

SOL-GEL SYNTHESIS OF WHITE MINERAL TRIOXIDE AGGREGATE WITH POTENTIAL USE AS BIOCEMENT

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White mineral trioxide aggregate (WMTA) for dental applications was synthesised by sol-gel route due to the advantages of this method as compared with the conventional one i.e. lower thermal treatment temperatures and higher purity of the product. Tetraethyl-orthosilicate ($C_6H_{16}O_3Si$ - TEOS) and soluble salts i.e. $Ca(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as precursors for WMTA synthesis. The material was obtained by a single step thermal treatment at 1200°C and 1350°C, for 30 minutes. Thermal analysis (DTA/TG/DTG), X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to investigate the WMTA synthesis. The biocompatibility was assessed in vitro, by soaking of WMTA powder in simulated body fluid (SBF) for 14 days. The XRD results indicated that one of the main mineralogical phases formed was hydroxyapatite, compound with good bioactivity.

(Received July 24, 2012; Accepted October 19, 2012)

Keywords: White mineral trioxide aggregate, Biocement, Sol-gel synthesis, In-vitro test

1. Introduction

Mineral trioxide aggregate (MTA) is a new cement used in endodontology as a root-end filling material [1-7]. MTA has a mineralogical composition similar with the one of portland clinker (PC), both materials being manufactured from similar raw materials [3-7].

The white MTA (WMTA) consists of three main mineralogical phases: $3CaO \cdot SiO_2$ (C_3S), $2CaO \cdot SiO_2$ (C_2S) and $3CaO \cdot Al_2O_3$ (C_3A) [3, 4]. The silicates are responsible for development of mechanical strength, while the aluminate compound is mainly responsible for cement setting [8, 9].

The conventional preparation of pure cement phases i.e. C_3S , C_2S and C_3A , is performed through solid-state reactions and involves the sintering of stoichiometric mixtures of oxides or carbonates at high temperatures for prolonged time [8, 9]. Therefore in this study a sol-gel method was used to synthesize WMTA. The main advantages of this synthesis route (as compared with the conventional one) are lower thermal treatment temperatures and higher purity of the product [10-13].

In order to assess the biocompatibility of synthesized WMTA, an in-vitro study was performed; WMTA powder was soaked in simulated body fluid (SBF) and kept at 37°C for 14 days and the newly formed mineralogical phases were assessed by X-ray diffraction analysis.

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2. Experimental

2.1. Sol-gel synthesis of WMTA

The raw materials were calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.0\%$, Reag. ACS., Sigma-Aldrich, Germany), aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98.5\%$, Reag. ACS, Sigma-Aldrich, Germany) and tetraethyl-orthosilicate ($\text{C}_6\text{H}_{16}\text{O}_3\text{Si}$, 99.0%, Reag. ACS., Sigma-Aldrich, Germany-TEOS). These materials were dosed in order to obtain a stoichiometric mixture corresponding to the following composition - 70% C_3S , 24% C_2S and 6% C_3A . The corresponding oxide composition is 70.95% CaO , 26.78% SiO_2 and 2.27% Al_2O_3 .

The main steps of the WMTA processing route are presented in fig.1. The calcium nitrate, followed by aluminium nitrate, were dissolved in 180 ml water, under magnetically stirring, until a clear solution was obtained. TEOS was hydrolysed - molar ratio TEOS: water was 1:4. The clear solution was continuously stirred at 60°C for 4 hours, than kept the next 96 hours at 70°C , to facilitate the water evaporation and to accelerate the polycondensation reaction, resulting in the formation of a viscous gel. This gel was then dried at 120°C for 420 hours and the final product was a white powder.

The powder was pressed in pellets and thermally treated at 1200°C or 1350°C , for 30 minutes. Rapid cooling of the thermally treated material was performed in air. The WMTA obtained by thermal treatment at 1350°C for 30 minutes was grinded for two hours into a laboratory planetary mill ($v=150$ rot/min) up to a fineness corresponding to $1.51 \text{ m}^2/\text{g}$ specific surface area assessed by laser granulometry by means of a Malvern Mastersizer 2000 laser granulometer.

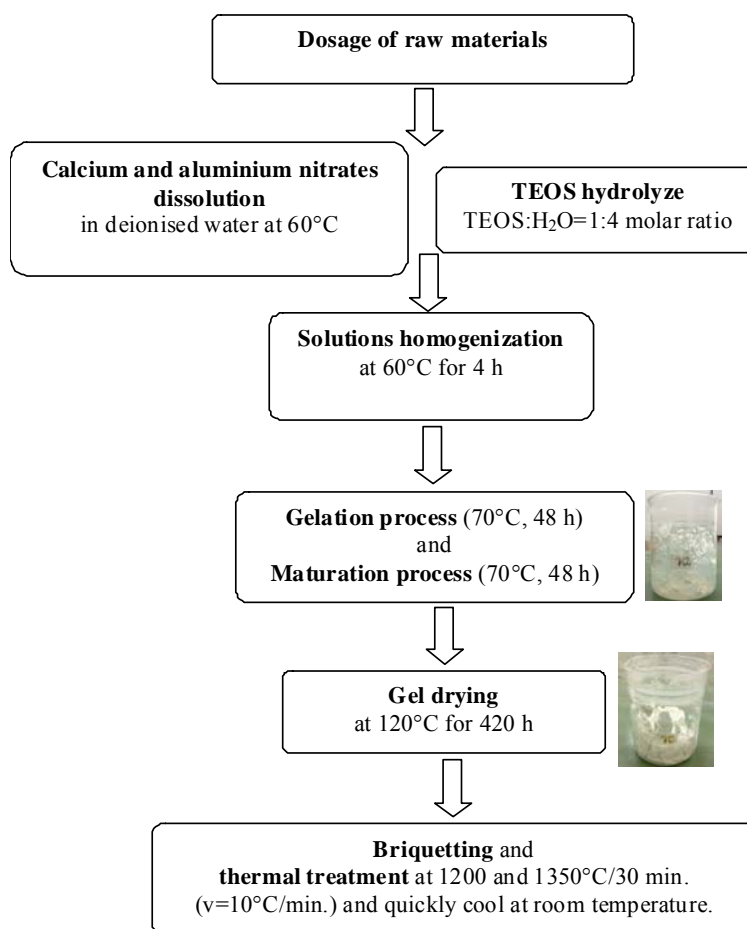


Fig. 1 Main steps of WMTA synthesis by sol-gel method

2.2. WMTA characterization

The white powder resulted by gel drying, was analysed by thermal analysis (DTA/TG/DTG) and by X-ray diffraction analysis (XRD). Thermal analysis (DTA/TG/DTG) was performed using a Shimadzu DTG-TA-60, in the 20-1000°C temperature range, with a heating rate of 10°C/min, in air. X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer, with Ni-filtered CuK α radiation ($\lambda=1.5406$ Å), with scan step of 0.02° and counting time of 0.6 s/step.

The free lime (CaO_{free}) content of WMTA thermally treated at different temperatures was assessed by titration of calcium (II) with 0.1 N hydrochloric acid solution, as prescribed in the European and corresponding national norm - SR EN 196-2:2006 [14].

The mineralogical composition of WMTA obtained by thermal treatment at 1200°C and 1350°C, was assessed by XRD. The morphology was investigated by scanning electron microscopy (SEM) using a HITACHI S2600N equipment. The specimens for SEM analysis were covered with a thin silver layer deposited by dc-sputtering.

The simulated body fluid (SBF) had a similar composition with human blood plasma (table 1).

Table 1 Composition of SBF.

Ionic concentration (mM)								Buffer	pH
Solution	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻		
SBF	142	5	1.5	2.5	148.8	4.2	1	7.25	

The WMTA, obtained by thermal treatment at 1300°C, was soaked in SBF solution (solid/liquid ratio of 0.5 mg/ml) and kept for 14 days at 37°C (in a water bath), without SBF refreshing. After 14 days the powder was filtrated, washed with ethanol and dried at 40°C for 24 h. After drying, the powder was analysed by XRD and Fourier transform infrared spectroscopy (FTIR). FTIR spectra in the range of 400-4000 cm⁻¹ wave number were recorded on a Shimadzu FTIR 8601PC spectrometer, using KBr pellets.

3. Results and discussion

Fig. 2 shows the DTA, TG and DTG curves of the white powder resulted by gel drying. The total weight loss recorded up to 1000°C was 84.04% (w/w). The DTA curve shows the presence of endothermic effects and the DTG-TG curves revealed four effects and corresponding mass losses:

- the effect with maximum at 331°C and corresponding mass loss of 45.61% is due to aluminium and calcium nitrates dehydration and decomposition [15, 16];
- the large effect with maximum at 497°C is due to the water loss from portlandite (calcium hydroxide) [17]; the corresponding mass loss for this effects is 19.18%; the “shoulder” from 551°C is due to the anhydrous Ca(NO₃)₂ melting [15, 16], the mass loss recorded between 535-600°C was 11.80%;
- the effect from 843°C corresponding to a weight loss of 1.77% is attributed to the decomposition of calcium carbonate, accidental formed by partial carbonation of portlandite [17].

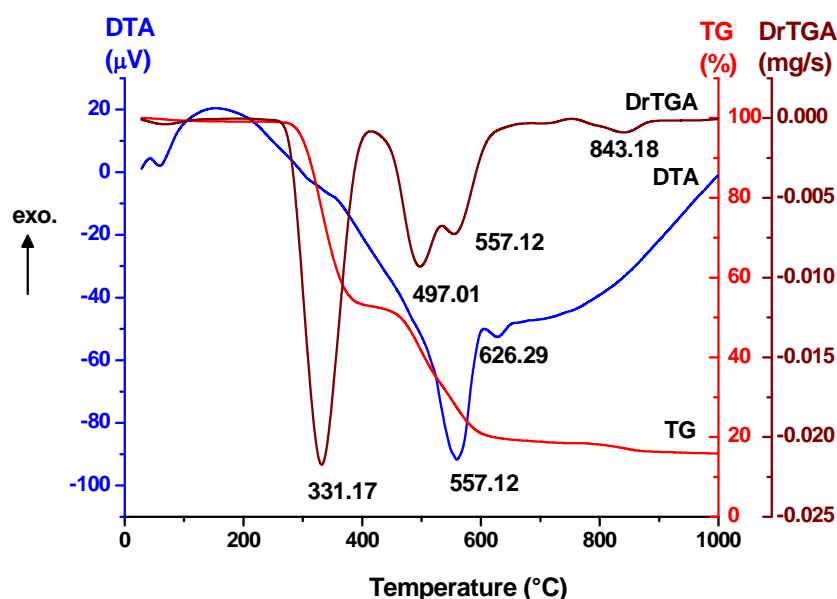


Fig. 2. The DTA, TG and DTG curves of dried gel.

Fig. 3 presents the XRD pattern of the white powder obtained by gel drying. The crystalline phases assessed by this method are calcium nitrate - anhydrous (JCPDS [07-0204]) and dihydrate (JCPDS [27-0087]). The presence of calcium nitrates in this material is mainly due to the partial re-precipitation from solution.

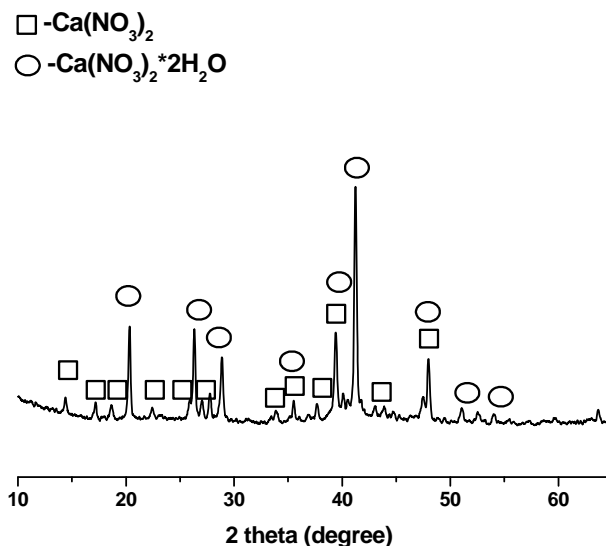


Fig. 3 The XRD pattern of the white powder resulted by gel drying.

The XRD analysis of WMTA obtained by thermal treatment at 1200°C and 1350°C (fig.4) shows the presence of three mineralogical phases i.e. dicalcium silicate (C_2S , JCPDS [20-0237]), tricalcium silicate (C_3S , JCPDS [42-0551]) and tricalcium aluminate (C_3A , JCPDS [32-0150]). The height of tricalcium silicate peaks increases with the increase of thermal treatment temperature suggesting the increase of this compound amount and/or crystallinity degree.

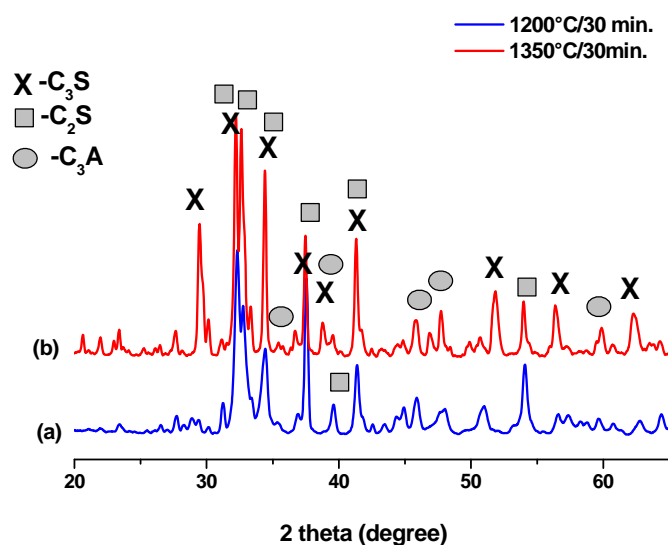


Fig. 3 The XRD patterns of the obtained clinkers at:
 a- 1200°C/30 min. and b- 1350°C/30 min.

The free lime (CaO_{free}) values assessed on WMTA masses obtained by thermal treatment at 1200°C and 1350°C are presented in table 2. As it can be seen for both studied thermal treatments the free lime values are below the 2% limit. Higher values of free lime can have a detrimental effect on the compressive strength values [18].

Table 2. Free lime content of WMTA masses.

Temperature/time of thermal treatment	1200°C/30 min.	1350°C/30 min.
CaO_{free} (%)	1.58	1.05

The microstructure of WMTA masses is presented in fig. 5. For the specimens obtained by thermal treatment at a lower temperature (1200°C) agglomerations of small crystals (1-2 μm) are present on the SEM micrographs (fig. 5a,b). In the micrograph presented in fig. 5b can be observed also calcium hydroxide crystals with their specific shape of “cauliflower” (see arrows) [19]. The increase of thermal treatment temperature at 1350°C, leads to the formation of polyhedral shape alite crystals with average size of 6-8 μm (see arrows, fig.5 c,d).

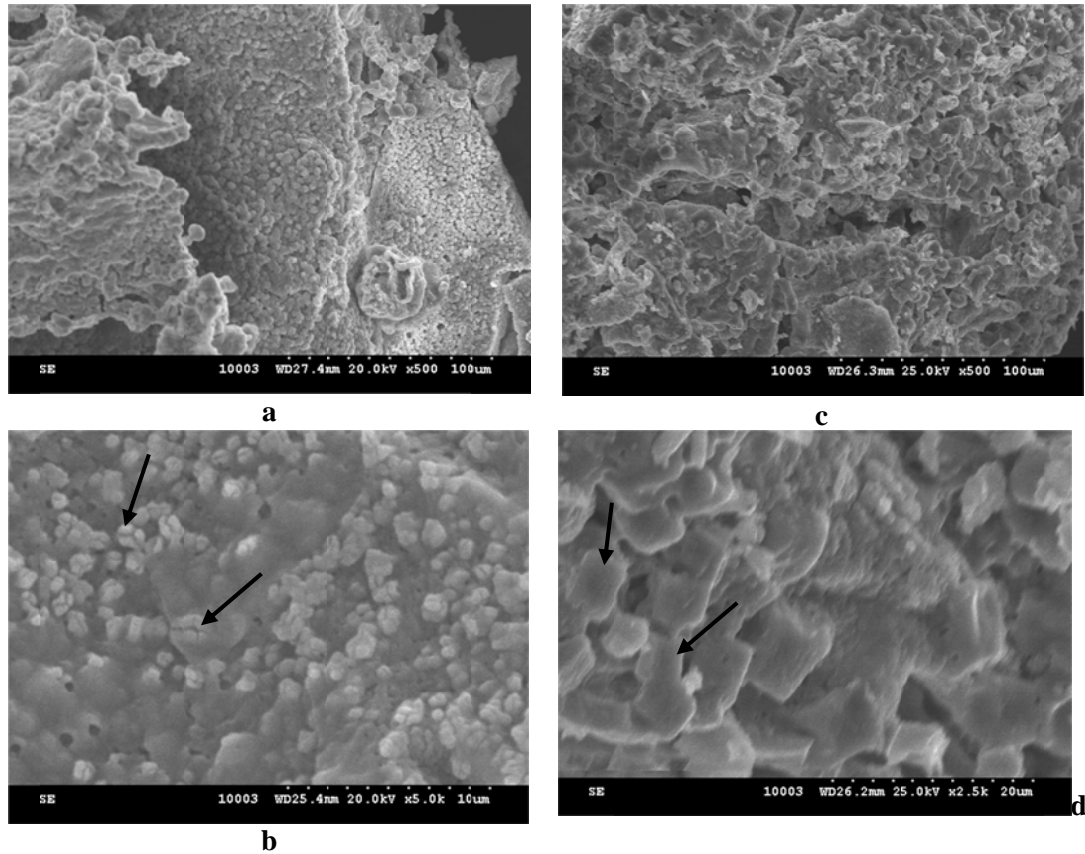


Fig. 5 SEM images for clinkers obtained at 1200°C/30 min. (a,b) and 1350°C/30 min. (c,d).

In order to assess the biocompatibility of the WMTA obtained by thermal treatment at 1350°C, an in vitro test was performed: the powder was soaked in SBF for 14 days at 37°C and then analysed by XRD. The XRD pattern is presented in fig. 6 and shows the presence of the following mineral phases: hydroxyapatite (JCPDS [84-198]; JCPDS [76-0694]), calcium hydroxide (JCPDS [84-1264]), calcium silicates hydrates (JCPDS [33-0306]) and calcium carbonate (JCPDS [05-0586]), last one formed by portlandite carbonation.

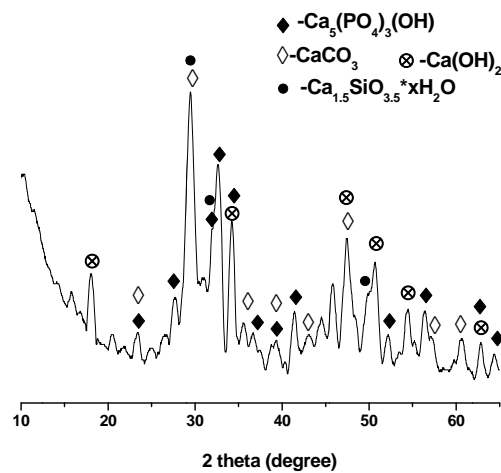


Fig.6 XRD patterns of WMTA powder soaked in SBF for 14 days.

The results of the FTIR analysis (Fig. 7) are in good agreement with those obtained by XRD. On the FTIR spectra are presents the specific bands of PO_4^{3-} - stretching and bending mode (461cm^{-1} ; 678cm^{-1} , 975cm^{-1}), and OH^- (678cm^{-1} ; 3559cm^{-1}) from hydroxyapatite [20, 21] and also CO_3^{2-} (1468cm^{-1}) band specific for carbonated hydroxyapatite [21]; the bands for SiO_4^{4-} (461cm^{-1} ; 522cm^{-1} ; 975cm^{-1}) and OH^- (3856cm^{-1} ; 3745cm^{-1} ; 2925cm^{-1} ; 2859cm^{-1}) specific for calcium silicates hydrates are also present on the FTIR spectrum [22-24]. The specific bands of CO_3^{2-} bond from CaCO_3 (1422cm^{-1} ; 1516cm^{-1} ; 870cm^{-1} [22-24]) were also identified.

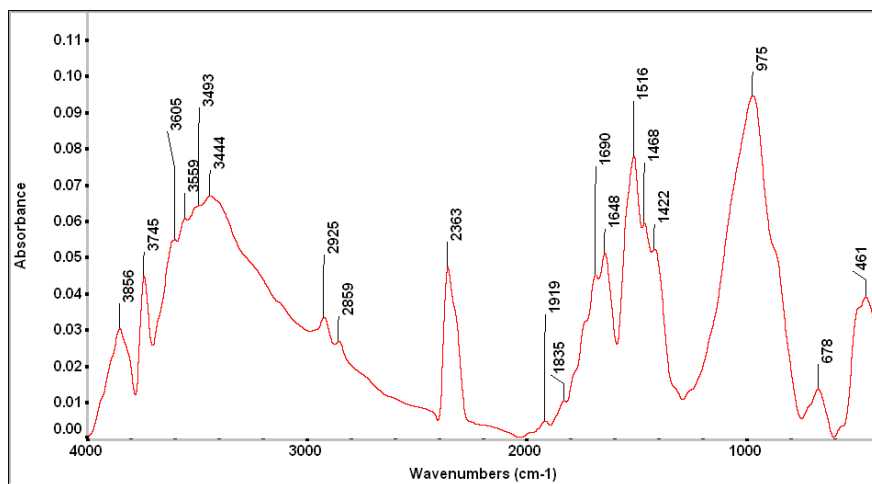


Fig. 7 FTIR spectrum of WMTA powder soaked in SBF for 14 days.

4. Conclusions

The results presented in this paper show that white mineral trioxide aggregate (WMTA) can be synthesized by sol-gel method. This route of processing permits the reduction of calcining temperature and thermal treatment time (as compared with the conventional route – solid state reactions) and the synthesis of a high purity material. The main mineralogical phases, present in WMTA obtained by thermal treatment at 1350°C for 30 minutes, are calcium silicates ($3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}_2$) and calcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$).

The soaking of WMTA powder in simulated body fluid (SBF) for 14 days at 37°C , leads to the formation of hydroxyapatite (along with other reaction products - calcium silicates hydrates, calcium hydroxide and calcium carbonate); the formation of hydroxyapatite gives a good biocompatibility of the synthesised WMTA.

Acknowledgements

This paper is supported by the Sectoral Operational Programme Human Resources Development, financed from the European Social Fund and by the Romanian Government under the contract number POSDRU/89/1.5/S/64109.

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