BIO-BASED SILICON CARBIDE CERAMICS FROM EXTRUDED THERMOSET-BASED WOOD POLYMER COMPOSITES

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Abstract
This work investigates the preparation of silicon carbide ceramics (C/Si/SiC ceramics) from extruded thermoset-based wood polymer composites (WPC). The extruded WPC green bodies are carbonised forming open porous carbon templates (C-templates). These C-templates are converted by liquid silicon infiltration into bio-based C/Si/SiC ceramics. The materials over the whole process chain (WPC → C-template → C/Si/SiC ceramic) are characterised by density and porosity measurements, mechanical testing, light optical microscopy, scanning electron microscopy and X-ray computed tomography.

Extruded thermoset-based WPC can successfully be used for the production of C/Si/SiC ceramics. Different 3D geometries have been processed by profile extrusion. The main impact factor on the quality of the porous C-templates and subsequent C/Si/SiC ceramics is the distribution of the constituents as well as the density distribution in the green bodies. Variations in the composition of WPC, especially the thermoplastic content, allow adjusting the porosity of the C-templates formed after pyrolysis. From optimised WPC green bodies, C-templates without distortion (isotropic shrinkage) and homogeneous pore distribution and subsequent C/Si/SiC ceramics with SiC contents up to 90 vol% (95 wt%) could be produced.

1. Introduction

Silicon carbide (SiC) is one of the most important engineering ceramics for use at high temperatures under aggressive conditions. Fibre reinforcement of the monolithic ceramic results in high performance composite materials with increased impact resistance and damage tolerance. However, cost reduction is needed for a wider scope. One approach is the development of bio-based C/Si/SiC ceramics.

Natural fibre composites can serve as green bodies and be transformed by a carbonisation step into C-templates. In a further step, bio-based SiC ceramics are produced by liquid silicon infiltration of the porous C-templates. The use of thermoset bonded natural fibre boards (chipboards, MDF) as green bodies is sufficient for planar geometries [1-4]. 3D structures can only be produced by time-consuming joining and machining.

The use of thermoplastic-based WPC is an interesting approach [5]. Green bodies are produced by extrusion or injection moulding, which make 3D geometries easily accessible. However, the common

thermoplastic matrices of WPC limit the use in the carbonisation process due to low carbon yield and limited dimensional stability.

Wood K plus owns more than 10 years of know-how in extrusion of wood thermoset composites mainly based on specially modified melamine resins [6, 7]. After carbonisation, melamine resin based green bodies result in too dense C-templates (silicon uptake low) with a low carbon yield. To solve this problem, Wood K plus has developed an extrusion process for phenolic resin based WPC. The change from melamine to phenolic resins significantly increases carbon yield and dimensional stability in the carbonisation process. The addition of thermoplastic modifiers as placeholders in the green body, which almost completely decompose during the carbonisation, leads to a porous structure during the carbonisation process [8].

2. Materials and Methods

2.1. Materials

All materials used are commercially available. The wood fibres are based on spruce with an average fibre length of 0.1 to 0.5 mm and a L/D ratio of up to 3. The thermoset matrix is based on novolac and urotropin is used as hardener. As thermoplastic modifiers, polyvinyl alcohol derivatives, polyolefins and polylactones are used. As processing aids stearates and fatty acid derivatives are used. Technical grade silicon (Si) with a purity of > 98.5% is used.

2.2. Methods

The bulk density of the green bodies and ceramics is determined by means of a pycnometer, the bulk density of the porous carbons is determined geometrically. The flexural strength is determined using the 3-point bending test (EN ISO 178, Messphysik Beta 50, bars: 80x10xd mm^3). The porosity of the carbons, as well as the microstructure and composition of the ceramics are determined by light microscopy (LOM) of embedded samples and the determined densities. Sample preparation and polishing was done at a Struers LapPol5 and for light optical microscopy an Olympus device was used. Scanning electron microscopy (SEM) was done on a TESCAN VEGA LMU 2 equipped with energy-dispersive X-ray spectroscopy (EDS) from Oxford. Mercury porosimetry investigations were done on a Pascal Mercury Intrusion Porosimeter from Thermo Scientific. X-ray computed tomography (XCT) was performed either on a RayScan 250 E device or, for smaller samples, on a GE phoenix|x-ray nanotom 180 NF device. Synchrotron computed tomography was done at DESY in Hamburg with energy of 18 keV. Tomograms were reconstructed with $(1.2\ \mu m)^3$ voxel size.

2.3. Compounding and Profile Extrusion

The compounding and profile extrusion of the thermoset-based WPC is performed on a Cincinnati Fiberex Konos 38, a counter-rotating conical twin-screw extruder (Fig. 1). The extrusion line is equipped with a gravimetric 6-fold dosing system of Motan Colortronic. For the production of the compounds, the extruder is combined with an Erema KG80 hot-cut granulating system. The compounds are prepared in a temperature range of 150-210 °C. For profile extrusion, various profile tools (hollow profiles, decking profiles, tubes) with calibration devices are used. The dies and calibration devices used are designed mainly for thermoplastic-based WPC. The profile extrusions are carried out in the temperature range of 130-160 °C.

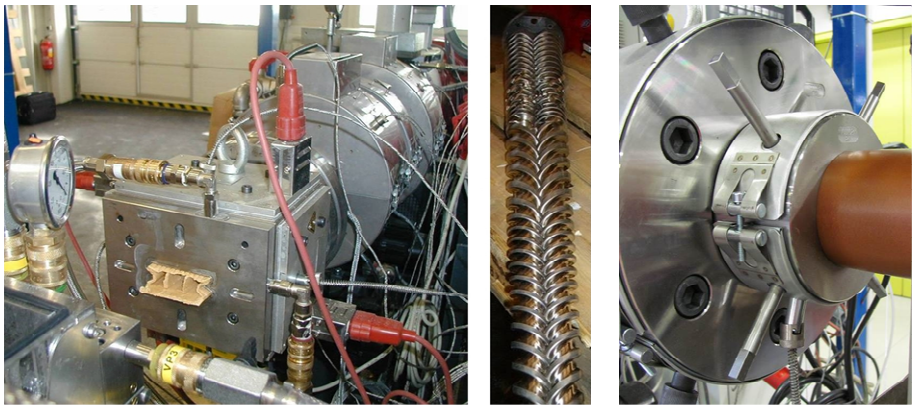

Figure 1. Cincinnati Fiberex Konos 38 with different profile dies and extruder screw (middle).

2.4. Carbonisation and Liquid Silicon Infiltration

The carbonisation and liquid silicon infiltration are carried out in a GERO HTK8 high-temperature chamber furnace equipped with a graphite pyrolysis retort. The carbonisation of the green bodies is carried out under an inert gas stream (nitrogen, argon) at 900 °C or 1600 °C (up to 500 °C: 1 K/min, 1 h at 500 °C, up to 900 °C: 5 K/min, 2 h at 900 °C, up to 1600 °C: 5 K/min, 1 h at 1600 °C). The liquid silicon infiltration is carried out under vacuum (1-5 mbar) at 1600 °C (up to 1300 °C: 5 K/min, up to 1600 °C: 2.5 K/min, 1 h at 1600 °C).

3. Results and Discussion

3.1. Compounding and Extrusion of Green Bodies

The WPC mixtures consist of 50 to 62 wt% of wood fibres between 0.1-0.5 mm, a matrix of 6 to 16 wt% thermoplastic modifier, 25 to 40 wt% phenolic resin and processing aids. With higher wood content, extrusion hardly is possible, because flow properties, friction and melt pressure are limiting. The goal is to transform a thermoset-based but thermoplastic processable mixture within the extrusion process into a shaped and cured profile. Due to the ongoing curing process, the extrusion of thermoset-based WPC is quite different to thermoplastic-based WPC. The basis for the reactivity of the mixtures is given by the resin type and the amount of hardener.

The higher the extrusion temperature, the lower is the thermoplastic processing window (possible residence time) of the mixture in the extruder. In addition, the curing enthalpy is set free during the process and also friction of the wood-based mixtures takes place. All these effects not only influence the reactivity but also the flow properties of the mixture. The flow properties further are influenced by the wood content and the type and amount of modifiers and processing aids. The moisture of the mixture has a great influence on both the reactivity and the flow properties.

Stress and density differences in the green bodies caused by differences in the flow behaviour in the tool then have an effect on the carbonisation: distortion, cracks and blistering can occur. The homogeneity in the green bodies is of central importance in order to be able to achieve a high SiC content in the ceramic. At the end, a composition is needed where the reactivity, the flow properties and the composite strength are in balance to receive a good quality green body. The aptitude of green body compositions for receiving suitable C-templates can be evaluated after the pyrolysis step. Good quality green bodies do not necessarily implicate appropriate C-templates.

Figure 2. Different profile geometries, green bodies (ochre coloured), porous C-templates (lying on top, right picture: in between) and C/Si/SiC-ceramics (right side).

In principle, profile extrusion can be done without a separate compounding step before. In this so called „direct extrusion“, compounding and profile extrusion are performed in one procedure excluding a separate compounding step. For a better homogeneity, a prior compounding step is necessary. In the compounding, a mixture of novolac, wood and thermoplast is processed. The hardener and the processing aids are added in the profile extrusion step. The highest SiC contents in the ceramics could be reached by performing two homogenisation steps before the profile extrusion.

3.2. Porous C-Templates und Bio-Based C/Si/SiC-Ceramics

The carbonisation of the green bodies is performed under inert gas at 900 °C or 1600 °C. During the carbonisation, open porous carbons are formed. The wood fibres in combination with the thermoset give the structural stability during carbonisation. The decomposition of the thermoplastic modifiers leads to pore formation in the matrix. The bulk density/porosity of the C-templates can be adjusted by the proportion of thermoplastic modifiers and is directly proportional to the thermoplastic content of the green bodies, regardless of the wood/thermoplastic combination. The mechanics, on the other hand, depend on the type of thermoplastic, which, moreover, has a decisive influence on the flow properties and the extrusion pressure.

During the carbonisation process, a shrinkage of 25-30% occurs (Fig. 2). Due to the random distribution of the wood fibres in the WPC, no significant anisotropy occurs during shrinking which is in contrary to the carbonisation of solid wood. Density differences and stresses in the green bodies can cause distortion in the C-templates during carbonisation. These deficiencies are caused by tools that are not optimised for phenolic resin extrusion (melt distributer, profile die, calibration).

The liquid silicon infiltration is a standard process [2, 4] and has only limited influence on the resulting properties and composition of the ceramics. The porous C-templates are put into a graphite crucible and the bottom is covered with the calculated amount of silicon lumps (2-5 mm). The optimum amount depends on the porosity of the carbon and lies between 180 wt% and 350 wt% calculated on the carbon mass. 233 wt% of silicon is the theoretical amount of silicon needed for a 100% transformation of C to SiC. The silicon infiltration is then performed at 1600 °C in vacuum.

3.3. Characterisation of WPC, Porous C-Templates und Bio-Based C/Si/SiC-Ceramics

3.3.1. Microscopy, density measurements and mechanical testing

The homogeneous distribution of the components and, derived from that, the homogeneous density distribution in the green body is the central factor to reach a high SiC content in the bio-based C/Si/SiC ceramics. In the green body, the distribution of the components is difficult to visualise.

However, the homogeneity can be clearly seen in micrographs of the C-templates and C/Si/SiC ceramics (Fig. 3).

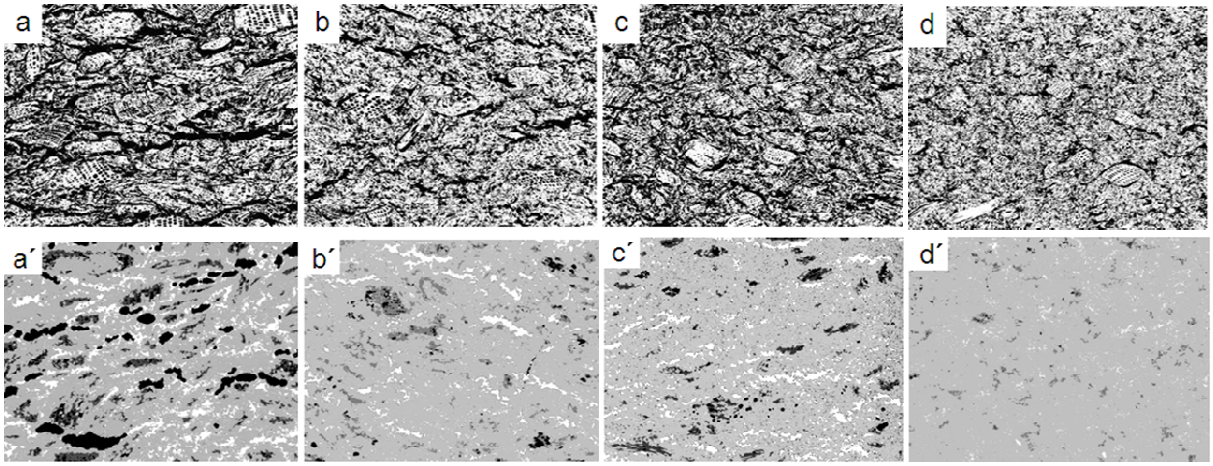

Figure 3. Micrographs 1.46x1.10 mm^2; **a-d**: C-templates from green bodies with 12% thermoplast (black: pores); **a**: direct extrusion, wood fibres 0.3-0.5 mm, **b**: one compounding step, wood fibres 0.3-0.5 mm, **c**: one compounding step, wood fibres 0.1-0.3 mm, **d**: two compounding steps, wood fibres 0.1-0.3 mm; **a´-d´**: corresponding ceramics (white: Si, black: pores, light grey: SiC, dark grey: C)

Table 1. Properties and composition of ceramics and C-templates from Fig. 3

	SiC	Si	C	Pores	Bending Strength	Bending Modulus	Density ceramic	Density C-template	Porosity C-template
	[vol%]				[MPa]	[GPa]	[g/cm^3]	[g/cm^3]	[vol%]
a/a´	67.3	12.7	12.4	7.6	168	148	2.67	0.80	44.8
b/b´	81.3	10.1	7.4	1.2	218	161	2.95	0.86	40.7
c/c´	85.1	8.3	4.5	2.1	231	141	2.96	0.87	40.0
d/d´	89.2	5.1	4.3	1.4	245/390*	184/280*	3.03	0.91	37.2

** values for surface polished specimens*

From the micrographs in Fig. 3 and Tab. 1 it can be seen that the homogeneity in the green body is decisively influenced by the compounding quality and the wood fineness. Direct extrusion with coarser wood fibres produces inhomogeneous carbons and ceramics with low SiC contents. Through an additional compounding step and the use of finer wood, the homogeneity and the achievable SiC contents are increased. The best carbon homogeneity and 90 vol% SiC content in the corresponding ceramics were received by two compounding steps before extrusion and wood fibres with 0.1-0.3 mm. The bending strength of the ceramics correlates with the SiC content and the density.

3.3.2. XCT and Synchrotron measurements, REM/EDX, LOM and Mercury Porosimetry

For the C-templates the quantification by XCT with an ISO62 threshold algorithm leads to quite the same results as obtained with LOM and mercury porosimetry (max. deviation ~1.2 vol%). Due to the low contrast differences and the small dimensions of the phase structures in C/Si/SiC ceramics, only an estimation of SiC content with XCT was possible. For the C/Si/SiC-ceramics LOM is the better method to gain meaningful quantitative results of Si and SiC content.

Table 2. Grey values and threshold for XCT-evaluation of C-templates. Results of XCT and reference methods for porosity evaluation with LOM and mercury porosimetry.

C-template carbonisation temperature	Grey Value		Threshold		XCT ISO50 [vol%]	XCT ISO62 [vol%]	LOM [vol%]	Mercury Porosimetry [vol%]
	Air	Carbon	ISO 50 %	ISO 62 %				
900 °C	21.8	35.5	28.7	30.3	26.5	33.7	34.6	34.0
1600 °C	25.6	41.1	33.3	35.2	27.8	34.9	35.9	33.7

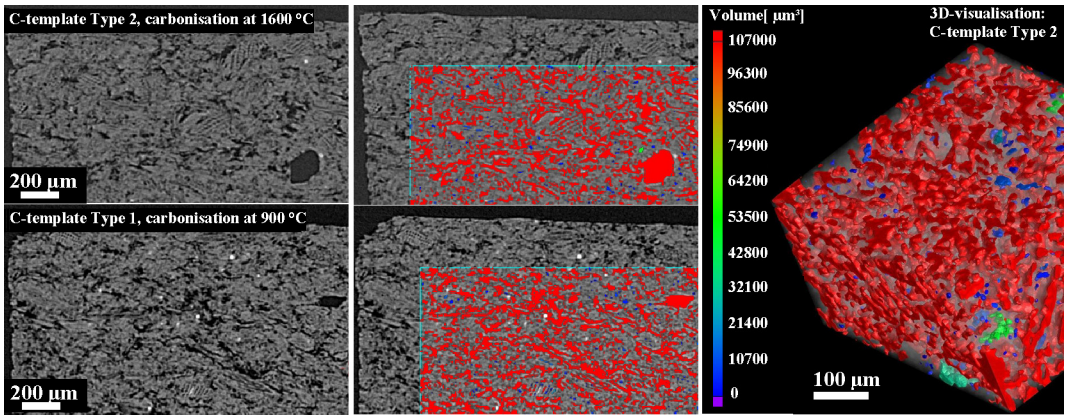

Figure 4. C-Template 900 °C, 1600 °C. Voids segmented with ISO50 threshold (middle). Right: 3D pore network of interconnected pores (red colour)

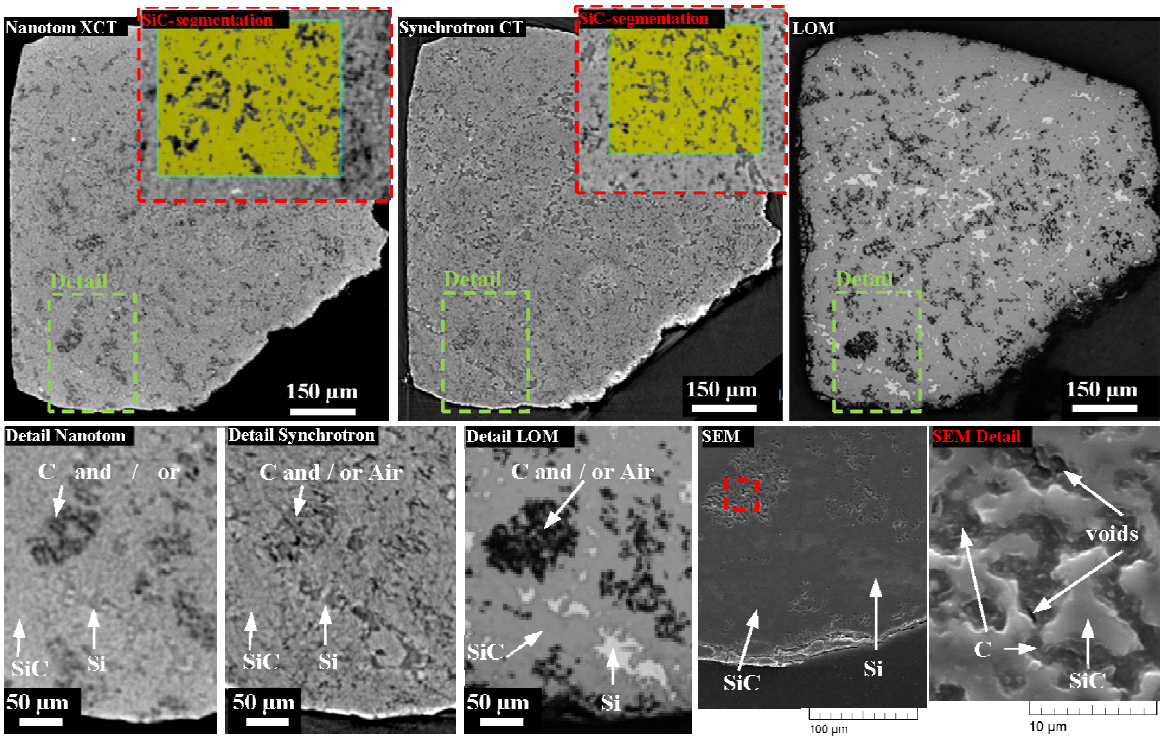

Figure 5. C/Si/SiC-ceramic: XCT slices generated on Nanotom XCT (0.8 µm)³ and synchrotron CT (1.2 µm)³ vs. LOM and SEM image after target preparation of C/Si/SiC-ceramic.

4. Conclusions

It has been shown that extruded WPC profiles based on thermosets can be successfully produced and used as green bodies for bio-based silicon carbide ceramics. The achievable qualities are comparable with the literature data [1-4]. The main impact factor on the quality of the porous C-templates and subsequent C/Si/SiC ceramics is the distribution of the constituents as well as the density distribution in the green bodies. This requires optimal compounding prior to profile extrusion and an even melt flow of the material into and in the profile die.

Quantitative characterisation of the green bodies is partly possible with XCT as an estimation of the wood content can be obtained. The quantitative characterisation of the C-templates leads to quite the same results with LOM, XCT and mercury porosimetry. For the C/Si/SiC-ceramics LOM is the better method to gain meaningful quantitative results of Si and SiC content than with XCT.

Acknowledgments

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