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Biomorphous SiOC/C-ceramic composites from chemically modified wood templates

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Abstract

Anisotropic, biomorphous SiOC/C-ceramic composites with different porosities and designed microstructure were manufactured from native beech and pine wood. In a first step, biotemplate/polysiloxane composites were prepared by infiltration and reaction of the wood preforms with a Si–H functionalised preceramic polymer (polymethylhydrosiloxane—PMHS). Curing of the infiltrated PMHS was achieved by temperature treatment at 120 °C for 12 h. Subsequent pyrolysis of the biopolymer/polysiloxane hybrid materials in inert atmosphere at 800 °C yields a biomorphous SiOC/C-ceramic composite. FTIR, TGA and SEM analysis was applied to monitor structural changes and phase formation processes during thermal treatment. The esterification of the wood with maleic acid anhydride (MA) was used to alter the chemical properties of the wood cell wall and to introduce CC-double bonds for further reaction with PMHS. The PMHS-infiltration reduced the anisotropic shrinkage associated with the thermal decomposition of the biopolymers compared to the native wood. MA-modified, PMHS-infiltrated samples exhibit an improved ceramic yield after pyrolysis, which may be attributable to a facilitated penetration of the PMHS into the wood cell wall. Additionally, the influence of low-molecular weight wood compounds on the PMHS-infiltration as well as on the microstructural evolution was assessed by extraction techniques. Extraction of the low-molecular weight wood compounds yielded an additional porosity and finally void formation inside the SiOC-phase, which stabilizes the specimen during the pyrolysis and prevents the sample from cracking.

Keywords: Biomorphous ceramics; Biotemplating; Chemical modification; Lignocellulosics; Preceramic polymers; SiOC

1. Introduction

Anisotropic ceramic materials with a hierarchical pore structure ranging from the nanometre to the millimetre scale are interesting for applications as filter, catalyst support or micro reactor device structures. While conventional extrusion technologies can be used for manufacturing of cell diameters down to below 1 mm, smaller uni-directed pore morphologies are accessible from native, lignocellulosic tissues. The cellular architecture of native lignocellulosic materials, such as biological fibres and wood tissue, was optimised from nature in respect to their mechanical and functional properties by evolution over a long time period.[1]

Over the last years, various high-temperature biotemplating techniques were developed to convert biological tissue into dense and porous SiC-based ceramics.[2] Considerable efforts have been devoted to the production of SiC-ceramics from organic fibres.[3–5] Reactive melt infiltration with liquid Si of different species of pyrolysed wood preforms yields dense or nearly dense biomorphous SiSiC-ceramics.[6–9] Highly porous, cellular, single-phase SiC-ceramic were obtained by vapour phase reaction with gaseous Si, SiO and H_3CSiCl_3.[10–12] An alternative technique for manufacturing of porous, biomorphous ceramics was studied by infiltration of biocarbon (C_B-)templates with metal-organic solutions. The C_B-templates were infiltrated repeatedly with metal-organic solutions, e.g. tetraethyl orthosilicate (TEOS) or titanium tetra-isopropoxide (TTiP) and subsequently converted into porous SiC- or TiO_2-ceramics by high-temperature treatment in air or inert atmosphere.[13,14] However, all of the previously developed techniques require at least a two-step high-temperature treatment to obtain the final microcellular ceramic material: (i) pyrolysis of the biotemplate into biocarbon, and (ii) an infiltration step with an additional high-temperature treatment, e.g. reactive melt, vapour or metal-organic solution infiltration.

In a former work,[15] the processing scheme for conversion of wood tissue into a microcellular C/SiOC-ceramic composite material in one single high-temperature step was developed. The porous structure of the

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native wood tissue was used for infiltration with a low viscous preceramic polymer and subsequently pyrolysed by annealing in inert atmosphere. Polymeric ceramic precursors such as silicone resins (e.g. polysilsesquioxanes—$RSiO_{1.5}$) can be transformed into an amorphous silicon oxycarbide (SiOC-phase) by thermal treatment in inert atmosphere at temperatures above 600 °C.[16] The capability of preceramic polymers as potential material for near-net shape manufacturing of complex parts are well-known.[17,18] The manufacturing of an ordered array of macro-porous SiC from templated preceramic polymers was recently described.[19]

The aim of the present work was to evaluate the influence of pre-processing steps, e.g. chemical modification and extraction, on the infiltration and pyrolysis behaviour of the preceramic polymer infiltrated native wood in order to reduce the shrinkage, to increase the ceramic yield and to design the microstructural morphology of the biomorphous SiOC/C-ceramic composites. Polymethylhydrosiloxane (PMHS) of low-viscosity and high ceramic yield was chosen as preceramic polymer, beech and pine wood as C_B-template. During PMHS-infiltration and curing, the SiH-functional groups of the polymeric precursor are able to react with the OH-groups of the biopolymers lignin and cellulose from the native wood in a dehydrogenative condensation reaction to form SiO–ether bonds.[20,21] The influence of low-molecular weight substances present in native wood was assessed by extraction of the solid wood before PMHS-infiltration. Modification of the wood with maleic acid anhydride (MA) was applied, because MA esterifies the OH-groups of the biopolymers and thus varies the chemical properties of the wood cell wall. The applied pre-processing treatments changed the chemical properties of the native wood template and results in a variation of the microcellular morphologies of the biotemplate/polysiloxane composite as well as the final SiOC/C-ceramic composites obtained after the pyrolysis process.

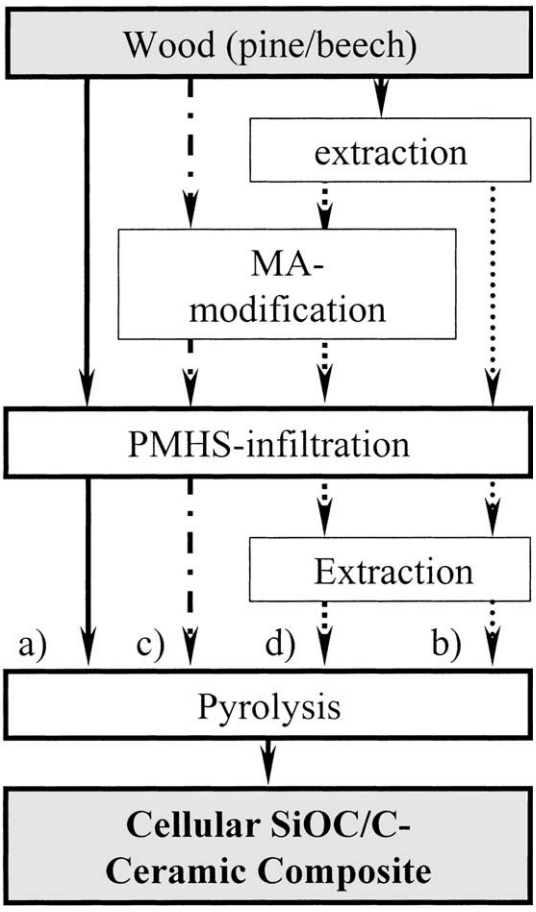

Fig. 1. Processing scheme for manufacturing of cellular SiOC/C-composites including the extraction, chemical modification and infiltration of PMHS: (a) infiltration of untreated wood with PMHS, (b) untreated wood was modified with MA, infiltrated and reacted with PMHS, (c) the wood was extracted prior to the infiltration with PMHS and extracted again after curing of the PMHS, (d) the wood was extracted prior to the modification with MA and subsequently infiltrated with PMHS and extracted again after curing and reaction of the PMHS. All samples were pyrolysed in a N_2-atmosphere at 800 °C.

2. Experimental

2.1. Processing scheme

The developed processing scheme for manufacturing of biomorphous SiOC/C-ceramic composites is shown in Fig. 1. First, untreated wood was infiltrated with PMHS, cured and pyrolysed, route (a) in Fig. 1. In a second route, the low-molecular weight substances present in native wood were extracted according to standard procedures used in wood chemistry.[22] Furthermore, the PMHS-infiltrated wood was a second time extracted to remove un-cured PMHS, route (b) in Fig. 1. In a third route, the modification of the wood with maleic acid anhydride (MA) was applied, route (c) in Fig. 1. Again the influence of pre- and post-extraction of MA-modified specimen on the PMHS-infiltration was studied, route (d) in Fig. 1.

2.2. Sample material

Oriented cubes of beech wood (*fagus sylvatica*) and pine wood (*pinus sylvestris*) with average dimensions of axial, radial and tangential directions of $10\times10\times10$ mm^3, were used throughout this study. The wood samples were dried at 105 °C for 24 h before processing. Part of the wood cubes were extracted with a mixture of toluene/ethanol 2:1 for 24 h in a Soxleth apparatus to remove low-molecular weight substances.[22] All chemicals were used as received without further purification.

2.3. Chemical modification of wood

Non-extracted and extracted wood samples were reacted with MA according to the procedures described by Timar et al.[23] Thirty samples of wood (15 samples of each wood species, total: 15 g) were places in a 250 ml round-bottom Schlenk flask equipped with dropping funnel without a pressure equalisation. The flask was evacuated with a water-jet vacuum pump. A solution of 40.86 g maleic acid anhydride (420 mmol) and 2 ml of triethanolamine (TEA) as a catalyst in 100 ml dimethyl acetamide (DMA) was slowly added from the funnel. The wood cubes were immediately infiltrated with the reaction solution. The mixture was then stirred for 3 days at room temperature (RT) and subsequently heated for 1 h to 100 °C. After cooling the reaction mixture to room temperature, the supernatant was decanted and the MA-modified wood cubes were extracted with acetone in a Soxleth apparatus for 24 h to remove un-reacted educts and by-products, which are not covalently bound to the biopolymers. After MA-modification the irreversible volumetric swelling $\Delta V/V_o$ was calculated according to:

$$\Delta V/V_o = (V_{MA} - V_o)/V_{o\cdot} \times 100 \quad [\%] \tag{1}$$

where V_{MA} is the volume of the MA-modified sample, and V_o is the volume of the native sample. The reaction of the MA with the biopolymers in the cell wall caused an average irreversible volumetric swelling of 11–13%.

2.4. Preceramic polymer infiltration

Non-extracted and extracted as well as unmodified and MA-modified wood samples were infiltrated with the pure liquid PMHS (Polymethylhydrosiloxane, Fluka, Germany). The composition and properties of PMHS are given in Table 1. The wood cubes were placed in a Schlenk tube equipped with a dropping funnel without pressure equalisation containing the PMHS. The tube was evacuated with a water-jet vacuum pump and the PMHS was slowly added. The infiltrated wood samples were removed from the liquid and excess polysiloxane was wiped off from the sample surface using filter paper. The infiltrated PMHS was cured in an oven at 120 °C for 12 h. Part of the cured biopolymer/polysiloxane composite were extracted with acetone in a Soxleth apparatus for 24 h. The mass loss after extraction of the cured PMHS-infiltrated samples accounted for only 1 wt.%

2.5. Characterisation of the weight gain

The individual weight gain (WG) and length changes in the major wood direction of each sample were measured before and after each infiltration or reaction step. The dimensions were determined using a calliper accurate to 0.025 mm. The fractional weight gain $\Delta m_o/m_o$ after infiltration of the PMHS with respect to the previous reaction/extraction step was calculated according to:

$$\Delta m_o/m_o = (m_{inf} - m_o)/m_{o\cdot} \times 100 \quad [\%] \tag{2}$$

where m_{inf} is the weight of the PMHS-infiltrated sample, and m_o is the weight of the native or modified sample.

2.6. Pyrolysis

The pyrolysis was performed in a electrically heated tube furnace, which was continuously flushed with nitrogen. The furnace was heated at a rate of 1 °C/min from room temperature to 500 °C and from 500 to 800 °C at rate of 5 °C/min. The peak temperature was held for 4 h. After cooling down to room temperature, the individual weight loss (WL) $\Delta m/m_{inf}$ was calculated according to Eq. (3):

$$\Delta m/m_{inf} = \left(m_{pyr} - m_{inf}\right)/m_{inf} \times 100 \quad [\%] \tag{3}$$

where m_{pyr} is the weight of the pyrolysed sample. The linear dimensions of the pyrolysed samples were measured.

The TGA measurements were performed with a Netzsch STA 409 instrument in the temperature range from 20 to 1000 °C at a rate of 5 °C/min (N_2-atmosphere) to determine the weight loss as function of the temperature.

2.7. Microstructure analysis

FTIR-spectra were recorded on a Nicolet Impact 420-T instrument operated in the directed reflection mode from the bulk after axially cleaving the cubes. 1024 scans at a resolution of 8 cm^{-1} were taken to obtain a spectrum with an improved signal to noise ratio. For the FTIR-spectra recorded with KBr technique 1 mg was scraped off the sample surface and mixed with 300 mg KBr. After grinding in a mortar, the mixture was axially pressed into a transparent tablet. The spectra were recorded at resolution of 4 cm^{-1} and 32 scans were taken per spectrum.

Table 1
Formula and properties of the polymethylhydrosiloxane (PMHS)

Polymer	Formula	M_W	Structure	Viscosity (20 °C)
PMHS	$(CH_3)_3SiO[CH_3HSiO]_{25–35}Si(CH_3)_3$	1500–1900	Linear	15–40 MPa·s

The microstructures of the pyrolysed SiOC/C-ceramic composites were characterised by scanning electron microscopy (SEM, Stereoscan S 250 MK3, Cambridge Instruments, Cambridge, UK) operated the BSE-mode at 25 kV and elemental analysis by EDX/SEM. The samples were prepared by grinding off one third of the bulk in axial direction. The surface was then carefully polished. The samples were mounted onto Al-sample holders with double-side adhesive carbon tapes and sputtered with gold.

3. Results and discussion

3.1. PMHS-infiltration

The results for the weight changes after the PMHS-infiltration with the different pre-processing treatments (MA-modification, extraction) are given in Table 2. Significant higher weight gains during the PMHS-infiltration and the MA-reaction were achieved for pine wood applying extraction steps in contrast to the untreated samples. The removal of the low-molecular weight extractives may improve the wettability for the PMHS enhancing the infiltration results for pine. However, the chemical modification with MA induced a irreversible volumetric swelling of 13% for the pine and 11% for the beech wood samples. The high WG for MA of 38.3 wt.% in extracted pine results in an increased swelling of the cell wall, which reduced the pore diameter of the wood cells. Thus, a lower amount of PMHS can be infiltrated into the wood template and the weight gain of extracted PMHS-MA-pine is reduced by 18% compared to non-extracted pine.

The extraction of the beech wood has a minor effect regarding the PMHS-infiltration and the weight gain for the MA-reaction. In contrast to the pine wood the weight gain of PMHS for extracted beech is slightly decreased by 7%, whereas the weight gain for the MA-reaction is increased by 9%. Due to the enhanced weight gain for the MA-reaction and the swelling of the cell wall, the weight gain for the PMHS-infiltration is reduced by 6%.

3.2. FTIR-spectroscopy

The infiltrated SiH-functionalised polysiloxane may react in three different ways with the MA-modified wood: (1) curing by temperature treatment (120 °C, 12 h) in the presence of moisture due to hydrolysis of the Si–H-groups to Si–OH and further dehydrogenative condensation with other Si–H functions; (2) dehydrogenative condensation of (non-esterified) OH-function of the biopolymers resulting in the formation of covalent Si–O-bonds; (3) hydrosilylation of the C=C-double bond of the MA residue. The FTIR-spectrum of pure PMHS after treatment at 120 °C using the KBr-technique is given in Fig. 2a. The most prominent signals are found at 2966 cm^{-1} [$\nu(sp^3CH)$], at 2166 cm^{-1} [$\nu(sp^3SiH)$], and in the fingerprint region. The signal at 1260 cm^{-1} is assigned to the $\nu Si\text{-}CH_3$). The strong bands from 1099 to 1059 cm^{-1} are assigned to the $\nu(Si\text{-}CH_3)$. The strong bands from 1099 to 1059 cm^{-1} are assigned to the SiO-framework[21]. The strong absorption below 1000 cm^{-1} is derived from the $SiCH_3$ side chain and partly of the SiO framework due to cross-linking. The FTIR-spectra from bulk beech sample of PMHS-infiltrated pine wood using the KBr technique are shown in Fig. 2b. The spectra for PMHS-pine and the extracted specimens are substantially the same. The absorption bands derived from the wood are visible in region from 1750 to 1275 cm^{-1}. The signals are weak compared to the strong signals derived from the polymer. The PMHS derived signals in Fig. 2b match the

Table 2
Weight gains (WG) after PMHS-infiltration and the different pre-processing steps, and weight loss (WL) after pyrolysis at 800 °C for the infiltrated wood samples

	Non-extracted		Extracted	
	WG [wt.%]	WL [wt.%]	WG [wt.%]	WL [wt.%]
Pine				
PMHS-	30.7	−59.3	75.4	−54.1
MA-	14.6	–	38.3	–
PMHS-MA-	79.7	−38.1	65.2	−44.9
Beech				
PMHS-	59.3	−56.5	55.2	−56.4
MA-	25.3	–	27.5	–
PMHS-MA-	40.7	−46.9	38.2	−49.4

The native wood exhibits a weight loss of 72% for pine and 76% of beech. The weight loss of pure PMHS accounts for 33%.

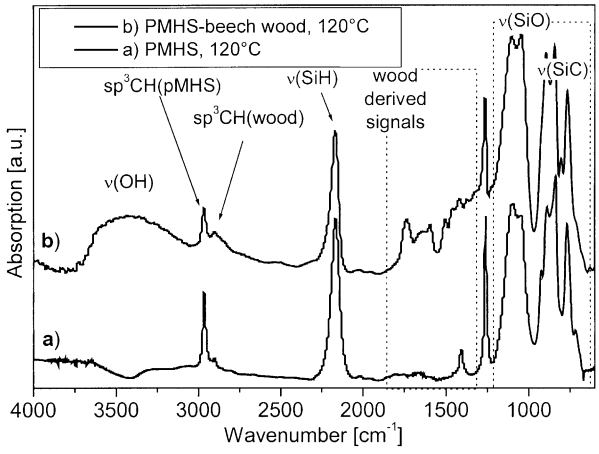

Fig. 2. FTIR-spectra (KBr-technique) of: (a) temperature-cured PMHS, (b) temperature-cured PMHS-infiltrated beech wood.

signals found for pure PMHS. The strong polymer derived bands superimpose the weak vibrations from the wood.

FTIR-spectra of the MA-modified wood and PMHS-MA-wood compared with native wood are depicted in Fig. 3 for pine wood and in Fig. 4 for beech wood. The spectra were obtained in the directed reflection mode from the sample surface after cleavage. The ratio between wood derived bands and those from the polymer are more equally distributed in this mode. Compared with the FTIR-spectrum of native softwood (Fig. 3a) and hardwood (Fig. 4a), the FTIR-spectrum of MA-modified wood (MA-wood) exhibits new absorption bands, Figs. 3b and 4b indicating esterification. The signal at 1750 cm^{-1} is derived from the vibration of the ester group [ν–C(=O)O–)]. Virtually, the OH-region appears to be contracted compared to native wood, which confirms disappearance of hydroxyl function due to ester formation. The signals at 1654 cm^{-1} [(ν(–C=C–)] and 824 cm^{-1} [δ(*cis*(–CH=CH–)] are attributed to the carbon double bond of the maleic ester residue. The spectra obtained from PMHS-MA-modification and temperature curing for pine (Fig. 3c) and beech (Fig. 4c) exhibit both the features of MA-modification and the bands typical for PMHS. The SiH vibration for both is strong, indicating a low extent of reaction and curing. Since the signals for the C=C-double bond (824 cm^{-1} [δ(*cis*(–CH=CH–))] and the SiC-core vibrations (837 cm^{-1}) are in the same range, differentiation is not possible. The extracted FTIR-spectra for the samples exhibit the same signals.

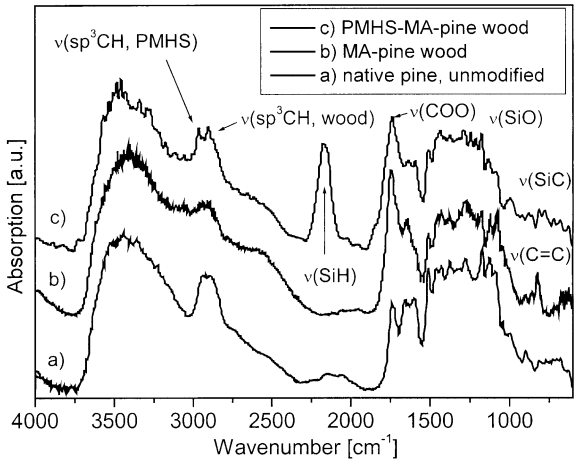

Fig. 3. FTIR-spectra (directed reflection) of pine wood: (a) native, (b) MA-modified pine, c) temperature-cured PMHS-infiltrated, MA-modified pine wood.

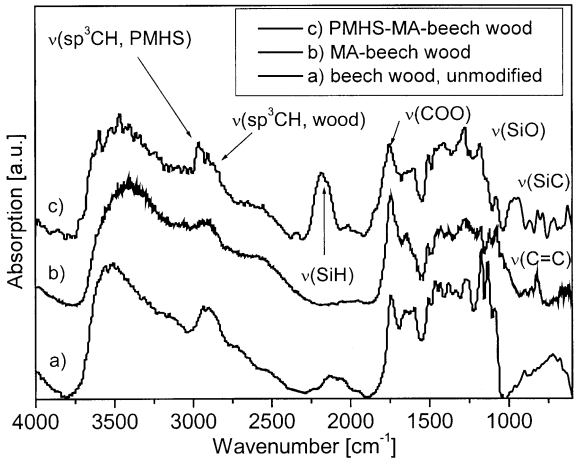

Fig. 4. FTIR-spectra (directed reflection) of beech wood: (a) native, (b) MA-modified beech, (c) temperature-cured PMHS-infiltrated, MA-modified beech wood.

3.3. Weight loss and shrinkage

After pyrolysis in N_2-atmosphere at 800 °C, the PMHS-infiltrated wood composites were transformed into SiOC/C-ceramic composites. The bioorganic matrix of the wood is thermally decomposed and forms carbon struts from the former cell walls.[15] The observed weight loss for the polymer infiltrated and modified wood specimens after pyrolysis are given in Table 2. Generally, an increasing amount of PMHS tends to result in an enhanced ceramic yield of the SiOC/C-composite.

TGA measurements showed, that the weight loss during heating of native and infiltrated wood started at 220 °C (Fig. 5). The maximum of weight loss occurred between 260 and 360 °C. Char yield for the native pine wood is 78 wt.% after pyrolysis at 800 °C. The thermal decomposition of the MA-modified wood already started at 200 °C with a lower decomposition rate compared to the native wood, but with a similar final yield. The PMHS-infiltrated wood exhibited similar behaviour as

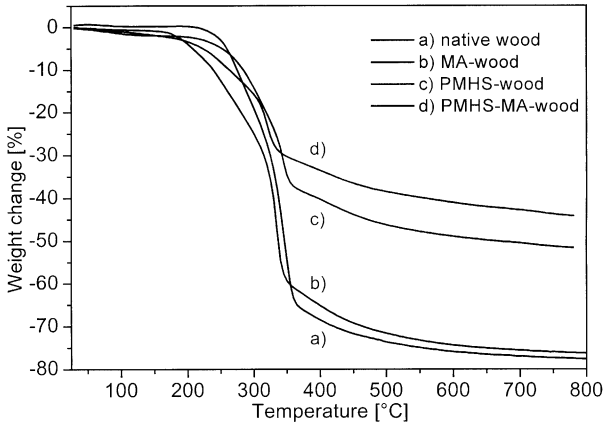

Fig. 5. Thermogravimetric analysis of (a) native pine wood, (b) MA-modified wood, (c) PMHS infiltrated wood, and (d) MA-modified and PMHS-infiltrated wood.

the native wood, however, a reduced weight loss due to the higher ceramic yield of the infiltrated preceramic polymer. The pyrolysis of PMHS-MA-wood started at 200 °C similar to the MA-wood accompanied by an even lower decomposition rate and reduced weight loss.

In Fig. 6 the weight loss after pyrolysis is plotted as function of the weight gain after PMHS-infiltration and compared to the theoretical weight loss of a separated mixture of the two compounds wood and PMHS. An independent pyrolysis for each compound was assumed in the calculation of the theoretical value (average weight loss of wood: 72%, PMHS: 33%). It can be deduced from the graph, that the experimental data points for PMHS-beech and -pine are close to the theoretical values, meaning that the PMHS and the wood are pyrolysed independently. However, the data obtained for the PMHS-MA-beech and -pine are shifted to significant lower weight loss than the theoretical value for a given weight gain of PMHS.

The main difference during pyrolysis between the unmodified and the MA-modified wood is the improved ceramic yield for the MA-reacted samples. Although the confirmation of the reaction with FTIR-spectroscopy due to superimposed absorption bands was ambiguous, covalent linkage of the PMHS to the wood biopolymers is considered based upon the decomposition results. The ceramic yield of the PMHS-MA-wood compared to the theoretical values calculated for the same composite, when separate and independent decompositions of the wood and the PMHS-components are assumed, is improved by 25% for beech and 26% for pine. Due to possible covalent bonding as discussed above, the wood polymers and the preceramic polymer are assumed to behave like a new compound with lower weight loss and reduced anisotropic shrinkage during pyrolysis.

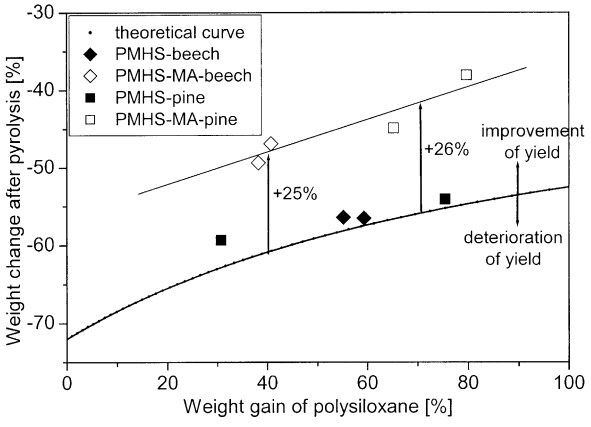

Fig. 6. The WL after pyrolysis is plotted as a function of the WG of PMHS, for the infiltrated (and MA-modified) extracted and non-extracted samples. The dotted line corresponds to the calculated theoretical values.

The length changes in the major directions of the native wood after pyrolysis and the pre-processed and PMHS-infiltrated wood are summarised in Fig. 7a,b. The shrinkage of non-extracted specimens appears more uniform, independent of the kind of modification. The MA-modification has only a small effect in addition to the reduced anisotropy of the shrinkage for the non-extracted—as well as for the extracted-specimens. The degree of shrinkage anisotropy as well as the overall shrinkage for the non-extracted-beech sample after PMHS-infiltration decreased even more with additional MA-modification.

3.4. Microstructure of the SiOC/C-ceramic composites

SEM-micrographs of the various PMHS-infiltrated and at 800 °C pyrolysed biomorphous SiOC/C-ceramic composites are shown in Fig. 8a–d. The dark contrasted phase corresponds to the former cell walls, which are transformed into carbon, whereas the regions of brighter contrast correspond to the pyrolysed polymer,

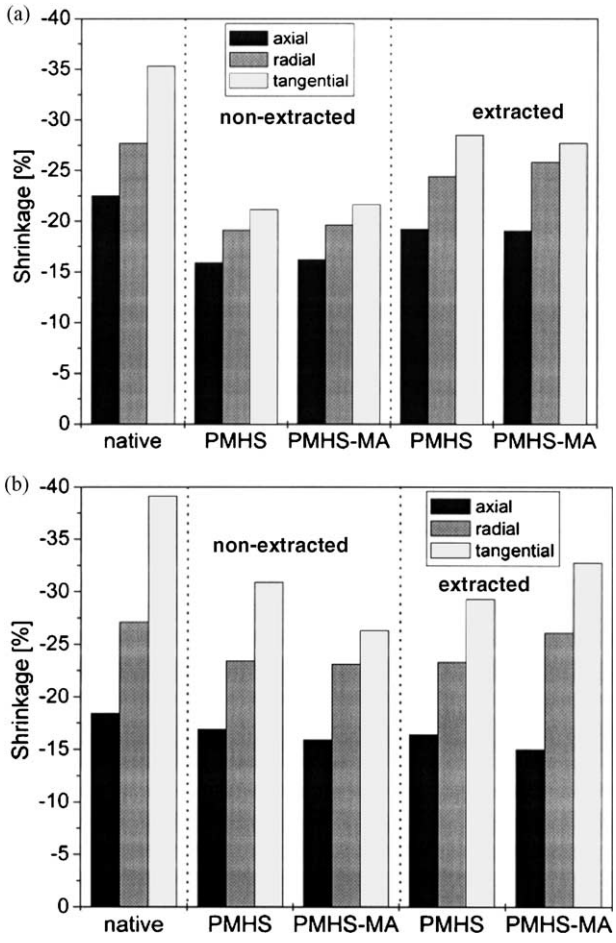

Fig. 7. Shrinkage values in the major directions of wood for: (a) (non-) extracted and modified pine wood samples, (b) (non-)extracted and modified beech wood samples.

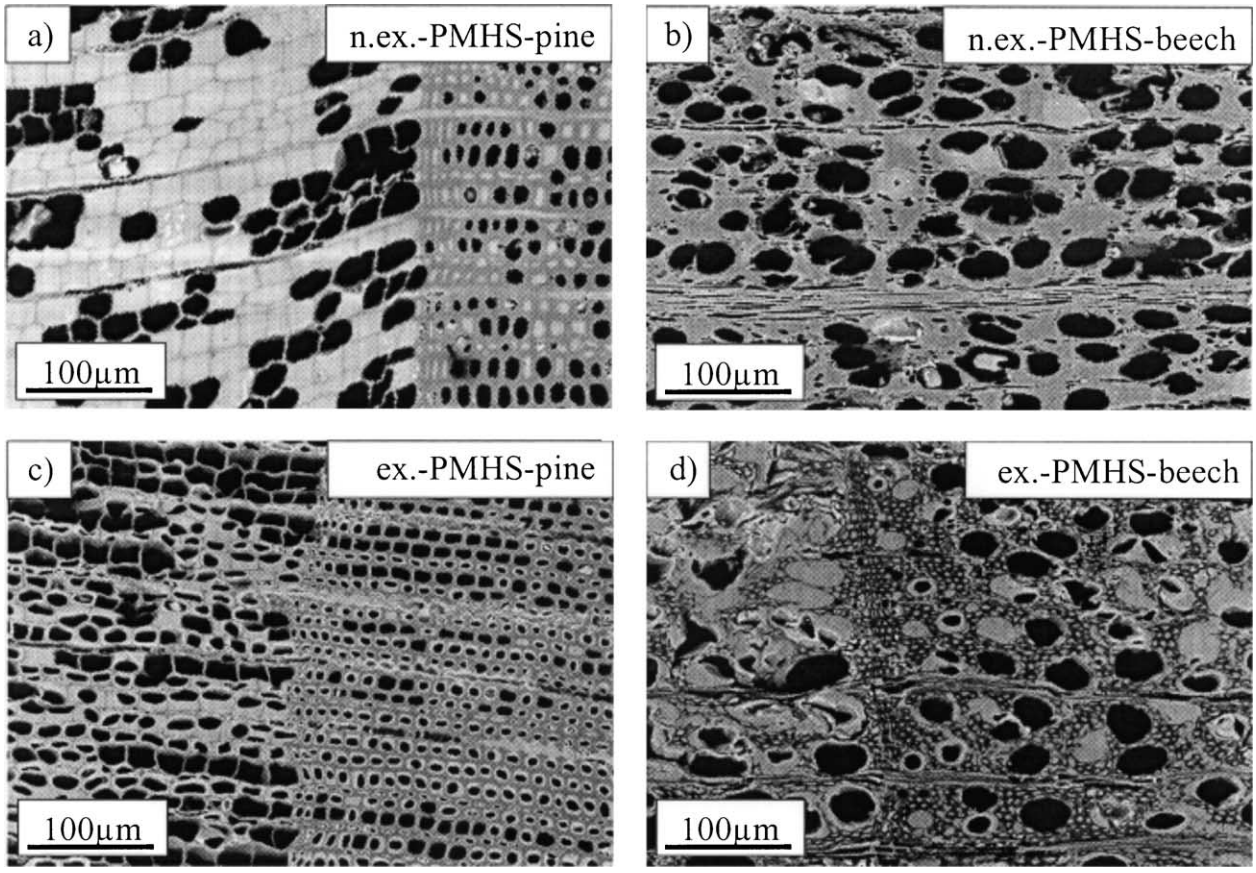

Fig. 8. SEM-micrographs of biomorphous SiOC/C-ceramics after pyrolysis at 800 °C: (a) non-extracted, PMHS-infiltrated pine and (b) beech, (c) extracted, PMHS-infiltrated pine and (d) beech.

which was transformed into a SiOC-glassy phase. The main structural features of the biotemplate are retained after pyrolysis in the ceramic composite. However, most of the tracheids in pine (Fig. 8a), and the basic tissue of libriform fibres and part of the vessels in beech are completely filled with the SiOC-phase (Fig. 8b). Only a few regions of the pine wood were not infiltrated with PMHS and thus after pyrolysis not filled with SiOC. Different characteristics in the SiOC-phase were observed, when the wood was extracted prior and after the PMHS-infiltration. The SiOC-phase exhibits holes in the compact in contrast to the non-extracted-PMHS-wood (Fig. 8c and 8d). In some cases, the pore walls seem to be solely coated with the pyrolysed polymer. Small pores in beech wood are completely filled with the SiOC-phase.

The microstructures of the PMHS-MA-modified pine and beech wood after pyrolysis are shown in Fig. 9a–d. Again, the extracted PMHS-MA pine (Fig. 9a) and beech (Fig. 9c) show large voids in the SiOC-phase. These pores in the SiOC-phase avoid the formation of macro-cracks during pyrolysis, which are frequently observed in samples with a WG of more than 50 wt.% (see Fig. 9a and b). The constraints due to the volumetric changes during pyrolysis are compensated by the voids, because the cellular system has room to counteract against the shrinkage. In the samples with a high weight gain (>50 wt.%), the not infiltrated empty cells are clearly extended in volume compared to the SiOC-phase filled cells, due to shrinkage compensation during the pyrolysis process. The pyrolysed SiOC-phase is stiff and inhibits shrinkage of the biopolymer moiety, the lack of voids in high density samples results in the formation of macro-cracks.

4. Conclusions

Pre-processing by extraction and chemical modification with MA can significantly change the processing parameters and the microstructural morphology of biomorphous SiOC/C-ceramic composites. The extraction of low-molecular weight substances from the native wood and the extraction of un-reacted PMHS after curing increases the porosity and mechanical stability of the composite material. While non-extracted specimens show morphologies with a dense SiOC-phase inside the

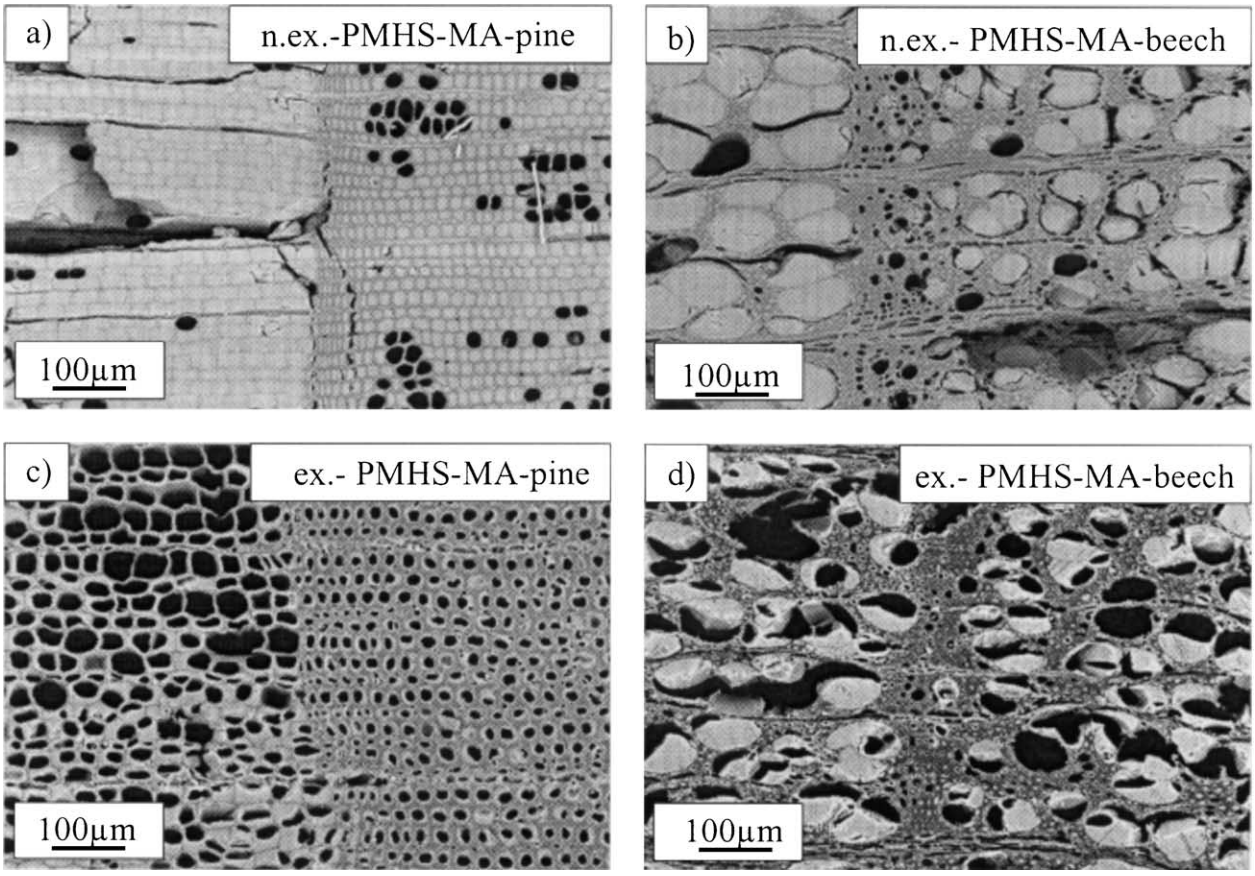

Fig. 9. SEM-micrographs of biomorphous SiOC/C-ceramics after pyrolysis at 800 °C: (a) non-extracted MA-modified PMHS-infiltrated pine and (b) beech, (c) extracted, MA-modified PMHS-infiltrated pine and (d) beech.

wood cells that often result in macro-cracks, the SiOC-phase in the extracted samples exhibits voids inside the SiOC-phase which avoid the cracking. The esterification with MA on the other hand decreases the weight loss during pyrolysis, and thus the absolute values as well as the anisotropy of the shrinkage. Here, the possible covalent bonding of the PMHS polymer to the wood biopolymers yields a significant change of the pyrolysis behaviour.

The large variety of biological available preforms together with the controlled microstructural design by advanced processing techniques allows the manufacturing of novel, microcellular SiOC/C-ceramic composites which may be interesting for micro-tools as well as chemical reaction or catalyst support structures.

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