

PROCESSING-MOISTURE RESISTANCE AND THERMAL ANALYSIS OF MACRO-DEFECT-FREE MATERIALS

S. C. Mojumdar^{*}

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravská Cesta 9, SK-842 36 Bratislava, Slovakia

Abstract

The system of sulfoaluminate ferrite belite (SAFB) clinkers premixed with Portland cement (PC) in mass ratio 85:15 in combination with hydroxypropylmethyl cellulose (HPMC) or polyphosphates (poly-P) was used for the syntheses of Macro-Defect-Free (MDF) materials. The subsequent moisture treatment and thermal stability of these MDF materials were investigated. The effect of individual humidity upon the evolution of mass is more intensive than the effects of composition of MDF materials or duration of the original MDF material synthesis. Detailed values of mass changes at 100% relative humidity (RH) and under ambient conditions are strongly affected by the nature of polymer used. A significant improvement of moisture resistance of MDF materials is achieved when the materials are dried after 24 h of finishing the pressure application. In the inter-phase section of MDF material samples, the content of $C-(A,F)-\bar{S}$ hydraulic phases, mainly tetracalcium aluminate ferrite monosulphate hydrate (AFm) decomposing by 250°C and CaCO_3 decomposing at 600–700°C increase after the moisture attack, while cross-links in AFm-like section with typical thermoanalytical traces in temperature region 250–550°C remain intact.**

Keywords: Al(Fe)–O–C(P) cross-links, MDF materials, thermal stability, moisture resistance

Introduction

The term ‘Macro-Defect-Free’ (MDF) refers to the absence of relatively large voids or defects that are normally present in conventional cement pastes because of entrapped air or inadequate mixing [1]. MDF materials display unique properties relative to traditional cement pastes. For example, their flexural strength is roughly 200 MPa as compared to 5–10 MPa for hardened PC pastes. MDF materials also have several other attractive features such as low fabrication temperature (<100°C), high toughness and good dielectric properties [2]. In an early patent in this field, Birchall *et al.* [3] outlined the use of aluminous, PC and sulfate clinkers, and a wide range of wa-

* E-mail: uachmoju@savba.sk, scmojumdar@hotmail.com

** The use of cement chemistry notation is as follows: C=CaO, A=Al₂O₃, F=Fe₂O₃, S= SiO₂, \bar{S} =SO₃, H=H₂O, \bar{C} =CO₂, AFm=C₄(A,F) \bar{S} H₁₂, w/s=water : solid mass ratio.

ter-soluble carbonaceous polymers. Drabik and co-workers have reported MDF materials processability of particular components/phases arising in potential sulfoaluminate ferrite belite (SAFB) clinkers, as well as the SAFB clinker itself, in combination with hydroxypropylmethyl cellulose (HPMC) and/or sodium polyphosphate (poly-P) [4–9]. Studies demonstrate the potential of low-energy clinkers and cements for the MDF material process. The results have pointed to (a) the involvement of Al, Fe, P and C atoms in Al(Fe)–O–C(P) cross-links within amorphous AFm-like reaction product/intergranular gel, (b) thermoanalytical characteristics of above mentioned cross-links, giving the temperature of decomposition from 250–450°C and (c) the influence of cross-link chemistry on porosity, electrical impedance as well as the moisture resistance.

The present work is focused on MDF material systems in SAFB clinkers with PC and HPMC or poly-P dried at 50°C immediately or after 24 h of finishing the pressure application (delayed dried). Blends of SAFB clinkers with PC exert upgraded properties against SAFB clinkers alone, i.e. setting times and mortar making technological procedures [10]. The aim of our study was to check the effects of PC in the raw mix and delayed drying on MDF material processes and also on subsequent moisture resistance and thermal stability.

Experimental

The process to obtain MDF materials was as follows:

- a) Initial dry premixing of SAFB clinker and PC was followed by either
- b) addition of HPMC or $\text{Na}_5\text{P}_3\text{O}_{10}$ (5% of total mass) and water to give $w/s=0.2$ or
- c) addition of an aqueous solution of sodium polyphosphate (poly-P) to incorporate 5% (by mass) of poly-P and give $w/s=0.2$ ('s' includes clinker and mass equivalent of the dissolved poly-P).
- d) Traces of glycerol were used as plastifier/processing agent.
- e) Twin-rolling was employed until the mixture reached the consistency of dense dough (up to 5 min),
- f) Static 5 MPa pressure in a pellet die (diameter 10 mm) was applied for intervals ranging from 0.5, 1, 3 and 5 h and
- g) Chemical reactions were completed by air drying at 50°C either immediately (x_{di}) or 24 h after finishing the pressure application (x_{dd}). HPMC (Aldrich) used corresponds to the viscosity of a 2% aqueous solution 80–120 cP. Sodium polyphosphates (Aldrich) were of formulae $(\text{NaPO}_3)_n$ and $\text{Na}_5\text{P}_3\text{O}_{10}$.

The moisture resistance of model MDF material samples was investigated at two different RHs. Cylindrical samples were kept in dessicators with controlled RH values, namely (a) above saturated $\text{NaHSO}_4(\text{aq})$ (52% RH) and (b) above deionized water (100% RH).

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were conducted from ambient temperature to 1000°C by using the T.A.I. SDT 2960

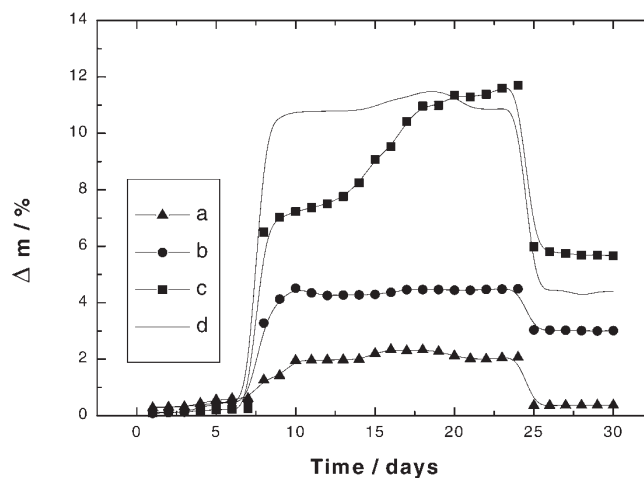


Fig. 1 Mass change Δm as a function of time for delayed dried MDF material test pieces fabricated from mixture of SAFB clinkers and PC with a – dissolved poly-P-(NaPO_3)_n, b – powdered poly-P- $\text{Na}_5\text{P}_3\text{O}_{10}$, c – HPMC and d – HPMC without PC, and treated at 52% RH (until the 8 day), at 100% RH (from the 9 to 21 day) and under the ambient conditions (from the 22 to the 30 day)

instrument (sample mass 10–20 mg (recommended by TA Instruments, Inc.), heating rate $10^\circ\text{C min}^{-1}$, in flowing air). Thermoanalytical studies were made on powders of two series of MDF material samples (as synthesized and after the moisture attack and re-equilibration under ambient conditions).

Results and discussion

Mass changes as the measure of the moisture resistance of MDF materials

The mass changes as the function of duration of the exposure in the environments with given RHs are displayed in Fig. 1. These, as the measure of the moisture resistance, give a powerful tool for an effective check of the attack of various levels of humidities on a variety of MDF material relevant compositions [5–7]. The evolution of mass (Fig. 1) to the equilibrium values enlarge the information about the effects of various levels of humidity as well as composition upon the moisture resistance of MDF materials. The equilibrium is achieved in any of the studied humidities within 8 to 13 days, it is in accordance with data about MDF materials where cementitious phase is exclusively SAFB clinkers [5–7, 9, 13]. The effect of individual humidity upon the evolution of mass is more intensive than the effects of composition of MDF materials or duration of the original MDF material synthesis. However, detailed values at 100% RH and re-equilibrated at ambient conditions are strongly affected by the nature of polymer, in both in SAFB clinker-based MDF materials [7, 9, 13] and in MDF materials, based on blends of SAFB clinkers and PC. The most important im-

provement of moisture resistance of MDF materials is achieved in probes containing poly-P and delayed dried (Fig. 1, curve a).

The results are discussed in details as follows:

- a) the effect of 52% RH and
- b) the effect of 100% RH, the latter being subdivided into irreversible change (the residual mass after decrease under ambient conditions) and reversible change (difference of the mass at 100% RH and the residual mass). The results show nearly negligible mass change of studied MDF material probes at 52% RH. An equilibrium mass increase after the treatment at 100% RH strongly depends on the nature of polymer, $\Delta m(\text{HPMC}) > \Delta m(\text{poly-P})$ and on drying, $\Delta m_{(\text{di})} > \Delta m_{(\text{dd})}$.

Thermoanalytical identification of the environmental deterioration in moist atmosphere

Data relating to the whole range of the studied compositions during thermal treatment are presented in Table 1. The effects of polymer used in the original synthesis upon the TG curves of moist attacked probes (Fig. 2) remain the same as we discussed earlier [9]. Individual sequences, as well as total mass changes (15–17.5% if poly-P is present vs. 23–26% if HPMC is present, cf. Fig. 2) for MDF materials attacked by extreme moisture do support the hypothesis about the impregnation/barrier effect of poly-P. Thus, presence of poly-P minimizes the scope of irreversible mass as well as phase changes due to the moisture uptake of MDF materials of SAFB clinkers, PC and HPMC or poly-P at 100% RH.

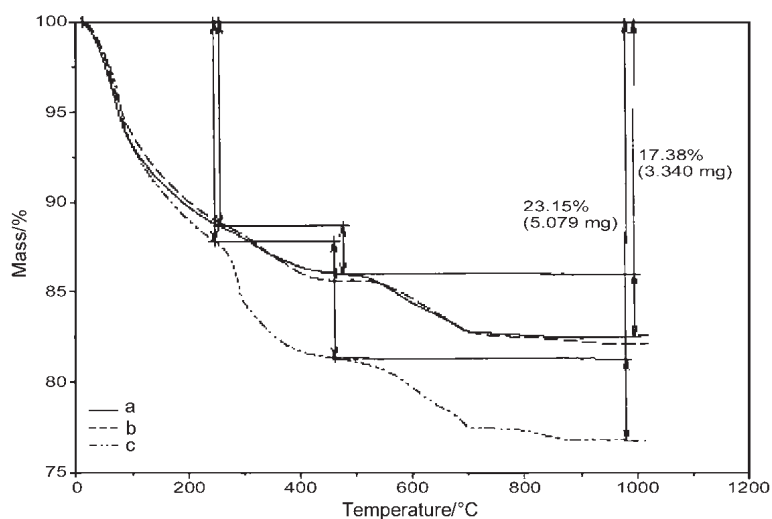


Fig. 2 Effect of polymer identity on TG steps during heating of the model MDF materials irreversibly attacked in the environment with 100% RH. Polymer additions are a – dissolved poly-P-(NaPO_3)_n, b – powdered poly-P- $\text{Na}_5\text{P}_3\text{O}_{10}$ and c – HPMC

Table 1 Summary of indicative TG intervals (°C) and DTA peak temperatures (°C) of MDF material samples based on SAFB clinkers and Portland cement

Polymer additives	MDF probes			
	As synthesized		After irreversible attack at 10% RH	
	TG	DTA	TG	DTA
HPMC	20–250	180–190	20–250	90
	250–550*	280–300*	250–400*	290–300*
	550–700 (CH)		500–700 (CH) (CC ⁻)	680 (CC ⁻)
poly-P	20–250	180–190	20–250	60–80
	250–550*	300–320*	250–450*	310–320*
	550–700* (CH)		500–720* (CH) _x (CC ⁻)	670–680 (CC ⁻)

Indicative thermal events: * – decomposition of cross-linked section of MDF materials.
 CH – decomposition of Ca(OH)₂, CC⁻ – decomposition of CaCO₃.
 The values in presence of poly-P ((NaPO₃)_n or Na₅P₃O₁₀) are almost identical.

Thermoanalytical treatment supports the differences of attacked and non-attacked MDF material probes (Table 1, Figs 3 and 4). The temperature intervals of thermal events (TG as well as DTA curves) are similar to that reported for MDF materials in system of SAFB clinkers and HPMC or poly-P [9, 13]. Totally, three distinct temperature regions in the thermoanalytical traces of both series of MDF materials (as synthesized and re-equilibrated after the moisture attack) are seen:

i) Upto 250°C – temperature region of ‘classical’ AFm hydrate decomposition [14, 15], where TG curves exert in moisture attacked probes by 1.5–7% higher mass loss (depending on the nature of polymer and delayed dried condition). It clearly displays an increase of the content of ‘classical’ cement hydrates. They arise due to the

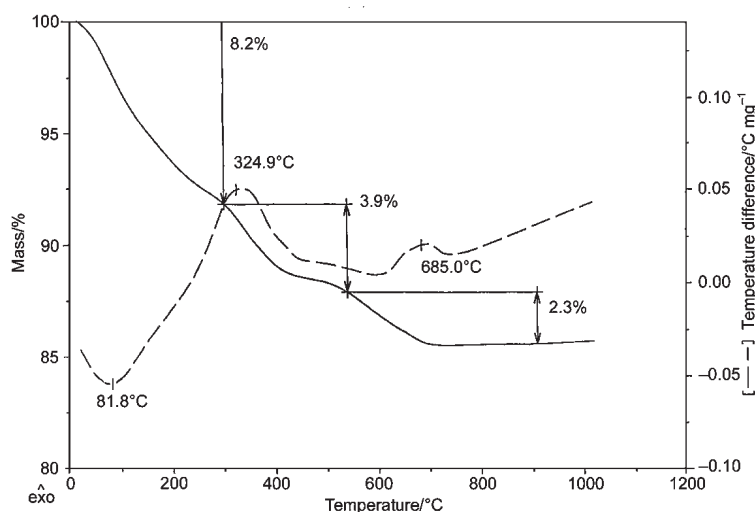


Fig. 3 Thermoanalytical curves of the delayed dried MDF materials. The sample was synthesized from mixture of SAFB clinkers and PC with powdered poly-P (Na₅P₃O₁₀)

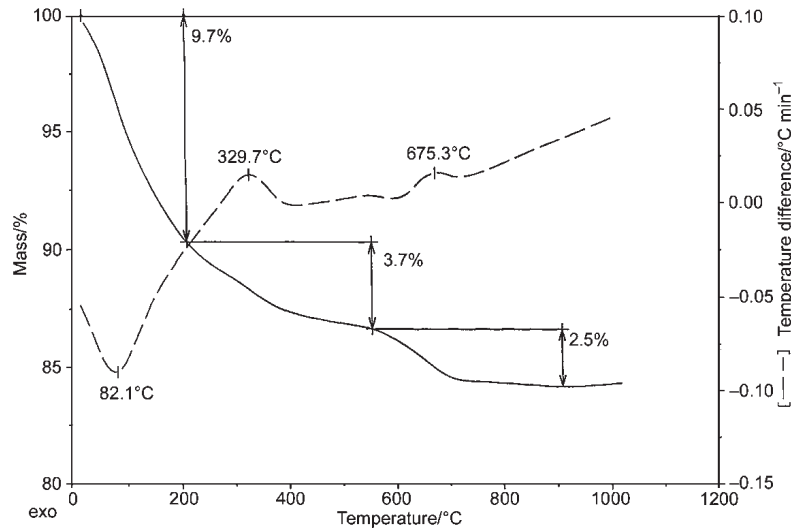


Fig. 4 Thermoanalytical curves of the delayed dried MDF materials. The sample was synthesized from mixture of SAFB clinkers and PC with powdered poly-P ($\text{Na}_5\text{P}_3\text{O}_{10}$) and irreversibly attacked by extreme levels of moisture (100% RH for 13 days and ambient conditions for additional 8 days)

moisture attack of clinker grains converted only partly in original MDF material samples [7, 9].

ii) 250–550°C – temperature region of cross-links decomposition [7, 9, 13]. Closely identical TG and DTA characteristics in both series of MDF materials confirm that the clusters of $\text{Al}(\text{Fe})\text{--O--C}(\text{P})$ cross-links appear unaffected by the moisture under test conditions. Thus, if PC properly mixed with SAFB clinkers, does not affect the moisture resistance of AFm-like cross-linked section of MDF materials and the impregnation / barrier effect [5, 9] of $\text{Al}(\text{Fe})\text{--O--P}$ cross-links remains conserved.

iii) Above 600°C – temperature region of carbonates decomposition [14–16], seen in the moisture attacked probes only as the additional mass loss, 0.5–4%, with maximum of typical DTA effect at 670–680°C. TG and DTA characteristics in this temperature region provide an evidence that the other crucial phase change of MDF material probes in the moist environment is the carbonation. Generally, cement-based materials with inter-phase region containing portlandite, free lime and/or partly converted clinker grains suffer frequently for this type of phase change [14, 15].

Conclusions

1. The scope of moisture attack on MDF materials, synthesized from the blends of SAFB clinkers, PC and HPMC or poly-P has been quantified using the values of mass changes as the measure of the moisture resistance. The method was proved as a powerful tool for an effective check of moisture attack on various MDF materials.

2. The effect of individual humidity upon the evolution of mass is more intensive than the effects of composition of MDF materials or duration of the original MDF material synthesis. However, detailed values of mass change at 100% RH are strongly affected by the nature of polymer, where irreversible portion ranges from 0.5 to 10% of mass gain. The lowest values correspond to the delayed dried MDF materials with poly-P.
3. The thermoanalytical data showed that Al(Fe)-O-C(P) cross-links in AFm-like region remain intact in the moist environment of either ambient or extreme levels of humidity.

* * *

The author would like thank the Slovak Grant Agency for Science for the financial support of the project (VEGA 6039).

References

- 1 J. A. Lewis and P. G. Desai, Proc. of MAETA Workshop on High Flexural Polymer-Cement Composite, Sakata 1996, p. 49.
- 2 K. Kendal, A. J. Howard and J. D. Birchall, Philos. Trans. R. Soc. London, A310 (1983) 139.
- 3 J. D. Birchall, A. J. Howard, K. Kendal and J. H. Raistrick, European Pat. Spec., B1 (1988) No. 0055035.
- 4 M. Drabik, L. Galikova, Z. Sadleikova and M. Kubranova, J. Therm. Anal. Cal., 46 (1996) 479.
- 5 M. Drabik, L. Galikova, G. B. Hix, A. G. Pearce, R. C. T. Slade and K. E. Young, Ce. Concr. Res., 27 (1997) 127.
- 6 M. Drabik, P. Zimmermann and R. C. T. Slade, Advances in Cement Research, 10 (1998) 129.
- 7 M. Drabik, L. Galikova, M. Kubranova and R. C. T. Slade, J. Mater. Chem., 4 (1994) 265.
- 8 M. Drabik and R. C. T. Slade, British Ceramic Transactions, 94 (1995) 242.
- 9 M. Drabik, L. Galikova and P. Zimmermann, J. Therm. Anal. Cal., 56 (1999) 117.
- 10 I. Janotka and L. Krajci, Advances in Cement Research, 11 (1999) 35.
- 11 T. Palou and J. Majling, Silikaty – Ceramics, 39 (1995) 41.
- 12 E. Dan and D. Popescu in Novel Low-Energy Cements Based on Belite, R&D EC Project (CIPA CT 94-0105), Ed.: J. H. Sharp, Sheffield 1996.
- 13 M. Drabik, L. Galikova, F. Hanic and J. H. Sharp, Chem. Papers, 51 (1997) 363.
- 14 F. W. Taylor, Cement Chemistry, 2nd Edn., Thomas Telford Publ., London 1998.
- 15 Lea's Chemistry of Cement & Concrete (Ed. P. C. Hewlett), 4th Edn., Edw. Arnold Publ., London 1998.
- 16 C. A. Strydom and J. H. Potgieter, Proceedings of 10th International Congress on the Chemistry of Cement (Ed. H. Justnes), Gothenburg 1997, p. 2ii049.