syntheses in the system $C_4AF - C_4A_3S - \text{hpmc} - \text{poly-P} - H$. Whisker-like reinforcing role of the cross-links is designed to explain the transfer of the chemical interactions into the level of particles and pores. Strength values indicate a further exploitation of C_4AF and C_4A_3S – based clinkers; in the MDF forming processes with hpmc and/or poly-P.

INTRODUCTION

Among the promising dispersed systems and materials that attract interest of researchers are also the so-called Macro-Defect-Free (MDF) materials. These belong to the group of chemically bounded ceramics – materials exhibiting properties comparable to those of ceramics, however, synthesized at ambient temperature and (in case of MDF's) at pressures 5MPa. Introductory studies [1–3] compare properties of MDF's so with ceramics as with hydraulic materials. Interactions and depths of chemical reaction of inorganic matrix with solidified polymer are discussed [2–4] as important factors influencing MDF properties. MDF's synthesized from aluminous cement and polyvinylalcohol-acetate (pva/ac) are the most superior examples [1–3], until now still far from an industrial production.

In addition to the study of "MDF processability" of various systems there is a strong need for experimental evidence of the links of chemical hypothesis and properties of MDF materials. Analysing the data in [1–4] one can treat MDF's as multicomponent systems containing compounds with various chemical background (minerals of cement clinker, products of its reaction with water, water-soluble polymers spontaneously solidified in basic environment, as well as regions exhibiting interactions among these components). Consequently, study of simplified models is

a necessary step if the progress in understanding and control of the new MDF-related systems are to be achieved.

Our study of phase composition, cross-linking atoms and thermal stability of system $C_4AF - \text{hydroxypropylmethyl cellulose (hpmc)} - H$, $C_4A_3S - \text{hpmc} - H$ and $C_4AF - C_4A_3S - \text{hpmc} - H$ [4–6] is in this paper completed by comparison of chemical interactions, porosity and strength values with these data reported for the most frequent MDF system (Secar 71-pva/ac- H). The choice of more complete systems mature for future analysis of MDF processability is appended based on the discussed results.

EXPERIMENTAL

Methodology of samples preparation and investigation we describe elsewhere [4,5], steps of the synthesis are close to that reported by Birchall and co. [1,2], in particular:

(i) Dry pre-mixing of clinker phase (C_4AF , C_4A_3S) or clinker (Secar 71) with 5% (by mass) of hpmc or pva/ac.

(ii) Addition of water giving $w/s = 0.2$, or addition of the solution of sodium polyphosphate (poly-P) introducing 5% (by mass) of the poly-P and ratio of $w/s = 0.2$ into the system.

(iii) Twin-rolling until the mixture reaches consistency of dense dough (upto 5 minutes).

(iv) Static 5 MPa pressure in a pellet die (diameter 20 mm) applied in durations ranging from 30 minutes to 6 hours. Chemical reactions were then kinetically frozen by drying at 80°C in air.

Strength of cylinders with the above diameter, porosity of broken samples and, finally, changes of

The work has been done under the project No 85/92 granted by the Slovak Grant Agency for Science, in part during the DAAD stay of M.D. at I.O.

Abbreviated notation: C – CaO, A – Al₂O₃, F – Fe₂O₃, S – SO₃, H – H₂O.

chemical and phase composition of powdered samples were estimated. The analysis of powders by methods of X-ray phase analysis (Diffractometer Philips PW 1050, CuK α or FeK α radiation), ^{27}Al MAS NMR spectroscopy (Bruker MSL 400 spectrometer, operating at 104.2 MHz, sample spinning rate 4.3 kHz) and ^{57}Fe mossbauer spectroscopy (standard constant acceleration spectrometer operating at the temperature of liquid nitrogen) are described in details in [5, 6]. Mercury intrusion porosimetry (Carlo Erba 2000) was used in investigation of open porosity characteristics, averages of three measurements are given for each sample. Shear strength measurements have been performed radially [7] on the original cylindrical probes, presented are averages of probes estimations (eq. 1) of each sample.

$$\delta = \frac{2}{\pi \cdot d} \cdot \frac{F}{h} \quad (1)$$

F/kN – force causing the colaps of the probe

d/mm – diameter of probe

h/mm – height of the probe

RESULTS AND DISCUSSION

A. $\text{C}_4\text{AF} - \text{C}_4\text{A}_3\text{S} - \text{hpmc} - \text{H}$, chemical interactions

Conversions of reagents upto 24 hours of reaction together with detection of the traces of crystallohydrates after more than 24 hours of reaction [5] displayed the exclusive presence of amorphous AFm-like hydrate upto 6 hours of the reaction duration. Resonance spectroscopies confirm octaedrally coordinated atoms of Al and Fe in the hydrate. Chemical shifts of Al atoms in ^{27}Al MAS NMR (9.5 ppm) and isomer shifts of paramagnetic doublet of Fe atoms in ^{57}Fe mossbauer spectra ($0.43 \text{ mm}\cdot\text{s}^{-1}$) exhibit differences against those of Al and Fe bonded through O to H [8–11]. Shifts are due to the variability of the second coordination spheres of Al and Fe; incorporation of not only H and S, but also C atoms in X-positions of $(\text{Al}, \text{Fe})[\text{OX}]_6$ in cationic part of the formed AFm skeleton [12]. Accounting for the structure of hpmc and positions of C atoms in it [13] leads to the desing of cross/links $(\text{Al}, \text{Fe})\text{-O-CR}$ in the studied systems (fig. 1).

Al and Fe environments, as displayed in fig. 1, are close to cross/links topical in interphase regions of clinker and polymeric parts of the other MDF's [3,14]. Cross-links of the atoms present in interphase regions are believed to exert the atomic level of the control of MDF related properties in Secar – pva/ac systems [2, 3, 14, 15]. The cross-links were postulated from IR and HREM results [3,14], however, experimentally have been restricted on aluminous systems. Our results show cross-linking potentials of Al as well as

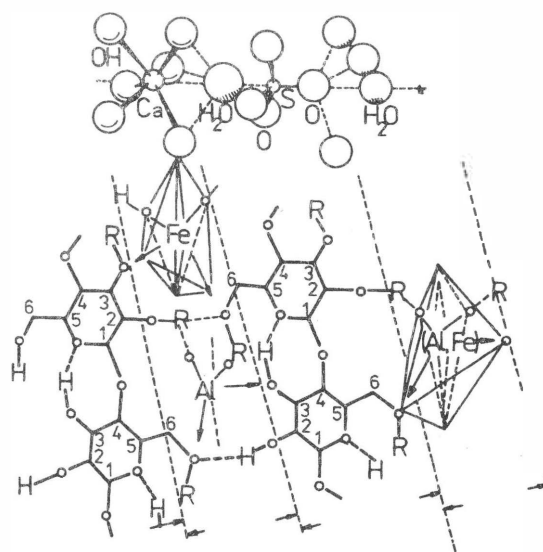


Fig. 1. Location of Al, Fe – O – XR cross-links in areas of the interaction between AFm phase [12] and chains of hpmc [13].

Fe atoms conforming to the frequent isomorphous Al \leftrightarrow Fe substitutions if both atoms are at the disposal during interactions of clinker and polymeric parts under MDF procedure conditions.

B. $\text{C}_4\text{AF} - \text{C}_4\text{A}_3\text{S} - \text{hpmc} (\text{pva/ac}, \text{poly-P}) - \text{H}$, Secar 71 – hpmc (pva/ac, poly-P) – H, porosities and strength

Consequences of the interactions of inorganic matrix with solidified polymers (hpmc, pva/ac, poly-P) have been followed on the level of particles of the individual studied reagent compositions. The data of mercury intrusion porosimetry and shear strength measurements are plotted in fig. 2. Results enable to discuss the extent of the controlling effect of cross-links on the porosities and strength of studied systems.

Incorporation of polymers and application of the pressure during syntheses densify the probe and minimize its open porosity to values between 2 and 12%. Furthermore, 80 to 90% of these pores are of the radii between 10 and 100 nm and consequently the medians (radii of pores at which the porosity is an half of the total value) are lower than 50 nm. The variety of reagents composition results in a large scaling of strength values. Despite it, common tendencies in evolution of these, of porosimetric parameters and of the cross-links occur, as discussed later.

Our data are in accord with the results of [15] concerning the length of particles of solidified polymers (from 100 to 1000nm) as well as with generally valid reciprocal relation between the pore volume and the

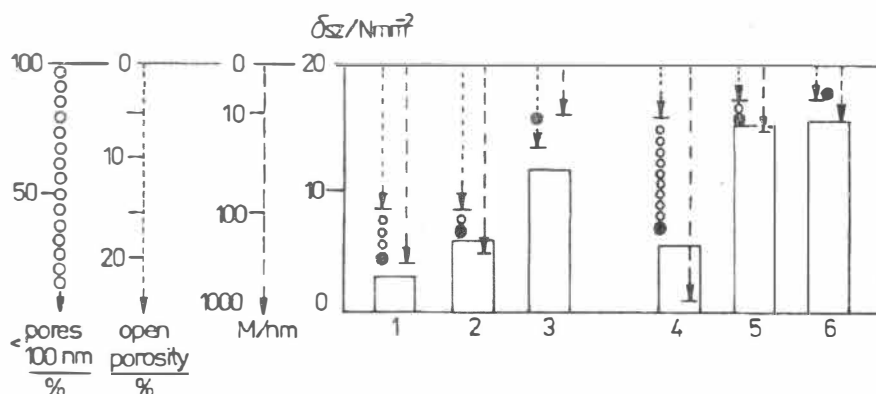


Fig. 2. Shear strength ($\delta_{sz}/N\cdot mm^{-2}$) and porosimetric parameters (open porosity / % , pores with radii < 100 nm / % , median M / nm) in the studied systems; 1: Secar 71 + pva, 2: Secar 71 + pva + poly-P, 3: Secar 71 + hpmc, 4: $C_4AF + C_4A_3S + pva$, 5: $C_4AF + C_4A_3S + hpmc$, 6: $C_4AF + C_4A_3S + hpmc + poly-P$.

density of the occupation of space. The results confirm the absence of large pores if mixture is properly processed [1–3]. Porosity of the particular sample determines its strength; medians and content of pores smaller than 100 nm exhibit the best relation with strength values in the studied system. The mixture of $C_4AF - C_4A_3S$ exerts the highest strengths in combination with hpmc and poly-P, it may be the consequence of comparable rates of polymers solidification and clinker hardening. From this point of view the pva/ac seems to be less compatible with C_4AF and C_4A_3S . Lower values of strength of Secar-based samples were introduced by the voids (shown by higher content of open pores of samples Secar 71 – pva/ac and Secar 71 – pva/ac – poly-P in fig. 2) during the synthesis process in presence of pva/ac. Strengths are slightly positively affected by the addition of the poly-P, similar effect has been recently reported in aluminous MDFs [17]. (Al, Fe) – O – P cross-links, as noted generally in [3,7,16] and in our latest study of this MDF-related system [6] might represent the atomic level source of observed effect. Study precisising the knowledge about P alternatives in X positions of (Al, Fe) [OX₆] is in progress.

Figs. 1 and 2 demonstrate two levels of the only change: MDF processing of studied systems leads to formation of cross-links and these, of solidified in originally free space among the grains, densify the reaction product, leading to the evolution of characteristic

porosities and strengths. Accepting a concept of the influence whiskers on the properties of ceramics one can attribute to the regions of cross-links a similar whisker-like reinforcing role. The differences against “innert” whiskers are obvious, i.e. reinforcing regions are of subparticle dimensions and form grains-scaled nearly homogenous body of the reaction product. Thus, fig. 1 may be considered as the design of the transfer of interactions including cross-links into the level of particles and pores in the studied system.

CONCLUSIONS

1. Al and Fe environments in products of the interactions of C_4AF and C_4A_3S with hpmc and poly-P are close to cross-links topical in interphase regions of clinker and polymeric parts of the aluminous MDF's. (Al, Fe)-O- R cross-links conform to the minimization of the amount and dimensions of pores during MDF syntheses in the system $C_4AF - C_4A_3S - hpmc - H$.
2. Despite the restriction of the porosity estimations to the open pores only, experiments display the relation of the porosity characteristics and the values of strength in studied system. Promising values of strength exert the mixtures of $C_4AF - C_4A_3S$ with hpmc and poly-P. Whisker-like reinforcing role of cross-links is designed to explain the transfer of chemical interactions in the level of particles and pores.

APPENDIX

Schematic review of the knowledge of MDF's and by it conditioned further study of models of MDF's is given below:

clinker	c-polymer	PVA		p(AM)		hpmc	
	poly P	0	+	0	+	0	+
Secar 71		1 a c-h	3 b d	-	-	1 b c-p	3 b d
PC 55		-	-	2	2	2	3 a d
C ₄ AF + C ₄ A ₃ S̄ mixtures		3 b d	3 b d	-	-	3 b c-h	3 b c-h
Š-clinker		4	4	-	-	4	4

0 - none

+

1 - MDF process already discribed

a - chemistry partly described

b - not described chemistry

c - impact of chem. hypothesis-h, possible-p

2 - unseccesfull

3 - MDF process sucessfull, not described before

a - high w/s

b - relative porosities and strength estaninated

c - chemistry studied, correlates with hypoth.-h

d - chemistry and correlations due to study

4 - following notes 1c, 3b-3d MDF processing anticipated to study

- [4] M. Drabik: Proc. Progmatech 91, 93 (Smolenice 1991)
- [5] M. Drabik, M. Kristofik, L. Galikova, S. Saňu: Proc. 9th Int. Congress on Cement Chemistry, vol. III., 386 (New Delhi 1992)
- [6] M. Drabik, R. C. T. Slade: Proc. "The chemistry and microstructure of cement and concrete", P 5 (Old Aberdeen 1993)
- [7] A. Zurz, I. Odler, B. Dettki: Mat. Res. Soc. Symp. Proc. 179, 69 (1991)
- [8] D. Muller, A. Rettel, W. Gessner, G. Shceller: J. Magn. Reson. 57, 152 (1984)
- [9] R. C. T. Slade, J. Č. Southern, A. Thompson: J. Mater. Chem. 1, 563 (1991)
- [10] G. D. Soraru, F. Baboneau, J. D. Mackenzie: J. Mater. Sci. 25, 3886 (1990)
- [11] T. Nishida, Y. Takashima: J. Non-cryst. Solids 94, 229 (1987)
- [12] F. Hanic, I. Kapralik, M. Drabik: Silikaty 33, 203 (1989)
- [13] M. Takahashi, M. Ookuko, H. Takenaka: Polym. J. 23, 1009 (1991)
- [14] S. A. Rodger, S. A. Brooks, W. Sinclair, G. W. Groves, D. D. Double: J. Mater. Sci. 20, 2853 (1985)
- [15] K. M. Atkins, R. N. Edmonds, A. J. Majumdar: J. Mater. Sci. 26, 2372 (1991)
- [16] D. M. Roy: Mat. Res. Soc. Symp. Proc. 13, 213 (1989)
- [17] W. Ma, P. W. Brown: Proc. 9th Int. Congress on Cement Chemistry, vol IV., 424 (New Delhi 1992)

Submitted in English by the authors

CHEMICKÉ INTERAKČIE, POROZITA A PEVNOSŤ NIEKOTRYCH MÔDELOV MDF MATERIÁLOV

MILAN DRÁBIK¹, ĽUBICA GÁLIKOVÁ¹, IVAN ODLER²

¹ Ústav anorganickej chemie SAV, 842 36 Bratislava, SR

² Institut für Nichtmetallische Werkstoffe TU Clausthal, 3392 Clausthal-Zellerfeld, SRN

We anticipate to perform the designed research jointly by our groups and Materials Chemistry Group of the Chemistry Dept. University Exeter, U.K. The joint research project would up-to-date our knowledge and specify if and how is the chemical hypothesis of MDF's generally valid (as for aluminous cement so for sulphoclinkers with polyphosphates, MDF processability of the latter not being studied till now). Moreover, at least the qualitative existence of close pores will be treated.

REFERENCES

- [1] J. D. Birchall, A. J. Howard, K. Kendal, J. H. Raistrick: Eur. Pat. Specs. No. 0055035 B1 and related
- [2] S. R. Tai, A. J. Howard, J. D. Birchall: Phil. Trans. R. Soc. London A 322, 479 (1987)
- [3] S. P. Shah, J. F. Young: Ceramic Bulletin 69, 1319 (1990)

Popri štúdiu spracovateľnosti nových systémov metódou MDF existuje v súčasnosti silná potreba experimentálne overiť význam a úlohu chemickej hypotézy o vzniku a vlastnostiach MDF materiálov. Pokúsili sme sa ukázať, že MDF materiály sú multifázové systémy obsahujúce zložky s rôznym chemickým pozadím; a to minerály cementového slínku a produkty jeho interakcie s vodou, vodorozpustné uhlíkaté polyméry spontánne tuhnuce v zásaditom prostredí, ako aj zóny vykazujúce produkty interakcie uvedených zložiek. Lokalizácia a spôsob sieťovania atómov v zónach sú načrtnuté na obr. 1. Rozsah spomenutých interakcií podmieňuje "MDF vlastnosti", čo predložená práca ilustruje hodnotami porozimetrických charakteristík a pevností v študovaných systémoch (obr. 2).

Diskusia poukazuje vo svojom závere na podobnosť úlohy sieťovania v MDF materiáloch s vystužovacím efektom whiskerov v keramických materiáloch. Význam štúdia zjednodušených modelov je nesporný, ak sa má dosiahnuť pokrok v pochopení chemizmu MDF materiálov, ale

aj vo výbere nových systémov, ktorých spracovateľnosť metódou MDF bude analyzovaná v budúcnosti.

Práca je jedným z výstupov projektu č. 85/92 Grantovej agentúry pre vedu v SR, časť výsledkov a námetov vznikla počas stáže (M.D. u I.O.) finične zabezpečenej nadáciou DAAD.

Skrátené značenie oxidov : C – CaO, A – Al₂O₃, S – SO₃, H – H₂O.

Obr. 1. Lokalizácia sietí (Al, Fe) – O – XR v zónach interakcií medzi fázou AFm [12] a reťazcami hpmc [13].

Obr. 2. Hodnoty pevností ($/N \cdot mm^{-2}$) a porozimetrických parametrov (porozita / % , obsah pórov s polomerom $< 100 \text{ nm} / \%$, median M / nm) v študovaných systémoch; 1: Secar 71 + pva, 2: Secar 71 + pva + poly-P, 3: Secar 71 + hpmc, 4: C₄AF + C₄A₃S + pva, 5: C₄AF + C₄A₃S + hpmc, 6: C₄AF + C₄A₃S + hpmc + poly-P.

Conference

THE WORLD CERAMIC CONGRESS, FLORENCE '94.

There was the 8-th CIMTECH- World Ceramic Congress held in Florence, Italy from June 28 to July 5, 1994. Congress took place under the endorsement of 44 national and international (resp. EC) ceramic, materials, engineering and physical societies, industrial companies and technical universities as well. The oral and poster sessions took place within the buildings of the Palace of the Florence Congress Centre, seat of the 8-th Cimtech, within the Palazzo dei Congressi and Palazzo degli Affari. The Palace is very appropriate place for the congress of such high level.

More than 2.5 thousands guests from more than 40 countries of the world participated on the Congress. After the opening meeting on Wednesday the plenary session (on Saturday afternoon) took place, and the programme ran parallelly in cca 10 individual sections on other days incl. Sunday. The presentations of the specialized literature publishers and various ceramics producers, and the exhibiton "Ceramics and cultural heritage" were the concomitant events of the Congress. International Symposia "Ceramics in Architecture" and "The Ceramics Heritage" combined with 8 Topical Congress Symposia in the form of lectures nad poster presentations as well as The Forum on New Materials together with basic scitons: Classical Ceramics (10 sessions), Advanced Technical Ceramics (14 sessions) and Special Sessions were held at the same time. The programme itself comprised 36 session blocks combined with 4 poster presentations (each of them lasted two days), and cultural and social events in the most attractive Florencia historical buildings on evenings. The leading executive personality was P. Vincenziny (Italy) the chairman of the international congress committee and well-known as a editor of various proceedings and author of numerous papers in the field of materials science and research management. Together with J. Andriolo (European Federation of Advanced Ceramics Industry - Groupisol), E. Andrete (EC Commision for Brite-Euram II Programme), A. G. Arroyo (CEE, Dir. XII, Science, R&D, Brusel), G. Lanzavecchi (Ministry of University and Research, Italy), H. Hausner (TU Berlin, BRD), H. Yanagida (Universi-

ty of Tokyo, Japan), I. J. Polmear (Monash University, Melbourne, Australia), E. R. Martuscelli (NRC Napoli, Italy), L. D. Pye and R. M. Spriggs (both Alfred University, USA), they directed the Congress and gave lectures within the opening event and plenary session.

The Congress '94 featured four in depth and interdisciplinary sections covered a broad range of current topics in ceramic science and engineering including composites, superconductors, bioceramics etc.:

1. Traditional Ceramics; topics of individual sessions were following: bases for the processing; product development; raw materials; technology; refractory materials; standards and certifications; overview of the ceramic industry in various regions of the world.
2. Advanced Technical ceramic; theme basic research in ceramics; mechanical and thermal properties; wear, erosion and corrosion; electric properties; testing. Synthesis and characterization of powders; forming and relating processes: sintering and relating processes. SHS ceramics; composite; joining ceramics/ceramics and ceramics/metal. Surface modifications. Ceramics for mechanical and thermal application; ceramics for chemical application; ceramics for electrical, magnetic, optical and nuclear applications.
3. Forum on New Materials; prospects in Materials R&D; progress in materials synthesis; computational modeling of materials; structure and property insight; progress in materials technology; standards and markets for advanced ceramics.
4. Symposia; advances in inorganic films and coatings; new diamond and diamond-like films; superconductive materials and technologies; high performance materials in engine technologies; intelligent materials and systems; advanced materials in optics, electro-optics and communication technologies; materials in clinical applications.

Evening and even night sightseeings were parts of the Congress, too. Participants visited the famous Palazzo Vecchio, organ concert in monumental Basilica di Santa Croce, and the Santa Maria Novella Church. The Party was held at the large square arcade court of the Chostro Grande (Large Cloister). The performance and a reception was