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DEVELOPMENT OF A MOLD FOR THERMOPLASTICS BASED ON A PHOSPHATE CEMENT

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ABSTRACT

In case of limited series or prototypes of thermoplastics, metallic molds are too expensive and time consuming to build. For that reason, a production strategy was developed to build a textile reinforced phosphate based cement mold with a thermal stability to at least 300°C. In this research, a composite mold is developed, based on glass fiber textile reinforced phosphate cement (TRC). This tooling system is combining the advantages of a thermoset mold with elevated temperature use. Since cement based molding systems contain water, major challenges are the reduction of porosity, the sealing of the surface and the limitation of the thermal shrinkage. The development of an isothermal curing method resulted in a more stable calcium phosphate cement, as confirmed by shrinkage measurements, X-ray Diffraction and Scanning Electron Microscopy. By adding fillers to the top coat, the surface permeability was decreased. The effects of thermal loading, composition of the matrix and the curing conditions were investigated by an experimental study including acoustic emission. To illustrate the potential of the proposed method, a thermoplastic prepreg was processed in both the conventional metal and the TRC equivalent. The proof of concept showed that a textile reinforced cement mold can be used to thermoform a thermoplastic prepreg to an acceptable part.

INTRODUCTION

This work presents an alternative tooling system based on a TRC. It is produced using calcium phosphate cement (Vubonite) [1]. Due to its structural water content, Vubonite will lose water when subjected to high temperatures, due to dehydration, which will result in mass loss and shrinkage, as mentioned in [2,3,4]. By using a textile, a controlled distribution and high fiber volume content can be obtained (vol. 20%), resulting in a high tensile strength and a very fine pattern of micron sized cracks. By using a reinforcement, the shrinkage will be restrained, resulting in cracks in the cement matrix. In the scope of the development of a textile-reinforced mold, restrained shrinkage is a major cause of concern because deformations and cracking due to this phenomenon can significantly affect the structural integrity, the surface state and the dimensional stability. Additionally a solution must be found to reduce the surface permeability. The success of tooling systems, based on TRC, depends on tackling these problems in combination with understanding the mechanical behavior of the TRC when exposed to elevated temperatures and the development of a simple and efficient production technique.

EXPERIMENTAL WORK

Different steps in the mold development will be discussed. Prior to mechanical study of the TRC, research was performed on increasing the stability of the calcium phosphate cement matrix when exposed to an elevated temperature (300°C). The composition of the cement matrix was modified to the specific needs to produce a TRC mold. Additionally a method based on a

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sealer was developed to reduce the surface permeability. Finally, a method is presented to produce a TRC mold, used to thermoform a thermoplastic prepreg.

Materials Used to Produce the TRC Mold

Matrix

The matrix used in this study was produced by mixing wollastonite (CaSiO_3) powder with a phosphoric acid based solution of metal oxides including a retarder (Vubonite liquid, supplied by Symbion, Belgium), as described in [1]. The mass ratio of liquid to powder was 1/0.8, which means that the molar ratio $\text{P}/\text{Ca} = r = 0.82$. The components were mixed using a Heidolph RZR 2102 overhead blade mixer. The mixing was performed in two stages starting at a speed of 500 rpm until homogenization, and continuing for another minute at 2000 rpm. Just after mixing, the fresh mixture is acidic ($\text{pH}=1$), resulting in a chemical attack of most types of metal. To avoid corrosion, the spindle and recipient of the mixer are made of stainless steel, while other production tools are in PVC. The mixture was left to rest for at least 30 s, in order to release the entrapped air, before casting.

Reference specimens are cured at room temperature (RT). To prevent important exothermic temperature peaks when cured at a more elevated temperature (40 and 60°C), specimens were cured between 15 mm thick preheated aluminum plates. This resulted in a nearly isothermal condition. The temperature was monitored with a TESTO 830T4 IR temperature scanner, revealing a variation of less than 1°C in the aluminum plates during the curing period.

Topcoat

A *thickener* is added to the wet Vubonite in order to modify the flow of the topcoat, so that it can cover and stick to an inclined surface, which is essential to develop a mold. A hydrophilic fumed silica type HL 200, supplied by Guangzhou GBS high-tech and industry [5], was used. Fumed silica will improve the lubrication of the Vubonite powder particles, being thousand times smaller. The high capillary forces are responsible for the thickening effect.

The permeability is reduced by using a *sealer*. In this case, the sealer is a powder, which can be mixed uniformly into the Vubonite paste. The heat resistant coating powder (PW), Alesta HR black matt “HR00044059021” was supplied by Dupont [6]. This coating is based on a silicone resin, which is developed to protect surfaces exposed to temperatures up to 550°C. The powder is a thermoset which will devitrify at about 200°C in order to form a heat resistant film. When the solidified Vubonite is heated, the powder becomes more liquid as the glass transition temperature (T_g) is exceeded and penetrates into the voids and cracks, reducing the surface permeability.

Reinforcement

The *E-glass fiber reinforcements* used in the composite molds are chopped glass fiber mats (CSM) with an aerial density of 300g/m² (type Vetrotex M5-300),[7].

Thermoplastic

To demonstrate the potential of the developed mold concept, a Twintex prepreg sheet [11] was used to be thermoformed. In this case a consolidated plate is used with a thickness of 2 mm, made from Twintex® commingled polypropylene and continuous glass fiber. The glass content is 60% by weight. The prepreg is thermoformed at 190°C and a pressure of 1.2 MPa.

Experimental techniques

Evolution of the reaction pH

The pH of the filtration water, recovered from washing the partially cured Vubonite specimens, was measured using a pHep 5 manufactured by Hanna instruments. This digital pH-measuring device with accuracy of 0.01 was cleaned with milli-Q water and calibrated with a pH 7 reference liquid before each measurement.

X-ray Diffraction (XRD)

X-ray diffractograms (XRD) of powdered samples of wollastonite and reaction products are registered on a Siemens D 5000 diffractometer, generating a Cu K α radiation with an applied voltage of 40 kV and a current of 40 mA

Shrinkage measurement using digital image correlation (DIC)

Digital image correlation (DIC) has major advantages compared to Thermo Mechanical Analysis (TMA) [8]: the method can be used on large specimens that are fabricated in realistic conditions, while the non-contact method can measure the full-field deformation at the surface of objects under mechanical or thermal loading. The experimental setup, shown in Figure 1, was designed to measure real time in-plane thermal deformations under thermal loading.

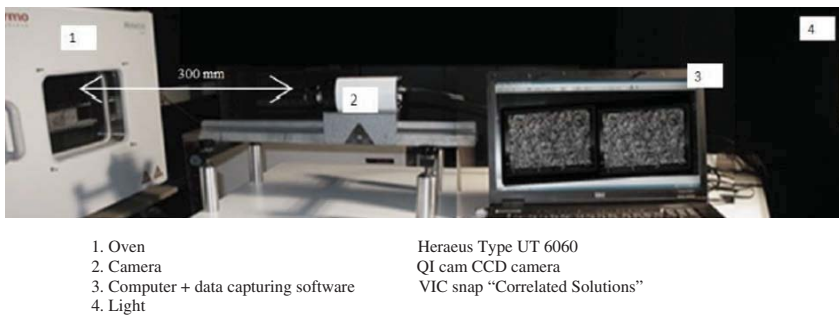


Figure 1. View of the digital image correlation (DIC) test setup.

The setup consists of an oven HERAEUS Type UT 6060 capable of heating the specimens up to 300°C, and a DIC capturing system. An electronic temperature control unit with an accuracy of 0.1°C for the interval 0-100°C and 1°C in the interval 100-300°C was applied to the oven. Because of the potential variation in thickness and refractive index, a quartz glass window was placed in the oven door. A QICAM 12-bit CCD camera was mounted on a sliding rail which is perpendicular to the specimen. A distance between camera lens and specimen of 300 mm was obtained. A Schneider compact VIS-NIR Xenoplan 1.4/23 lens was used.

Before placing the specimens in the oven, a heat resistant black paint speckle pattern was applied through a silkscreen print process. Each measuring cycle started with taking a reference image at RT using the image capturing software VIC snap supplied by Correlated Solutions Inc.. After taking the reference image, the temperature of the oven was increased to 100°C. Once this temperature reached, it was kept stable for 1 hour. During this period, every 5 min an image was made. The procedure was repeated for 200°C and 300°C. After heating, the specimen was cooled to RT using the same steps.

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The images were imported in the VIC2D software in order to correlate the undistorted and distorted images. After correlation, the linear deformation was computed at three different positions using a 20 mm virtual strain gauge.

Tensile testing

Stress-strain data were obtained from tests performed on five specimens, using a tensile testing machine (INSTRON 5885H) with a capacity of 100 kN. The rate of crosshead displacement was set to 1 mm/min. Strain was measured with a double averaging clip on extensometer with a gauge length of 50 mm.

RESULTS AND DISCUSSION

The evolution of the hardening reaction, depending on the different curing conditions described above, was studied by extracting samples at intervals of 1 hour. In order to stop the reaction, the sample was grinded and then washed with demineralized water. After washing, the samples were filtered using a Büchner funnel. Drying was performed by placing the samples in a vacuum oven. The experiment showed not only the relation between hardening, curing time and temperature but it also revealed a good correlation between the pH of the filtration water and the evolution of the heat flux obtained by Differential Scanning Calorimetry [3].

The effect of curing on the microstructure was studied using X-ray diffractometry on crushed samples. The XRD diffractograms for partially and fully cured specimens for the three curing temperatures are shown in Figure 2.

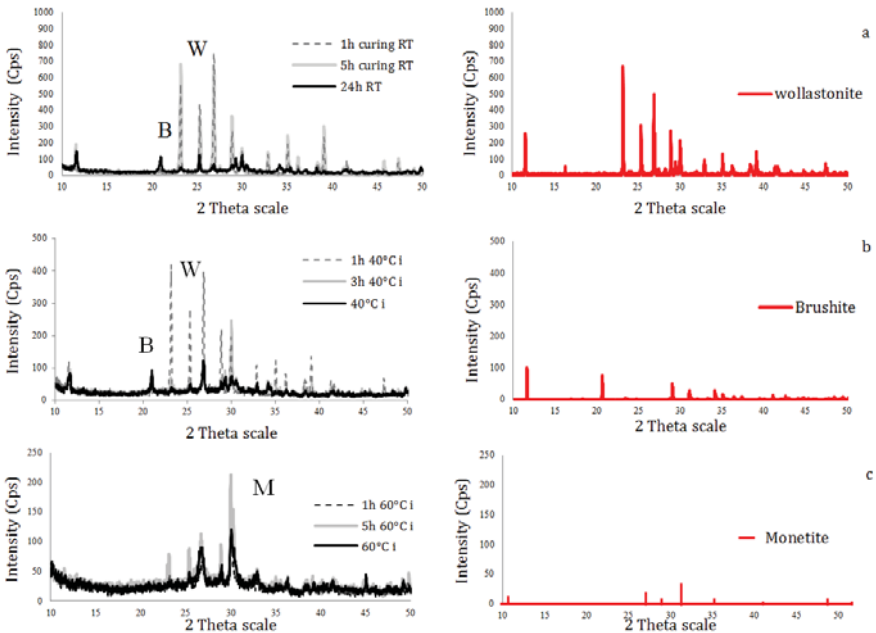


Figure 2. XRD diffractograms for partially and fully cured specimens for the three curing regimes, at the right hand side, reference diffractograms are given (<http://webmineral.com/data/>).

The RT curing led to non-solidified samples after 1 and 5 h. Their diffractograms showed a large similarity and indicated residual wollastonite, while after hardening (24 h) the wollastonite was converted into brushite (Figure 2a). Curing at 40°C for 3 h, resulted in hardening of the specimens. The diffractogram in Figure 2b showed that wollastonite (W) is converted after that curing time into brushite (B), according to Eq. (1) [2,3].

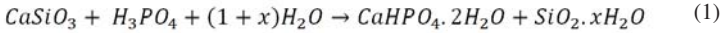
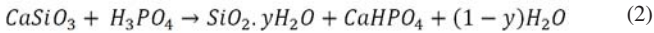


Figure 2c shows the formation of monetite (M) instead of brushite after 1h for the curing at 60°C. The reaction leading to monetite (CaHPO₄) is given in Eq. (2).



The XRD analysis indicates the presence of brushite as a reaction product for the curing at room temperature and at 40°C, while monetite is formed after a curing at 60°C, Figure 2. Increasing the curing temperature also shortens the time to solidify, from about 24 h at room temperature curing to less than 1 h at 60°C. The pH measurements of the filtration water indicate that hardening starts when the initial pH of three, immediately after mixing, has increased to five. The transition of wollastonite to brushite or monetite occurs at this pH value, as is confirmed by XRD and images obtained by SEM in combination with EDX [3].

For the design of a mold it is of utmost importance to know the shrinkage of the material resulting from the cure and from the drying. Further shrinkage takes place during the first heating to the molding temperature, which can be up to 300°C.

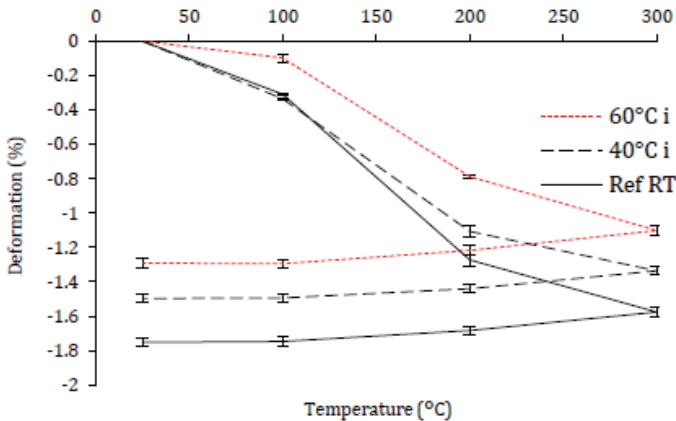


Figure 3. Average linear deformation during 1st heating and cooling cycle (RT - 300°C - RT) for different curing methods. As all specimen shrink only negative deformations are observed

The samples that were cured isothermally at 60°C, showed a significant reduction (25%) of the thermal shrinkage compared to samples cured at room temperature, figure 3. This difference is related to the direct formation of monetite at 60°C, which contains less water than

the brushite that is formed during curing at lower temperatures. Reduction of shrinkage and improving the thermal dimensional stability is only one of the challenges. In order to be useable, the viscosity needs to be adjusted so that the Vubonite can cover and stick on inclined surfaces, while surface permeability needs to be reduced. Adding hydrophilic fumed silica to the Vubonite liquid mixture with a weight ratio liquid to filler of 1/0.02 and a silicon resin based coating powder [6] with a weight ratio liquid to filler of 1/0.08, offers a solution for both the processing needs and the surface permeability. By adding these fillers, the matrix can be used as a topcoat to cover the inclined surfaces of the master mold.

It was demonstrated that curing at 60°C with controlled specimen temperature causes a reduction of composite stiffness by 20% compared to TRC specimens cured at room temperature, Figure 4. On the other hand, after exposing the specimens to 300°C, the stiffness of specimens cured at RT is reduced by 45%. The composite stiffness of specimens cured at 60°C, will be reduced by only 10% after the same heating. This lower degradation of the composite stiffness illustrates the increased thermal stability, due to the formation of more stable monetite when cured at 60°C. In this case, less restrained shrinkage will occur when exposing the specimens to 300°C. Thus, less matrix damage will be introduced, resulting in a lower reduction of the composite stiffness.

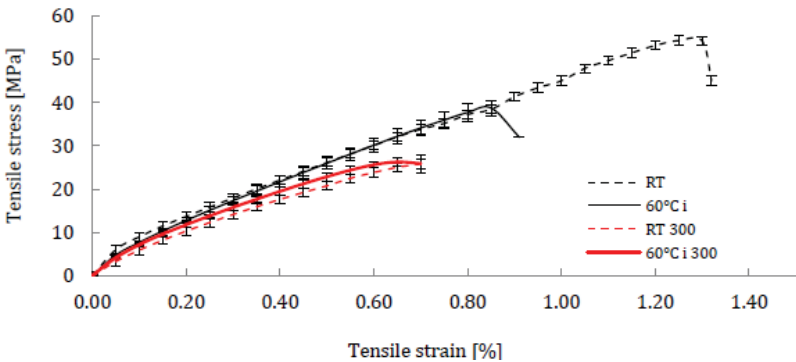


Figure 4. Comparison of tensile stress-strain curves cured at RT and 60°C

PROOF OF CONCEPT

To demonstrate the full potential of the TRC mold, a test was performed on an industrial press. The main steps to produce the female and male part of the matched die TRC mold will now be described.

A plastic tray was used as master model and placed in a wooden frame, Figure 5(a). The master model was covered with an adhesive wax. The wax was used to insure a smooth surface of the master mold, Figure 5(b).

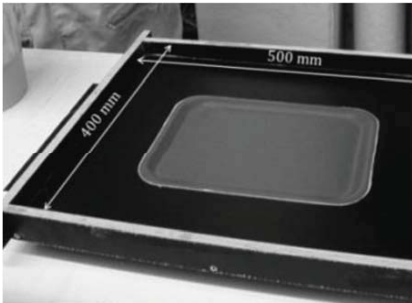


Figure 5(a). The master mold in wooden frame



Figure 5(b). Master model covered with wax sheet

The next step involves applying the topcoat, containing Alesta HR filler and fumed silica, with a brush to the waxed master model, Figure 6. A surfacing veil is used as first fiber layer to get a better surface quality (finishing) and to prevent the glass fibers of the next layers from penetrating through the matrix top surface, Figure 7(a). A water dissolvable veil binder is used (Owens Corning), solving molding problems in the corners. Another advantage of using a surface veil is a significant reduction of micro cracks when the composite is heated. In total two layers of surfacing veil are added and pressed in with a roller.



Figure 6. Workability of topcoat with AEROSIL and Dupont Alesta HR filler

The *textile reinforced cement* is a combination of Vubonite with addition of hydrophilic fumed silica [5] and an E-glass reinforcement.

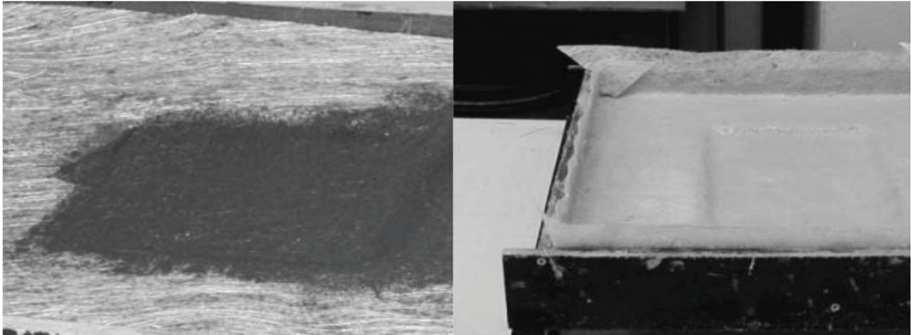


Figure 7(a). Impregnation of the CSM with topcoat.

Figure 7(b). Impregnation of the CSM with Vubonite matrix.

The E-glass fiber reinforcements used in the next six layers are chopped glass fiber mats (CSM) with a fiber density of 300g/m^2 , Figure 7(b). The average matrix consumption for each layer was 800g/m^2 . A standard hand lay-up method was used to apply the different layers. After laminating, the mold parts are cured isothermally at 60°C for 24h. Before using the mold it was preheated at 200°C for 4h. The two parts of the TRC mold are presented in Figure 8.



Figure 8. Matched die TRC mold

The TRC molds were mounted on 25 mm thick steel plates that could be attached to the press plates, figure 9. The Twintex prepreg sheets [9] were heated in an oven at 190°C for 10 minutes before placing the hot Twintex between the mold parts.



Figure 9. Mold placed in the industrial press

By using the industrial press, the Twintex sheet could be fully deformed to the desired shape, figure 10.

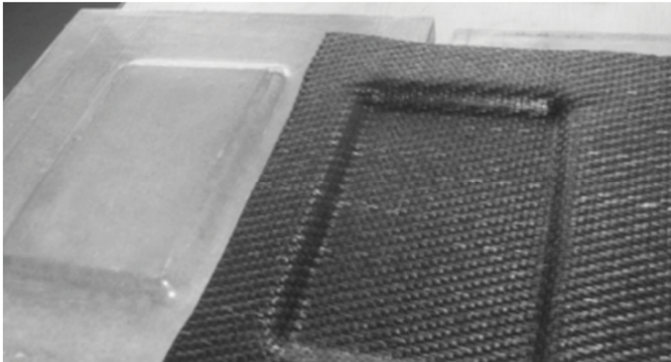


Figure 10. Thermoformed Twintex part.

CONCLUSIONS

The proposed curing at a controlled temperature of 60°C resulted in faster hardening into a more thermally stable calcium phosphate (monetite instead of brushite). This was confirmed by X-ray Diffraction (XRD) measurements. In the scope of this research, a non-contact method based on digital image correlation (DIC) was developed, indicating a significant reduction (25%) of the thermal shrinkage.

Adding hydrophilic fumed silica and a silicon resin-based coating powder to the Vubonite composition, provided a solution for both the thixotropic effect and for the reduced surface permeability. Curing at 60°C results in lower composite stiffness but also less mechanical degradation when exposed to an elevated temperature, compared to specimens cured

at room temperature. Thermoforming a prepreg with a TRC mold showed promising results, illustrating the potential of the method, even on a large scale using an industrial press.

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