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REVIEW ARTICLE

Tape casting of preceramic polymers toward advanced ceramics: A review

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Abstract

In the last 20 years, tape casting, a standard wet-shaping process to produce thin ceramics, has been applied to manufacture polymer-derived ceramics (PDCs). Si-based polymers, such as polysiloxanes and polysilazanes, also known as preceramic polymers (PCPs), have been used as precursors/binders replacing conventional raw materials and additives for tape casting process. Thermal processing of PCPs is carried out at lower temperatures in comparison with classical ceramic sintering, particularly of carbides and nitrides. Furthermore, polymeric precursors can be converted into hybrid or composite ceramics, when parts of the polymers remain unreacted. Inert or reactive fillers might be used to reduce both shrinkage and porosity inherently caused by the weight loss occurring during polymer pyrolysis while forming new ceramic phases in the final materials. Alternatively, pore formers might also be added to tailor pore shape, connectivity, and volume (macroporosity). Nevertheless, current equipment and process parameters for tape casting-based products must be eventually adjusted to fit the characteristics of ceramic precursors. Therefore, the aim of this review is focused on listing and discussing the efforts to produce PDCs using tape casting as a shaping technique. Interactions of system components and effects of treatment, particularly thermal stages, on final microstructure and properties are

Abbreviations: ADA, AzoDicarbonAmide, $C_2H_4N_4O_2$; AFCOP, Active Filler Controlled Polymer Pyrolysis; Al(acac)$_3$, Aluminum acetylacetonate, Al($C_5H_7O_2$)$_3$; Ceraset SN, polysilazane (Honeywell (https://www.lab-honeywell.com/products/brands/honeywell/), formerly AlliedSignal, USA), (C=O)(N-R)(CH$_3$)(H)(Si–NH)(C$_2$H$_3$)(CH$_3$)(Si–NH) [(CH$_3$)(R)Si–NH]$_n$ with n = 1-20 and R = H, CH=CH$_2$; CTE, Coefficient of Thermal Expansion; DBE, Di-n-ButylEther, $C_8H_{18}O$; DCP, DiCumyl Peroxide, $C_{18}H_{22}O_2$; DMF, DiMethylFormamide, HCO-N(CH$_3$)$_2$; Durazane 1800, (organo)silazane (Merck (https://www.merckgroup.com/en/brands/pm/az-products.html), Germany), [(C$_2$H$_3$)(CH$_3$)Si–NH)$_{0.2n}$(H(CH$_3$)Si–NH)$_{0.8n}$; Eucryptite, Li$_2$O·Al$_2$O$_3$·xSiO$_2$ with x = 2 for stoichiometric composition; FA, FormAmide, CH$_3$NO; FGC(s), Functionally Graded Ceramic(s); FGM(s), Functionally Graded Material(s); H44, solid phenylmethyl polysiloxane (Wacker (https://www.wacker.com/cms/en/products/productsearch/product-search.jsp), Germany),[(C$_6$H$_5$)$_{0.62}$(CH$_3$)$_{0.31}$(OR)$_{0.07}$SiO$_{1.5}$]$_n$, n < 20, where R can be either a hydroxyl (-OH) or a alkoxy group (-OC$_2$H$_5$); H62C, liquid methyl-phenyl vinyl hydrogen polysiloxane (Wacker[4], Germany), [(C$_6$H$_5$)$_{0.44}$(CH$_3$)$_{0.24}$(C$_2$H$_3$)$_{0.16}$(H)$_{0.16}$SiO$_{1.5}$]$_n$; Imidazole, C$_3$H$_4$N$_2$; LTCC, Low-Temperature Cofired Ceramics; MK, solid methyl polysilsesquioxane (Wacker[4], Germany), (CH$_3$SiO$_{1.5}$)$_n$ with n = 130-150; MSE100, liquid methoxy functional methyl polysiloxane (Wacker[4], Germany), [CH$_3$SiO$_{1.1}$(OCH$_3$)0.8]$_n$; MTES, MethylTriEthoxySilane, CH$_3$Si(OC$_3$H$_5$)$_3$; MTMS, MethylTriMethoxySilane, CH$_3$Si(OCH$_3$)$_3$; NTE, Negative Thermal Expansion; Oleic acid, (9Z)-octadec-9-enoic acid, CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH; PCP(s), PreCeramic Polymer(s); PDC(s), Polymer-Derived Ceramic(s); PHPS, PerHydroPolySilazane, (H$_2$Si–NH)$_n$; SOFC(s), Solid Oxide Fuel Cell(s); Spodumene, Li$_2$O·Al$_2$O$_3$·4SiO$_2$; TBC(s), Thermal Barrier Coating(s); TMIA, TriMethylIminoAlane; Xylene, C_8H_{10}; YSZ, Yttria-Stabilized Zirconia, xY$_2$O$_3$·yZrO$_2$; Zr(acac)$_4$, Zirconium acetylacetonate, Al(C$_5$H$_7$O$_2$)$_4$.

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stressed out. Gaps in the literature concerning processing optimization are pointed out, and suggestions are given for further development of PDCs produced by tape casting.

1 | INTRODUCTION

Tape casting is a standard wet-shaping process to produce thin ceramics.[1] Single dried tapes, with thickness ranging from 50 to 1000 μm,[2] are usually further submitted to lamination, debinding, and sintering.[3,4] Sintered tapes or laminates are applied mainly as electronic substrates,[5] multilayered capacitors,[6] multilayered packages,[7] piezoceramics,[8] and components for solid oxide fuel cells (SOFCs).[9] Novel tape casting applications include 3D printed laminates,[10] functionally graded materials (FGMs),[11] and porous membranes or supports.[12]

Typically, tape casting is carried out from slurries comprised basically by a ceramic powder, a liquid (organic solvent or water), and additives, such as dispersants, binders, and plasticizers.[13,14] Due to environmental and safety issues, the use of water-based systems is increasing in importance.[15–18] Nevertheless, the replacement of organic solvents by water presents some challenges in controlling the rheological and drying behavior of the slurry.[19,20] In addition, some raw materials, particularly nonoxides, can react adversely with water.[21] Thus, organic solvent-based tape casting remains used in the industrial shaping process for producing thin, flat ceramics.

Crystalline/amorphous, oxide/nonoxide, single/composite ceramics have been processed by tape casting. Alumina[22] and zirconia[23] are the most frequent tape cast oxides, not to mention many composites from them.[24] Silicon carbide and aluminum nitride are among the most common nonoxide ceramics shaped by this technique.[25–28] Nonetheless, glass-ceramics, particularly those related to low-temperature cofired ceramics (LTCC),[29] have been often processed by tape casting. Last but not least, Si-based polymers, such as polysiloxanes and polysilazanes, also known as preceramic polymers (PCPs),[30] have been also shaped by tape casting as precursors for fabricating Si-based ceramics, also known as polymer-derived ceramics (PDCs).[31]

Polymer-derived ceramics have been developed for over 50 years from polymeric precursors, which are able to be shaped by conventional polymer processing techniques such as injection molding or extrusion. PCPs are first submitted to shaping, followed by cross-linking and then by heating to temperatures high enough to consolidate them into non-oxide ceramics like SiC, Si_3N_4, AIN, BN, SiCN, or BCN,[32]

oxide ceramics like mullite,[33] or mixed non oxide ceramics like SiCO, SiCNO, or SiAlON.[34] The elimination of organic moieties occurring during pyrolysis results in the formation of an inorganic material. The ceramic material forms through a complex microstructural evolution, which depends on the PCPs molecular architecture and pyrolysis conditions, leading to nanosized crystalline phases embedded in an amorphous matrix.[35] The absence of a sintering step enables thermal processing at lower temperatures without the need for pressure, as compared with classical ceramic powder processing.[36] Furthermore, polymeric precursors can be converted into hybrid ceramics, when parts of the polymers remain unreacted.[37]

Shaping of PCPs by tape casting offers innovative composition, microstructure and mainly in terms of design possibilities, but poses new challenges in terms of process control. Conventional tape casting needs organic additives that are burned out in a subsequent step. If appropriately selected, PCPs have the advantage of a high ceramic yield (>70 wt.%) at moderate temperatures (as low as 1000°C).[38] However, the organic/inorganic transformation is accompanied by a density increase that gives rise either to a high shrinkage or to a high porosity. In this regard, reactive fillers might be used to form new ceramic phases and reduce both shrinkage and porosity.[39] Nevertheless, current equipment and process parameters for tape cast-based products must be eventually adjusted to fit the characteristics of ceramic precursors, for instance, with the use of a protective atmosphere.

Therefore, the aim of this review is focused on listing and discussing the efforts to manufacture PDCs using tape casting as a shaping technique. Interactions of system components and effects of treatment, particularly thermal stages, on final microstructure and properties are stressed out. Gaps in the literature concerning processing optimization are pointed out, and suggestions are given for further development of PDCs produced by tape casting.

2 | THE POLYMER-DERIVED CERAMICS ROUTE

2.1 | General concept

Chemical approaches based on well-defined precursors offer precise control over chemical compositions and

microstructures, as well as low processing temperatures and, therefore, they find a strong interest in the design of ceramic components. As an illustration, polymer-based routes to ceramics take advantage of precursor chemistry and structure to produce materials with a large range of functionality.[31,35,36] This route, better known as PDCs, is based on the synthesis of a preceramic polymer (PCP) from tailor-made molecular precursors. As-synthesized polymers provide a uniform chemical composition to the material at a molecular scale (Figure 1).

The main principle of the PDC route is to produce ceramics, in general nonoxide, through the thermo-chemical conversion of as-synthesized PCPs via four steps: shaping (to give the polymer a particular shape or form), curing (to further crosslink the polymer), pyrolysis (to transform the cured polymer into an amorphous ceramic), and optionally annealing (to crystallize the amorphous ceramics). This last step is optional because through an appropriate combination of the elements composing the ceramic (therefore the polymer) from which the binding energy is derived from covalent bonds, highly thermally stable amorphous ceramics, such as Si-B-C-N ceramics, can be designed.[40] Because of the possibility of controlling the cross-linking degree, the type of bonds linking monomeric units and the nature of functional groups in PCPs, polymers with tailored rheological properties can be designed.[41,42] This allows polymer shaping before curing to produce thin parts or complex architectures such as fibers, coatings, or dense monoliths.[43–45] If the PDC route is coupled with a macroporous network design method, at the polymer level, a control of the porosity can be achieved at various length scales.[46–50] Last but not least, the chemical characteristics (elemental composition and polymer network structure), the physical properties, and the reactivity (thermal and chemical) of the precursors can be adjusted to obtain, after pyrolysis and optional annealing, ceramics with the desirable composition and phase distribution. Hence, PDCs offer the possibility to prepare a vast range of functional materials.

Fundamental works have been conducted on the formation of inorganic (preceramic) polymers in the seventies[51,52] leading to commercial products. These pioneering works nicely marked the beginning of the new field of PCPs and illustrated the contribution of organosilicon precursor chemistry to PDCs. In the forthcoming years, there

has been much activity worldwide in the PDCs field, and the organosilicon precursor chemistry remained the highest active contributor to this topic, as illustrated in a majority of references.[36,53–69]

Organosilicon precursors, such as halogenosilanes, made an increasingly important contribution to the research development and manufacture of PDCs. For instance, chlorosilanes have been investigated for the synthesis of polysiloxanes by hydrolysis of Si-Cl bonds followed by subsequent condensation of the Si-OH intermediates to form Si-O-Si groups in polysiloxanes (Figure 2).[70] If ammonia is used instead of water, a similar reaction—known as ammonolysis—takes place and silylamines are formed, which can condense to give polysilazanes.[71] Concerning the synthesis of SiC precursors, the common approach, extensively developed by Yajima et al,[52] consists of the synthesis of polysilanes (PS), which are further converted into polycarbosilanes (PCS, $[SiR_1R_2CH_2-]_n$) and more precisely $[-SiH(CH_3)CH_2-]_n$ upon thermolysis through the Kumada rearrangement.[72] More complex structures containing Si, C, N, and/or O in the polymeric network such as polysilylcarbodiimides can also be synthesized.[73]
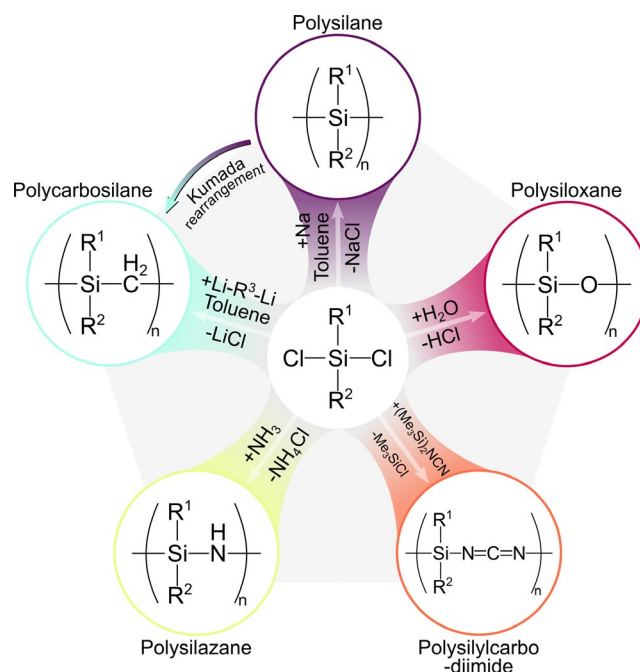

FIGURE 2 Organosilicon precursors in the Si-C-N-O system (R^1 or R^2 = H, CH$_3$, CH=CH$_2$, etc.)
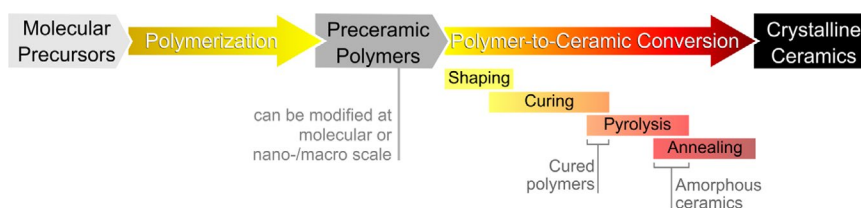

FIGURE 1 General procedure for the preparation of polymer-derived ceramics

Ceramics produced from these polymers such as the single-components SiC and Si_3N_4 (from polycarbosilanes and polysilazanes, respectively) display a number of favorable performance characteristics, which are appropriate for advanced component applications. More interestingly, these precursors can be modified at molecular and nano/microscale. This allows generating composites or nanocomposites made of (at least) one more phase in addition to SiC or Si_3N_4. Such materials often exhibit dramatically enhanced properties in terms of mechanical properties and/or structure stability.[74–78] In particular, this involves approaches based on the mixing of polymers with metal fillers.[79]

2.2 | The passive and active filler controlled polymer pyrolysis

Beside the use of ceramic powders as passive fillers, the use of active fillers in PCPs has been deeply investigated by Greil et al,[30,54,80] although pioneering works have been reported by Seyferth et al.[81,82] The first purpose of Greil's works was to investigate the limitations when producing polymer-derived bulk components. Indeed, the polymer-to-ceramic conversion (ie, polymer pyrolysis) involves a complex sequence of structural and chemical changes based on molecular rearrangements associated with the release of gaseous by-products.[55] This inherently induces both weight loss and a pronounced density increase from the polymers to the targeted ceramics. High volume shrinkage is therefore generated, which may result, if not controlled, in the collapse of the work piece that is produced. Through these reports, it has been suggested that the addition of active fillers such as metal powders to the polymers might significantly minimize the volume shrinkage (and porosity) that is developed upon pyrolysis of a polymeric green body due to the reaction of fillers with the gaseous and solid decomposition products.[83] Near net shape manufacturing becomes possible while the reactions allow influencing the ceramic composition by producing new phases, thus forming in general multicomponent ceramics.[84]

Seyferth et al[82] investigated this approach to prepare Si-C-W systems using polysilazanes and W powders. In the same study, Ti and Zr were combined with the polysilazane and pyrolyzed under Ar at 1500°C to form mixtures of TiN, ZrN, and SiC. Mixtures of metal (Me) powders with the respective polymers were prepared by ultrasonication in toluene, then they were removed from the solvent and dried. Therefore, this approach provides an easy access to composite materials, especially based on the chemistry of the organosilicon precursor. As an illustration, the pyrolysis of polycarbosilane (PCS) mixed with Ti, Zr, and Hf to 1500°C in a stream of argon delivered TiC/SiC composites, ZrC/SiC composites, and only HfC,

respectively.[85] Using a carbon-rich SiC precursor, for example $[Me_2SiC{\equiv}C]_n$, as a reagent, and Ti, Zr, and Hf as active fillers, different MeC/SiC compositions have been prepared. The pyrolysis of a Si-rich SiC precursor, for example $[(MeSiH)_{-0.4}(MeSi)_{-0.6}]_n$, under Ar at 1500°C led to TiC and Ti_5Si_3 phases. These results clearly emphasize the possibility to tune the composition of the composites through the chemistry of the organosilicon precursor. Based on these papers, it appears that SiC precursors represent appropriate reagents to successfully generate MeC/SiC composites via their mixture with metal powders. The use of nanoscaled metals such as titanium nanoparticles (Ti NPs) allows nanostructuring the composites and form nanocomposites.[86] As an illustration, allylhydridopolycarbosilane (AHPCS) was recently used as a reagent and Ti nanopowders as active fillers. Compared with PCS, AHPCS, with a nominal structure of $[Si(CH_2CH{=}CH_2)CH_2]_{0.1}[SiH_2CH_2]_{0.9}$,[87–89] can be processed much more easily: It is a liquid and the presence of allyl groups in its structure results in a precursor with an improved curing efficiency through hydrosilylation reactions. Therefore, an enhanced ceramic yield is obtained. During pyrolysis under Ar, Ti nanoparticles reacted with carbon-based gaseous by-products (methane, ethylene, etc.) that evolved from AHPCS during its decomposition and/or with carbon radicals to form TiC as a unique phase after pyrolysis to 800°C. The dominating crystalline TiC phase further crystallized in the temperature range 800-1000°C while marking the Ti_3SiC_2 and Ti_5Si_3 nucleation. Upon further pyrolysis above 1000°C, samples gradually formed composites made of TiC and SiC at 1400°C.

As aforementioned, the first purpose of the active filler controlled polymer pyrolysis (AFCOP) approach was to reduce the volume shrinkage when producing bulk components from PCPs. However, the use of active fillers has been mainly investigated to prepare composite and nanocomposite materials. An important aspect of the current AFCOP research is the extension of the underlying processing method to a wider range of shaping processes including tape casting. The following section describes the tape casting process with a special emphasis on the PDCs route coupled with passive and active fillers.

3 | TAPE CASTING USING PCPS: A CHRONOLOGICAL OVERVIEW

Table 1 lists the precursors, with respective active and/or passive fillers, mainly used in tape casting, to obtain polymer-derived ceramic tapes and laminates, as well as typical temperature ranges for cross-linking and pyrolysis of PCPs, and the respective ceramics phases obtained.

TABLE 1 Main raw materials, processing parameters, and products for manufacturing of PDCs from cast tapes

Preceramic precursors	Active fillers	Passive fillers	Cross-linking temperatures (°C)	Pyrolysis temperatures (°C)	Polymer-derived ceramics	Ref.
Trimethyliminoalane (TMIA)[a]	Al	AlN		600-700	AlN	[90]
Polysiloxanes (MK, MSE100, H62C)	Si	SiC	130	1200-1600	SiC, Si_2ON_2	[91]
Polysiloxanes (MK, H62C)[b]	Si	SiC	130	1400-1600	SiC, Si_2ON_2	[92]
Polysiloxanes (MK, MSE100, H44)[c]	Si	SiC	270	1000	SiOC	[93]
Polysiloxanes (MK, H62C)	Si	Al_2O_3	120	1400-1500	SiOC, SiC, Si_2ON_2	[94]
Polysilazane (Ceraset SN)[d]		Si_3N_4 (Y_2O_3, $Al_2O_{3)}$	150	1800	Si_3N_4	[95]
Polysiloxanes (MK, H62C)	Si	SiC	120-150	1000-1500	SiC, Si_2ON_2, MFI zeolite	[96]
Polysiloxanes (MK, H62C)	Si	SiC	120	950-1200	SiOC, SiC	[97]
Polysiloxanes (MK, H62C)	Si, Al		120	1000-1500	SiC, SiAlON, AlN, Al_2O_3	[98]
Polysilazanes (PHPS, Durazane 1800)[e]	$ZrSi_2$	YSZ	110	500, 1000	ZrO_2, YSZ	[99]
Polysiloxane (MK)		β-eucryptite, SiC	200	800-1100	β-eucryptite, β-spodumene, SiC	[100]
Polysiloxanes (H44, MK)		SiC	25	600, 1000	SiOC	[101]
Polysiloxanes (H44, MK)	$MoSi_2$	Graphite, carbon black, $NiCl_2$, $CoCl_2$	25	500, 600, 1000, 1200, 1500	SiOC	[102]

[a]TMIA used as precursor/binder for lamination of commercially available AlN cast tapes.

[b]MK, MSE100, H62C used as precursors/binders for centrifugal casting of multilayered tubes.

[c]MK and MSE100 used as precursors for tape casting; H44, for fabrication of a foam core.

[d]Ceraset SN used as precursor/binder for lamination of Si_3N_4 water-based cast tapes.

[e]PHPS used as precursor/binder for bond coat; Durazane, for top coat, respectively, on steel substrates.

Preceramic polymers associated to cast tapes were mentioned by Bitterlich et al in 2001.[90] They used trimethyliminoalane (TMIA) and AlN powder as an interlayer binder paste for laminating commercial AlN cast tapes into multilayered stacks. This work applied an adapted method of synthesis of AlN from a polymeric precursor (polyiminoalane), in which metallic aluminum is electrolytically dissolved. After pyrolysis, AlN nanopowder is produced (mean crystallite size of ~30 nm).[103] The laminates were pyrolyzed (600-700°C) and sintered in nitrogen atmosphere at 1800°C and 2 MPa, using AlN plates as a load to avoid warping. Sintered AlN laminates presented residual interlayer porosity, which led to lower thermal conductivity values when compared to single AlN tapes.

To the best of our knowledge, the earliest work found in the literature about ceramic tapes manufactured from PCPs was carried out by Cromme et al in 2002.[91] Active (Si) and passive (SiC) filler loaded silane/polysiloxane slurries were used for manufacturing ceramic tapes. Single tapes and multilayer laminates were submitted to cross-linking at 180°C and pyrolysis in Ar or N_2 atmosphere

at 1200-1600°C. Increasing the Si to SiC filler ratio led to higher porosities in Ar and to lower porosities in N_2, respectively. The pyrolyzed SiC/Si_2ON_2 tapes were characterized with respect to their geometrical accuracy, mechanical stability, and porosity.

Melcher et al[92] manufactured thin layers by centrifugal casting of a polysiloxane/filler suspension to produce ceramic tubes in the system SiOC(N). Since this method has similarities with tape casting of PCPs in terms of slurry composition and thickness of thin films obtained (100-2000 μm), it was included in this overview. In this case, Si and SiC powders were dispersed in polyorganosiloxane/MTES solutions. The samples were cross-linked at 130°C and pyrolyzed in Ar or N_2 at 1400-1600°C. The Si_2ON_2-SiC tubes were characterized in terms of shape stability, microstructure, and bending strength.

Hoefner et al[93] fabricated light weight ceramic sandwich structures with a foam core and surface cover tapes from filler loaded preceramic polymer systems. A polysiloxane loaded with Si/SiC filler powders was tape cast. Another polysiloxane-filler blend was foamed in situ between two green tapes

by a controlled heat treatment (blowing, curing, and stabilization) at 270°C. The sandwich element was subsequently pyrolyzed at 1000°C in N_2 atmosphere to form a SiOC microcomposite material. The microstructure and the mechanical properties of the sandwich structure were characterized.

Rocha et al[94] prepared suspensions with different contents of polysiloxanes and fillers (Si and Al_2O_3). The cured tapes were pyrolyzed in N_2 atmosphere at 1400°C/2 hours and 1500°C/2 hours, converting the material to PDCs in the SiAlONC system. The products were characterized according to phase formation, microstructure, density, and thermal conductivity.

Bitterlich et al[95] used PCPs to produce laminated Si_3N_4 tapes, as previously reported in a former work for AlN laminates.[90] This time, the authors used a liquid polysilazane and a powder mixture based on Si_3N_4 to obtain a binder paste, with variable precursor content, for laminating water-based Si_3N_4 cast tapes into multilayered stacks. Pyrolysis and binder burnout were carried out simultaneously under a flowing N_2 atmosphere 150°C for 1 hour. The pyrolyzed tapes were sintered at 1800°C for 1 hour under a N_2 pressure of 5 MPa. Microstructure, mechanical strength, and thermal diffusivity data of Si_3N_4 stacks laminated with precursor pastes were discussed.

Schefler et al[96] manufactured composite membranes by partial formation of zeolite on PDC tapes. The tapes, which act as mechanical support and chemical source for the zeolite framework, were prepared by tape casting with a slurry composed of polysiloxanes, and particles of inert (SiC) and reactive (Si) fillers, based on the method first described by Cromme et al in 2002.[91] The partial transformation of Si, contained in the tapes, into zeolite crystals was carried out by hydrothermal treatment of the tapes in an aqueous, alkaline solution containing a structure directing agent at 150°C for up to 96 hours. Pyrolysis was performed in Ar or N_2 atmosphere at 1000-1500°C. The products were subjected to solid state characterization, porosimetry, and chemical analysis.

Functionally graded ceramics (FGCs) were fabricated by Steinau et al[97] from laminated preceramic polymer cast tapes, consisting of MK, H62C, MTES, Si, and SiC. After drying at room temperature, the tapes were partially cross-linked at 120°C. Lamination was carried out by warm pressing at 230°C. In order to avoid cracking and warpage, rate controlled pyrolysis of the laminates was applied up to 950°C in flowing N_2. After this step, the samples were treated at 1200°C at an N_2 pressure of 1 MPa to improve the mechanical properties. Laminates, each consisting of eight layers with graded and ungraded grain size, were produced and characterized in terms of mechanical behavior.

Commercial polysilsesquioxanes filled with Si and Al particles were tape cast by Rocha et al[98] and pyrolyzed in N_2 atmosphere at various temperatures up to 1500°C. Substrates converted to SiC/SiAlON composites were characterized with respect to their microstructures, phase compositions, density, porosity, and thermal expansion coefficient.

Barroso et al[99] developed a double-layered PDC-based thermal barrier coating (TBC) system consisting of a polysilazane bond coat, and a top coat formed by the combination of passive (YSZ) and/or active($ZrSi_2$) fillers with a (organo) silazane. The top coat was applied on steel substrates by tape casting, due to its very good reproducibility and low suspension consumption. The resulting coatings and their components, after solvent removal at 110°C, were pyrolyzed for 1 hour at 500 and 1000°C, respectively, for the bond and top coat and then investigated by TGA, XRD, SEM, and EDX.

Fedorova et al[100] used a polysiloxane filled with β-eucryptite as a negative thermal expansion (NTE) filler and/or SiC as a second filler for obtaining PDC tapes with higher strength and controlled coefficient of thermal expansion (CTE). After drying, cross-linking was carried out stepwise from 40 to 200°C and pyrolysis was held at temperatures between 800 and 1100°C under argon flow. Microstructure, phase composition, and mechanical behavior were analyzed.

Nishihora et al[101] applied tape casting to produce porous hybrid and SiOC ceramic tapes using polysiloxanes as polymeric binders. SiC particles were used as inert fillers, and macroporosity was adjusted by varying the azodicarbonamide (ADA) content from 0 to 30 wt.%. Cross-linking was conducted at room temperature, and decomposition of the polysiloxanes at 600°C resulted in the generation of micropores and a predominant hydrophobic behavior; at 1000°C, meso/macroporosity was observed with increased hydrophilicity. The porous tapes with tunable surface characteristics and structure are promising for applications as membranes in microfiltration (0.1-10 µm).

Silva et al[102] prepared porous SiOC electrodes by tape casting for potential application in bioelectrochemical systems. Some of the raw materials (PCPs, cross-linkers, solvent, and pore formers) as well as the preparation steps were similar to the approach aforementioned.[101] Nevertheless, the fillers employed in this study were composed by conductive phases such as graphite, carbon black, $MoSi_2$, metal salts, and grids. The room temperature cross-linked tapes were pyrolyzed under N_2 atmosphere in the range of 500-1500°C. Macroporosity exhibited a broad distribution in the range of 0.1-100 µm with main peaks in the region of 0.1-1.0 µm. Increasing pyrolysis temperature shifted the pore size distribution to the upper range.

4 | MATERIALS AND METHODS OF PCPS FOR TAPE CASTING

Basically, two classes of PCPs have been used so far as a precursor and binder in the tape casting process: polysiloxanes

and polysilazanes. Main additives, such as catalysts, and optional fillers or porogenic agents were commonly employed for adjusting shrinkage and porosity to desired levels.

Conventional unit operations, such as milling/mixing, degassing, and cutting, as well as thermal treatments, which may or not involve chemical reactions, such as cross-linking, drying, and pyrolysis, were normally described for the manufacturing of precursor-based tapes. A typical flowchart for this process is shown in Figure 3.[101] Relevant details on materials and processing are given in this section.

4.1 | Precursors, solvents, catalysts, and fillers

Table 2 summarizes the slurry compositions based on PCPs, usually with active and/or passive fillers, with addition of solvents and cross-linking catalysts, used to obtain thin films (100-2000 μm), such as tape casting and processes alike.

Bitterlich et al[90] applied trimethyliminoalane (TMIA) as a binder paste to join AlN cast tapes into multilayered laminates. Solvents (dimethylformamide, DMF, and formamide, FA) were used to dissolve TMIA. Metallic Al, as active filler, was present in the synthesis of TMIA, and AlN powder was added to the slurry as passive filler. A volume ratio of 47:53 of the precursor to the AlN powder was employed.

Cromme et al[91] prepared slurries containing commercially available polysiloxanes (MK, MSE 100, H62C), two silanes as solvents (MTES, MTMS), and Si ($d_{90} = 2$ μm) and SiC ($d_{50} = 2$ μm) powders as fillers. In this case, either 10 vol.% Si + 30 vol.% SiC or 30 vol.% Si + 10 vol.% SiC was used. Two catalysts were used, respectively, for low (<100°C) and high temperature (>100°C): aluminum acetylacetonate and oleic acid (0.5 vol.% each).

In the work of Melcher et al,[92] a solid precursor (MK, melting point of 42°C) and/or a liquid precursor (H62C) was diluted in methyltriethoxysilane (MTES). Cross-linking catalysts (aluminum acetylacetonate and oleic acid) and the filler powders (Si, $d_{90} = 10$ μm and SiC, $d_{50} = 2$ μm) were added stepwise.

For tape fabrication, Hoefner et al[93] dissolved MK powder in MTMS (solvent) and MSE100 (liquid resin) was added subsequently with curing agents, oleic acid, and Al (acac)$_3$. The solution was stirred for 10 minutes, and then, Si ($d_{50} = 7.5$ μm) and SiC ($d_{50} = 1.6$ μm) were added as powder fillers. The filler content of the tapes was kept constant at 58 wt%.

Rocha et al[94] used two commercial polysiloxanes (MK and H62C), MTES as a solvent, and Zr(acac)$_4$ and oleic acid as catalysts. Fillers, active (Si, $d_{50} = 3$ μm) and passive (Al$_2$O$_3$, $d_{50} = 7.5$ μm), were added in a fixed concentration of 40 vol%.

The pastes used for lamination of Si$_3$N$_4$ green tapes by Bitterlich et al[95] consisted of a liquid polysilazane (Ceraset SN, Honeywell, formerly AlliedSignal, USA) with 1 wt% dicumyl peroxide as a catalyst, terpineol (C10H18O) as a solvent, a powder mixture (Si$_3$N$_4$, $d_{50} = 0.4$ μm, with 6 wt% Y$_2$O$_3$ and 4 wt% Al$_2$O$_3$ as sintering aids), and 1 wt% dispersant related to the powder content (polycarbonate-based, Trusan 450).

Schefler et al[96] followed a former procedure[91] to prepare slurries with polysiloxanes (MK, H62C), a silane (MTES) as solvent, and Si ($d_{50} = 8$ μm) and SiC ($d_{50} = 2$ μm) powders as fillers. Two catalysts were used: Al (acac)$_3$ and oleic acid (0.5 vol.% each). The slurry consisted of 60 vol.% liquid and 40 vol.% solids with a solid filler ratio adjusted either to 30 vol% Si and 10 vol% SiC or to 10 vol.% Si and 30 vol.% SiC.

Steinau et al[97] used a combination of PCPs (MK, H62C) with MTES (solvent), catalysts (Al(acac)$_3$, oleic acid) with 40 vol% solids relative to 10 vol% active filler (Si, 10 μm), and 30 vol% passive filler (SiC), from a formulation of the same group (1). In this case, the average size of SiC particles (d_{50}) was varied from 1.5 to 8.5 μm, though.

Rocha et al[98] employed commercial polysilsesquioxanes (MK, H62C) dissolved in MTES with two catalysts (Zr(acac)$_4$, oleic acid). Si powder ($d_{50} = 3.1$ μm) and Al powder ($d_{50} = 30$ μm) were added as reactive fillers. Three different slurries were prepared with 30 vol% active fillers, 24 vol% MTES, 1 vol% catalysts, and variable relative amounts of fillers and precursors.

Barroso et al[99] selected perhydropolysilazane (PHPS, NN120-20,20 wt.% in di-n-butylether) and liquid (organo) silazane (Durazane 1800, Merck, formerly AZ Electronic Materials, Germany) as preceramic precursors for coatings on steel substrates. Dicumyl peroxide (DCP) was added as a cross-linking catalyst at low temperatures (3 wt.%). Yttria-stabilized zirconia (YSZ, $d_{50} = 0.3$ μm) and zirconium disilicide (ZrSi$_2$, $d_{50} = 1.5$ μm) were chosen, respectively, as passive and active fillers, with volumetric fractions from 59% to 73%, in different combinations. Suspensions of each powder in di-n-butylether (DBE), using Disperbyk 2070(BYK-Chemie, Germany) as dispersant agent, were prepared and mixed with Durazane 1800 to obtain the mixtures.

Fedorova et al[100] employed a commercially available polysiloxane (MK) to prepare slurries with 49.5 vol% of fillers, related to different proportions of synthesized β-eucryptite (11 μm) and commercial SiC (3.7 μm). Oleic acid and Al (acac)$_3$ were used as catalysts for enhancing cross-linking, respectively, at temperatures lower and higher than 100°C.

Nishihora et al[101] used powders of methyl-phenyl polysiloxane (Silres H44) and methyl polysiloxane (Silres MK), both from Wacker (Germany), as binders and ceramic precursors. Two SiC powders ($d_{50} =6.5$ and 4.5 μm) were used as inert fillers corresponding to 59 wt% of the mixture, and azodicarbonamide (ADA) was used as pore former. Imidazole was applied as a cross-linking catalyst for the polysiloxanes.

Xylene was the solvent for the polysiloxanes and the liquid medium to disperse the other components.

Silva et al[102] employed a similar approach and raw materials (PCPs, cross-linkers, solvent, and pore former) than Nishihora et al[101] Nevertheless, the fillers in this study were conductive phases such as graphite, carbon black, metal salts, and grids. Molybdenum disilicide ($MoSi_2$) and azodicarbonamide (ADA) were added for controlling shrinkage and inducing formation of pores, respectively. The fillers content varied from 12 wt% ($MoSi_2$ only) to 42.2 wt% (29.2 wt% graphite + 8 wt% $MoSi_2$ + 5 wt% carbon black or metal salt).

4.2 | Tape casting parameters

The first step comprises the slurry preparation, which was conducted normally at room temperature using mechanical[91] or magnetic stirrer,[101] in one or more steps. Alternatively, ball milling was applied, as in the case of Hoefner et al,[93] who used Si_3N_4 balls in a 1-liter mill for 24 hours, or Steinau et al,[97] who employed ZrO_2 balls for 12 hours at 60 rpm. In another approach, the slurries were treated for 10 minutes with an ultrasonicator followed by mixing in a planetary centrifugal mixer for 20 minutes at 2000 rpm.[100] Degassing was eventually performed by applying vacuum (0.005 MPa for 3 minutes).[91]

The slurries were normally cast over a polyethylene terephthalate carrier film (Mylar), usually silicone-coated. Using variable doctor blade gaps, with casting speed up to 700 mm/min,[97] led to green tape thickness from 0.1 mm[91] to 1.5 mm.[100,101] Alternatively, a film of PCP slurry was applied as a top coat with a doctor blade on a steel precoated substrate at room temperature in air, obtaining green films up to 120 μm thick.[99]

Multilayered materials were prepared either by sequential casting or by thermopressing. In the first case, a second

TABLE 2 Typical compositions of preceramic polymer slurries for tape casting
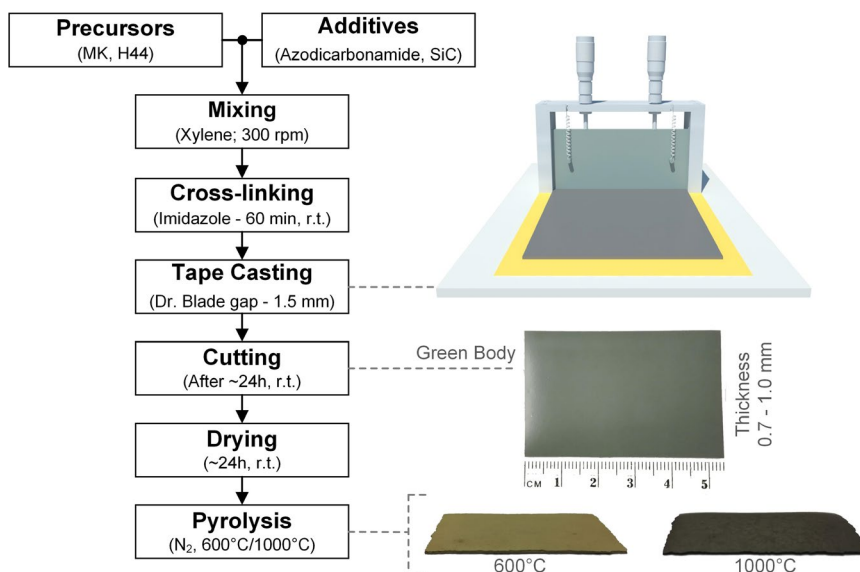
Preceramic precursors	Solvents	Active fillers	Passive fillers	Cross-linking catalysts	Filler contents (%)	Ref.
Trimethyliminoalane (TMIA)[a]	Dimethylformamide (DMF), formamide (FA)	Al	AlN		53 vol% (AlN)	90
Polysiloxanes (MK, MSE 100, H62C)	Silanes (MTES, MTMS)	Si	SiC	$Al(acac)_3$, oleic acid	40 vol%	91
Polysiloxanes (MK, MSE 100, H62C)[b]	Silane (MTES)	Si	SiC	$Al(acac)_3$, oleic acid	54.6-58.5 wt%	92
Polysiloxanes (MK, MSE100)	Silane (MTMS)	Si	SiC	$Al(acac)_3$, oleic acid	58 wt%	93
Polysiloxanes (MK, H62C)	Silane (MTES)	Si	Al_2O_3	$Zr(acac)_4$, oleic acid	40 vol%	94
Polysilazane (Ceraset SN)[c]	Terpineol		Si_3N_4 (Y_2O_3, Al_2O_3)	Dicumyl peroxide	38.5-41.9 vol%	95
Polysiloxanes (MK, H62C)	Silane (MTES)	Si	SiC	$Al(acac)_3$, oleic acid	40 vol%	96
Polysiloxanes (MK, H62C)	Silane (MTES)	Si	SiC	$Al(acac)_3$, oleic acid	40 vol%	97
Polysiloxanes (MK, H62C)	Silane (MTES)	Si, Al		$Zr(acac)_4$, oleic acid	30 vol%	94
Polysilazane (Durazane 1800)	Di-n-butylether	$ZrSi_2$	YSZ		59-73 vol%	99
Polysiloxane (MK)			β-eucryptite, SiC	$Al(acac)_3$, oleic acid	49.5 vol%	100
Polysiloxanes (H44. MK)	Xylene		SiC	Imidazole	59 wt%	101
Polysiloxanes (H44. MK)	Xylene	$MoSi_2$	Graphite, carbon black, $NiCl_2$, $CoCl_2$	Imidazole	12-42.2 wt%	102

[a]TMIA used as precursor/binder for lamination of commercially available AlN cast tapes.

[b]MK, MSE100, H62C used as precursors/binders for centrifugal casting of multilayered tubes.

[c]Ceraset SN used as precursor/binder for lamination of Si_3N_4 water-based cast tapes.

FIGURE 3 Typical manufacturing flowchart of tape casting-shaped preceramic polymers, with partial (600°C) or complete pyrolysis (1000°C), leading to hybrid or pure polymer-derived ceramics, respectively, where r.t. = room temperature.[101] (reproduced with permission)

layer was cast on the first one, and the procedure was repeated up to reaching the number of desired tapes, normally up to 3.[91,94]

After casting, the tapes were dried at room temperature for 12 hours[91] up to 72 hours[93] prior to cutting into pieces, from 25 mm × 25 mm[94,96] to 210 mm × 105 mm.[97] Sometimes, drying was performed in a saturated solvent atmosphere to avoid cracking.[93]

Thermopressing was eventually applied to produce laminates simultaneously with cross-linking, for instance, at 90°C and 0.3 MPa,[91] or at 230°C and 25 MPa for 20 minutes.[97] In addition, a surface modification might be applied to the cast tapes, such as a functionalization with a zeolite layer.[96]

4.3 | Thermal treatment parameters

Cromme et al[91] carried out cross-linking of polysiloxanes stepwise by heating to 60, 90, and 130°C as maximum temperature. Pyrolysis was performed in an electrically heated furnace with a sealed alumina tube at temperatures in the range of 1200-1600°C. Flowing Ar or N_2 atmosphere (3.5 L/min) was applied. Heating and cooling rates were adjusted to 3°C/min with holding times from 4 to 16 hours at the peak temperature.

In the work of Melcher et al,[92] polysiloxanes were pyrolyzed in Ar or N_2 atmosphere in an electrical furnace. A heating and cooling rate of 3°C/min and a dwell time of 4 hours at maximum temperature ranging from 1400 to 1600°C were applied.

For the sandwich structure fabrication, Hoefner et al[93] proceeded with pyrolysis in a preheated furnace in air at 270°C for 2 hours. The samples were pyrolyzed at 1000°C under flowing N_2. A heating rate of 3°C/min was applied up to 500°C, with a hold of 2 hours, and then up to 1000°C.

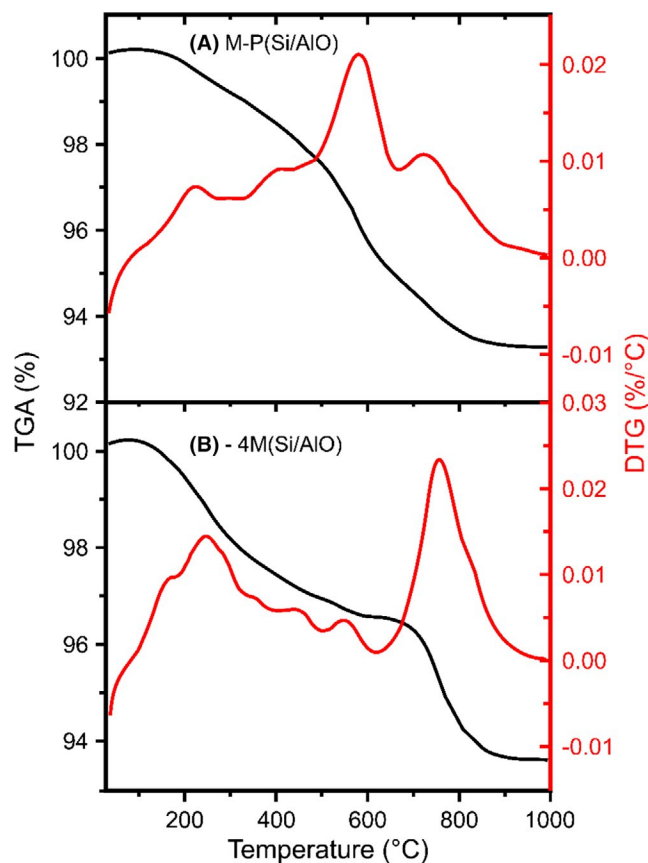Rocha et al[94,98] carried out the cross-linking of the substrates stepwise (60°C/1-4 hours, 90°C/1-4 hours and

FIGURE 4 TG and DTG curves of tapes with 40 vol% fillers (20 vol% Si + 20 vol% Al_2O_3) with: (A) 41 vol% MK [4M(Si/AlO)]; (B) 20.5 vol% MK + 20.5 vol% H62C [M-P(Si/AlO)][94] (adapted and reproduced with permission)

120°C/4 hours) to avoid the formation of cracks and bubbles caused by evaporation of the condensation products. Pyrolysis was performed in a tubular electric furnace in flowing N_2 up to 1400 and 1500°C for 2 hours at the peak temperature. The

heating rate was 3°C/min, and the cooling rate from 3 to 10°C/min. The loss of mass of the substrates with either 41 vol% MK or 20.5 vol% MK + 20.5 vol% H62C, both with 20 vol% Si + 20 vol% Al_2O_3, was monitored by TG up to the temperature of 1000°C, in N_2 atmosphere (Figure 4). The total mass loss at the end of the analysis is practically the same for the two substrates (~6.5%). However, this loss occurs differently in function of the composition of each polymer phase.

To obtain samples with different porosity and different amounts of Si, available for crystallization, Schefler et al[96] submitted the green tapes to pyrolysis at 1000, 1200, 1350, and 1500°C in Ar or in N_2 atmosphere. After pyrolysis at 1500°C, they observed that the relative Si amount, measured by XRD, decreases dramatically in all samples. The oxygen content, as measured by elemental analysis, also decreased with increasing pyrolysis temperature, independently from the atmosphere. This effect is attributed to the SiO2 constituent of the PDC matrix which undergoes a set of complex high-temperature reactions during pyrolysis in both atmospheres.

Steinau et al[97] employed a tailored two-step pyrolysis approach in N_2 atmosphere. The first part, from 20 to 950°C, was conducted in an electric heated furnace; in the second step, the material was heated at 3°C/min to 1200°C with a dwell time of 3 hours at 1 MPa N_2 in a gas pressure furnace.

Rocha et al[98] carried out pyrolysis of the stacked tapes in four thermal schedules (1000°C/1 hours, 1350°C/2 hours, 1400°C/2 hours, and 1500°C/2 hours) with heating and cooling rates of 3°C/min.

In the case of tape-coated steel substrates, a top coat polysilazane composite system was pyrolyzed in air at 1000°C/1 hour with heating rate of 3°C/min. A first pyrolysis for the bond coat substrate was performed in air at 500°C/1 hour with heating rate of 5°C/min to improve the bonding between the top and bond coating.[99]

Fedorova et al[100] employed a stepwise cross-linking schedule by heating the samples to 40, 60, 90, 120, 160, and 200°C with a heating rate of 1°C/min, for 4 hours each step. The tapes were then pyrolyzed at temperatures between 800 and 1100°C under flowing Ar. Heating and cooling rates were adjusted to 1 and 4°C/min, respectively.

Finally, Nishihora et al[101] pyrolyzed tapes at 600 and 1000°C in N_2 atmosphere, and Silva et al[102] pyrolyzed at 500, 600, 1000, 1200, and 1500°C under N_2. The heating rate was 120°C/h to 100°C below the final temperature and 30°C/h to the final temperature with a dwelling time of 4 hours.

5 | CHARACTERIZATION OF PCPS FOR TAPE CASTING

PCPs represent the key compound in the design of advanced ceramics via tape casting, so that they have to be characterized as such in the liquid (resin) or solid form, respectively,

in terms of rheological and mechanical properties. For PCPs used for tape casting, basically only the rheological behavior was (partially) studied so far. Nonetheless, additives (solvents and catalysts) and primarily solid loads (fillers) play an important role in modifying the rheology of liquid/solid mixtures and mechanical properties of intermediate (after cross-linking, before pyrolysis) polymer-based composites. A summary follows in this section.

Rheological measurements of the polymer/filler slurries were carried out by Cromme et al[91] using a rotational viscometer with shear rates from 10 to 500 s^{-1}. Figure 5 shows a typical flow curve of a mixture 60 vol.% polymers/solvents/catalysts + 10 vol.% SiC + 30 vol.% Si. The decreasing slope of the viscosity curve for increasing shear rate corresponds to a shear thinning behavior at shear rates <10 s^{-1} and >100 s^{-1}, with a Newtonian plateau of 2 Pa·s between 10 and 100 s^{-1}. This behavior is suitable for the casting process, although the viscosity value was slightly higher than a typical viscosity for traditional tape casting slurries, around 1 Pa·s, at the same shear rate range.[104]

The rheological behavior of the tape casting slurry must be adjusted according to the respective tape casting parameters. For instance, the viscosity of ceramic slurry is usually lower for the casting of thin tapes (ie, 10-50 μm) corresponding to Newtonian behavior in comparison with the casting of thick tapes (ie, 0.5-1 mm) corresponding to shear-thickening behavior. In case of preceramic polymer, the slurry viscosity required should be low enough to limit the stresses during drying of cast tapes. The main drawback of the application of PCPs is linked to the large shrinkage of tapes during drying and further heat treatments. This large shrinkage may lead to significant internal stresses and deformations, which may induce cracking of tapes.
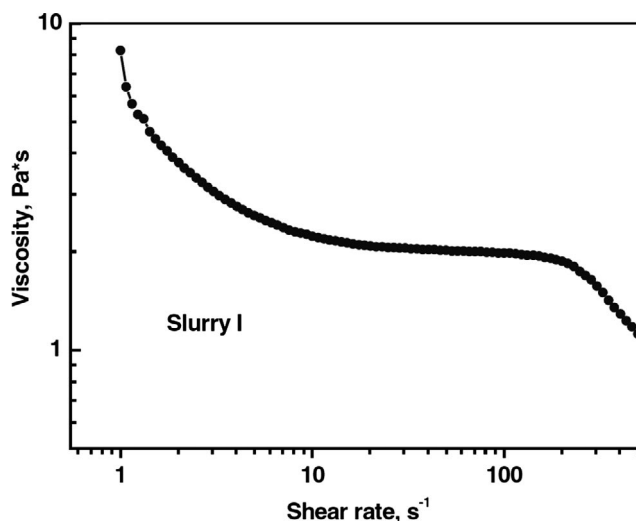

FIGURE 5 Typical flow behavior of preceramic polymer-based slurry for tape casting, comprised of precursors, solvents, catalysts, and fillers.[91] (reproduced with permission)

Fedorova et al[100] observed also a shear thinning behavior, however with even higher viscosities. Values of 50-20 Pa·s were measured, at shear rates from 10 to 100 s^{-1}, respectively, for a preceramic polymer/filler mixture with 40 vol% β-eucryptite:SiC (volume ratio of 2:1).

Melcher et al[92] also evaluated the rheological behavior of slurries comprising Si and SiC fillers dispersed in polysiloxane/ MTES solutions. They found that the centrifugal casting process could be conducted at room temperature between 1000 and 2600 rpm without sedimentation of the fillers when the viscosity was between 1 and 10 Pa·s in the shear rate range of 10-100 s^{-1}.

Rheological studies for optimizing the behavior of screen-printed pastes used as preceramic polymer binder for laminating Si$_3$N$_4$ cast tapes were also performed.[95] A viscosity of 6-10 Pa·s at a shear rate of 50 s^{-1} was found to be best suited for the screen printing process. The thickness of the dried screen-printed layers was around 30 μm, comparable to a thin cast tape.

6 | CHARACTERIZATION OF TAPE CAST PDCS

PCPs shaped by tape casting are further submitted to thermal treatments at different temperature ranges, leading either to a polymer/ceramic composite or to a "pure" polymer-derived ceramic. Obviously, structural and microstructural characterization has been carried out for those PDCs, as well as the relationship between their structure, properties and inferred applications have been well presented and discussed. A short summary on this issue is presented in this section.

6.1 | Phase composition

Figure 6 shows a typical composition, as detected by X-ray diffraction (XRD) of a polysiloxane-based tape submitted to thermal treatment at 1600°C in different atmospheres, as obtained by Cromme et al.[91] A strong influence of the furnace atmosphere on phase formation can be inferred: For pyrolysis in Ar, only SiC was identified, and for pyrolysis in N$_2$, both SiC and Si$_2$ON$_2$ could be found. Melcher et al,[92] working basically with the same system, found that after pyrolysis at 1400°C, metallic Si and SiC were detected, while pyrolysis at 1550 and 1600°C led to a complete conversion of the Si filler into Si$_2$ON$_2$-SiC composite ceramics.

According to Rocha et al,[94] after pyrolysis at 1400°C (Figure 7A) there is still metallic Si, indicating that the β-SiC phase, identified in the diffractogram of this sample, can be derived from the carbothermal reduction reaction between polymer decomposition products. The amorphous SiO$_2$ phase resulting from the pyrolysis process is formed in the range of carbon-rich composition. After pyrolysis at 1500°C, the phases identified by XRD (Figure 7B) are Al$_2$O$_3$, mullite, β-SiC, and Si$_2$ON$_2$ or O'-SiAlON, which is a Si-rich phase
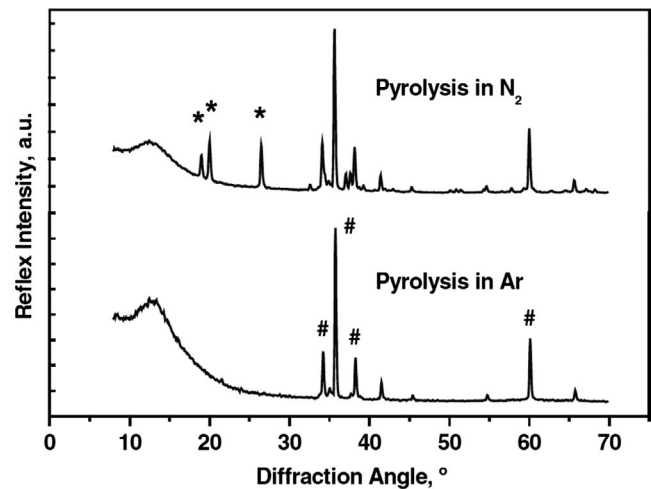

FIGURE 6 Typical phase composition of polymer-derived ceramics after pyrolysis of polysiloxane with Si/SiC fillers at 1600°C in different atmospheres. SiC: #; Si$_2$ON$_2$: *[91] (reproduced with permission)
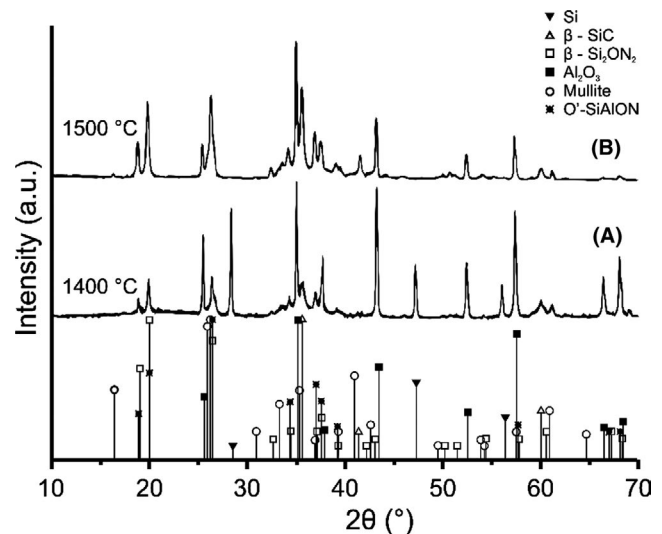

FIGURE 7 Phase composition of polymer-derived ceramics after pyrolysis of polysiloxanes with Si/Al$_2$O$_3$ fillers in N$_2$ atmospheres for 2 h at: (A) 1400°C and (B) 1500°C.[94] (adapted and reproduced with permission)

derived from Si$_2$ON$_2$. No Si peaks were identified, indicating that at this temperature, the active filler reacted completely.

When two active fillers are added to polysiloxanes, complex reactions take place during pyrolysis,[98] naturally as a function of temperature. At 1500°C/2 hours, a marked reduction in Si content and significant increase in β-SiAlON on substrates with Al:Si ratio of 1:1 is observed (Figure 8). SiAlON polytypoids were identified in all compositions, mainly on substrate with higher amount of Al (M(Si-3Al)). These polytypoids can be formed by direct reaction of AlN and SiO2, originated from the decomposition of polymer matrix.

Fedorova et al[100] analyzed the interaction of SiC particles with β-eucryptite, used as fillers, and the SiO_2 constituent of the PDC matrix at different pyrolysis temperatures. The diffusion of silica from the matrix into β-eucryptite particles was inhibited by SiC due to a reduced contact area, which preventing eucryptite from transformation into β-spodumene. In the samples with high SiC content, no β-spodumene was detected.

6.2 | Surface characteristics of hybrid and pure PDCs

Hydrophilicity and hydrophobicity characteristics of the pyrolyzed tapes were determined by Nishihora et al[101] from measurements of the vapor adsorption of polar (water) and nonpolar

FIGURE 8 Phase composition of polymer-derived ceramics after pyrolysis of polysiloxanes with two active fillers (Si/Al, in different proportions) in N_2 atmosphere for 2 h at 1500°C.[98] (reproduced with permission)

(n-heptane) solvents (Figure 9). The surface characteristic depends basically on the pyrolysis temperature: Beyond 600°C, most of the remaining hydrophobic methyl groups of the preceramic polymer are decomposed, resulting in higher hydrophilicity.[105] Both the SiC particle size and the amount of pore former (azodicarbonamide, ADA) do not play a relevant role in terms of hydrophilic/hydrophobic character, when compared to the pyrolysis temperature (600 and 1000°C).

6.3 | Porosity and pore morphology

The peak temperature and atmosphere of pyrolysis of PCP cast tapes play an important role on porosity and pore size. As an example, for pyrolysis of polysiloxane with 40 vol.% fillers at 1600°C in Ar, the highest values of both porosity (45%) and average pore radius (2.05 μm) were obtained, particularly for the 30 vol.% Si + 10 vol.% SiC. For the same composition, when the tapes were pyrolyzed at 1400°C in N_2, the values of both porosity (13.2%) and average pore radius (0.025 μm) were much lower.[91]

Rocha et al[94] found relatively high porosity values for pyrolyzed substrates (12 to 22%), depending on the composition and the heat treatment. The pyrolyzed samples at 1500°C presented, in general, higher density than those of the pyrolyzed substrates at 1400°C. The higher concentration of Si in the substrates provides a slight reduction in porosity, and this effect is more evident in the pyrolyzed substrates at 1500 °C.

Typical pore morphology in active filler pyrolyzed substrates can be seen in Figure 10.[94] The central layer of the substrate, with higher concentration of Si, presents higher density due to the reaction of Si with N_2, forming Si_2ON_2. The same figure contains enlargements of regions of the substrate layers, allowing better visualization of the differentiated microstructure depending on the composition of the substrate.
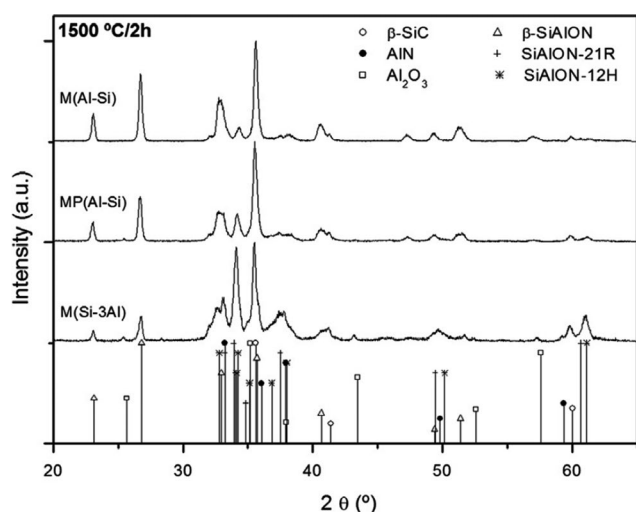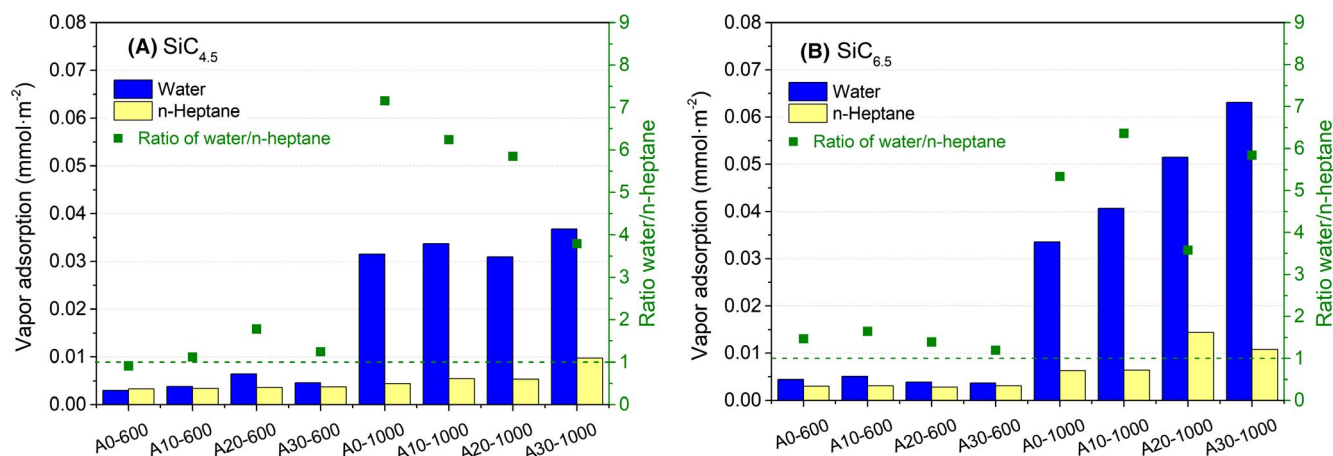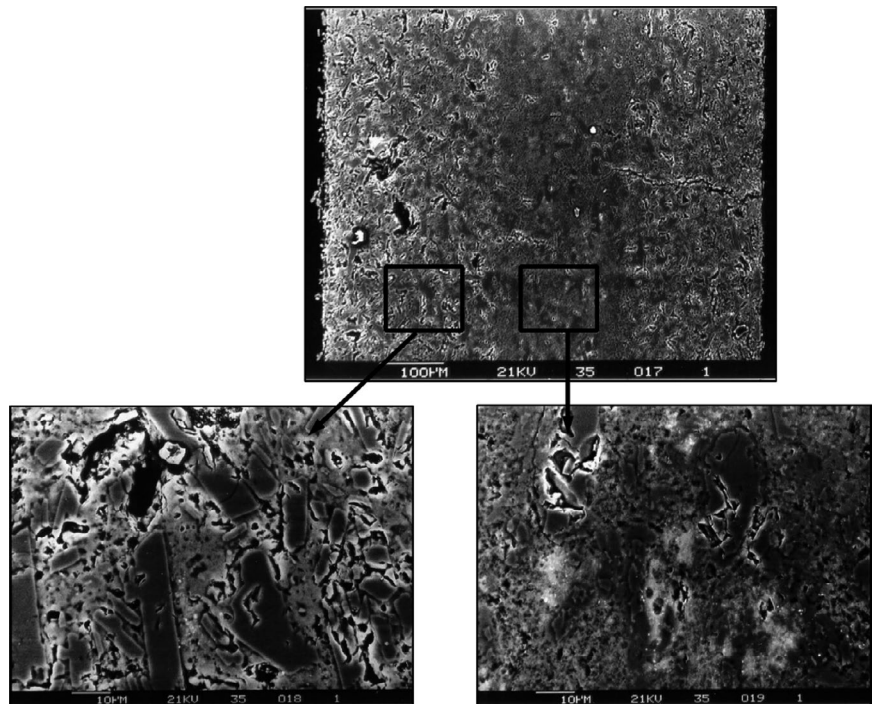
FIGURE 9 Water and n-heptane vapor adsorption at 25°C (left axis) and ratio of maximum water and n-heptane adsorption (right axis) for polymer-derived ceramic samples with different SiC particle size of 4.5 μm (A) and 6.5 μm (B), varying azodicarbonamide (ADA) amount (from zero, A0, to 30 wt%, A30) and pyrolysis temperature (600 and 1000°C).[101] (reproduced with permission)

FIGURE 10 SEM micrographs of
the three-layer polysiloxane tapes pyrolyzed
at 1500°C for 2 h. From left to right on
the top image: poor, rich, poor Si layers.[94]
(reproduced with permission)

In Figure 11, typical Hg porosimetry curves as a measure of the total porosity of the bilayered PDC tapes are presented.[96] While in Ar pyrolyzed tapes, the total porosity is always higher compared to the tapes pyrolyzed in N_2, the porosity also increases with higher pyrolysis temperature. In the samples pyrolyzed at 1500 °C, a pronounced bimodal porosity distribution was found, having a maximum at about 0.3 and 2 µm for Ar and at 0.2 and 0.3 µm for N_2 pyrolysis.

Rocha et al[98] obtained substrates in the SiAlONC system with skeleton density of pyrolyzed tapes of ~3.1 g/cm³, with an open porosity of ~25% and low linear shrinkage (~3.5%), which is suitable for near net shape applications.

As for PDC coatings applied on steel substrates by tape casting, with thickness of 50 µm and thermal stability up to 1000°C, a value of 27 vol.% porosity was measured.[99] This contributes on one hand, as a positive effect, to the reduction of stresses during thermal load, but, on the other hand, it has also a negative effect on the mechanical stability of the thermal barrier coatings.

Nishihora et al[101] and Silva et al[102] found that the main parameter responsible for creating open macroporosity in polysiloxane-based PDCs is the addition of ADA, especially for amounts larger than 10 wt.%. Moreover, an additional influence of filler particle size (SiC) on the average pore size was noticed. The increase in the pore size is more appreciable using 6.5 µmSiC particles in samples pyrolyzed at 1000°C. They also measured nitrogen sorption isotherms of polysiloxane samples pyrolyzed at 600°C, classified as a type I isotherm, typical for microporous solids (<2 nm). The shape of isotherms for samples pyrolyzed

at 1000°C, especially those with 4.5 µm SiC particles, was associated with type IV isotherm, corresponding to mesoporosity (2-50 nm), where capillary condensation takes place.[106] Recent advances in the design of mesoporous PDCs hold much promise for the development of novel catalysts or catalyst supports.[107]

6.4 | Mechanical behavior of ceramic tapes and laminates

Samples of ceramic tapes (polysiloxane with 30 vol.% SiC + 10 vol.% Si), pyrolyzed at 1550°C in N_2, reached
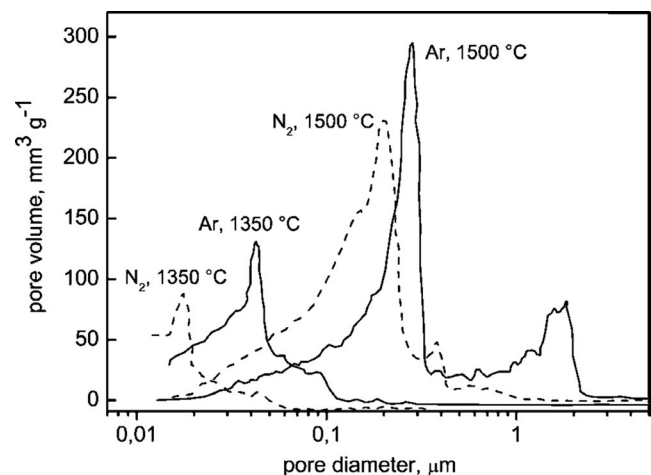

FIGURE 11 Pore size distribution of polymer-derived ceramic tapes after pyrolysis in Ar or N_2 at 1350 and 1500°C.[96] (reproduced with permission)

values of flexural strength of 115 MPa, for 29% porosity and average pore radius of 0.14 μm. When those samples were pyrolyzed in Ar atmosphere, the values of porosity and mean pore size were, respectively, higher (32% and 0.25 μm) and mechanical strength were lower (67 MPa).[91]

Steinau et al[97] evaluated the bending strength of PDC laminates in different configurations, according to the grain size of SiC (passive filler) employed (Figure 12). After pyrolysis at 950°C, samples presented ~15% open porosity and were thus relatively weak mechanically. A lamination of tapes with fine SiC in outer layers led to an increase of 25% in bending strength. On the other hand, when the tapes with coarse SiC were on the outside, a decrease in same amount was observed. Similar trends and better results were obtained after pyrolysis at 1200°C.

Finally, Nishihora et al[101] observed that mechanical stability of porous PDCs is directly related to the microstructure, porosity, type, and size of inert filler particles. The major influence on the flexural strength of the tape was associated to the pyrolysis temperature and porosity (ADA content). Increment in porosity means enlarging macrodefects in the structure, which drastically reduced the mechanical strength for both pyrolysis temperatures (600 and 1000°C). At 1000°C, high mechanical strength is expected due to ceramization or due to the presence of free carbon between SiOC bonds.[108]

7 | CONVENTIONAL AND PDC-BASED TAPE CASTING COMPARED

As in any innovative application of a standard shaping technique, the PDC-based tape casting route differs from the conventional route in terms of raw materials, additives,
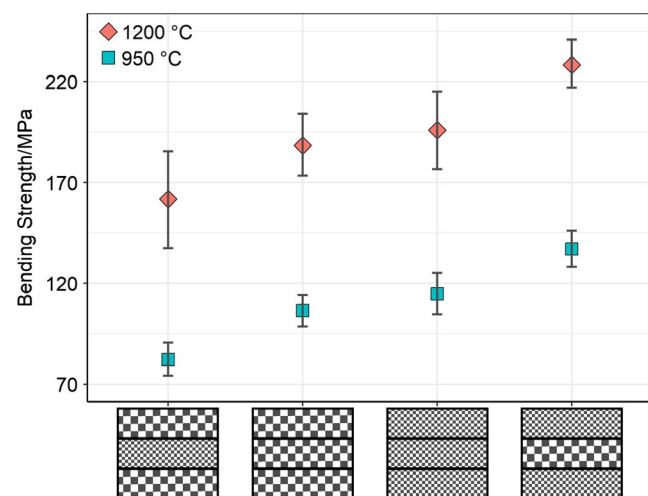

FIGURE 12 Bending strength of polymer-derived ceramic laminates with fine and coarse grain size treated at 950°C in 0.1 MPa N_2, or at 1200°C in 1 MPa N_2.[97] (adapted and reproduced with permission)

processing parameters, as well as unit operations before and after casting. Figure 13 depicts both routes compared, and Table 3 gives an overlook of each relevant difference.

In order to fabricate ceramic products from cast tapes, ceramic raw materials are naturally needed. In the standard case, ceramic powders are added to the batch and remain as the sole source for the final ceramic product. No reaction is normally expected or desired to occur in terms of changing chemical or phase composition in the next steps, particularly those involving heat (drying, debinding, sintering).

On the other hand, the PDC route is all about chemical transformations as explained in the first section of the present review paper. A preceramic polymer, especially based on silicon, is first designed to form a cross-linked structure after curing, which may occur at temperatures as low as at room temperature. Fillers, both passive and active, are usually added not only to control shrinkage and porosity of the final body, but also to form new compositions during pyrolysis. Eventually, the pyrolyzed bodies are yet submitted to crystallization at higher temperatures for reaching a certain phase or optimizing a specific set of properties.[31]

Tape casting is essentially a wet-based forming route. This means that the shaping medium is liquid and, as such, subject to the laws of fluid mechanics. Firstly, in the classical route, a liquid is both a solvent (in regard to the additives that need to be dissolved in it) and a dispersing medium (in the sense of providing a physical environment where the ceramic powders should remain "stable" for a necessary period of processing time). Conversely, in the PDC route, a liquid is not only a solvent for the preceramic polymer, which is a Si-based resin, but also a viscous medium to maintain powdered fillers in suspension, in the most part of cases.

Regarding conventional tape casting slurries, the literature is very rich in rheology studies, particularly as a function of additives composition and amount.[13,14,16,18,20] Correlations between the rheological behavior of the slips and the mechanical properties of green tapes or laminates may be drawn according to the type and amount of organic additives.[109]

For the PDC route, specific rheological investigations are limited to a few PCP systems.[56,110–113] Even less frequent are rheological studies with direct correlations to common shaping processes, such as extrusion or melt spinning.[114] To the best of our knowledge, no specific investigation on mechanical properties of cross-linked PCPs before pyrolysis was performed so far.

Moreover, the approach for PDC rheology is somehow unusual when compared to conventional tape casting flow analysis.[115] Rather than obtaining a typical shear stress vs shear rate rheogram, PDC rheology has a polymer science perspective. This is obviously correct, because when a polymer system is subjected to a chemical reaction, under the
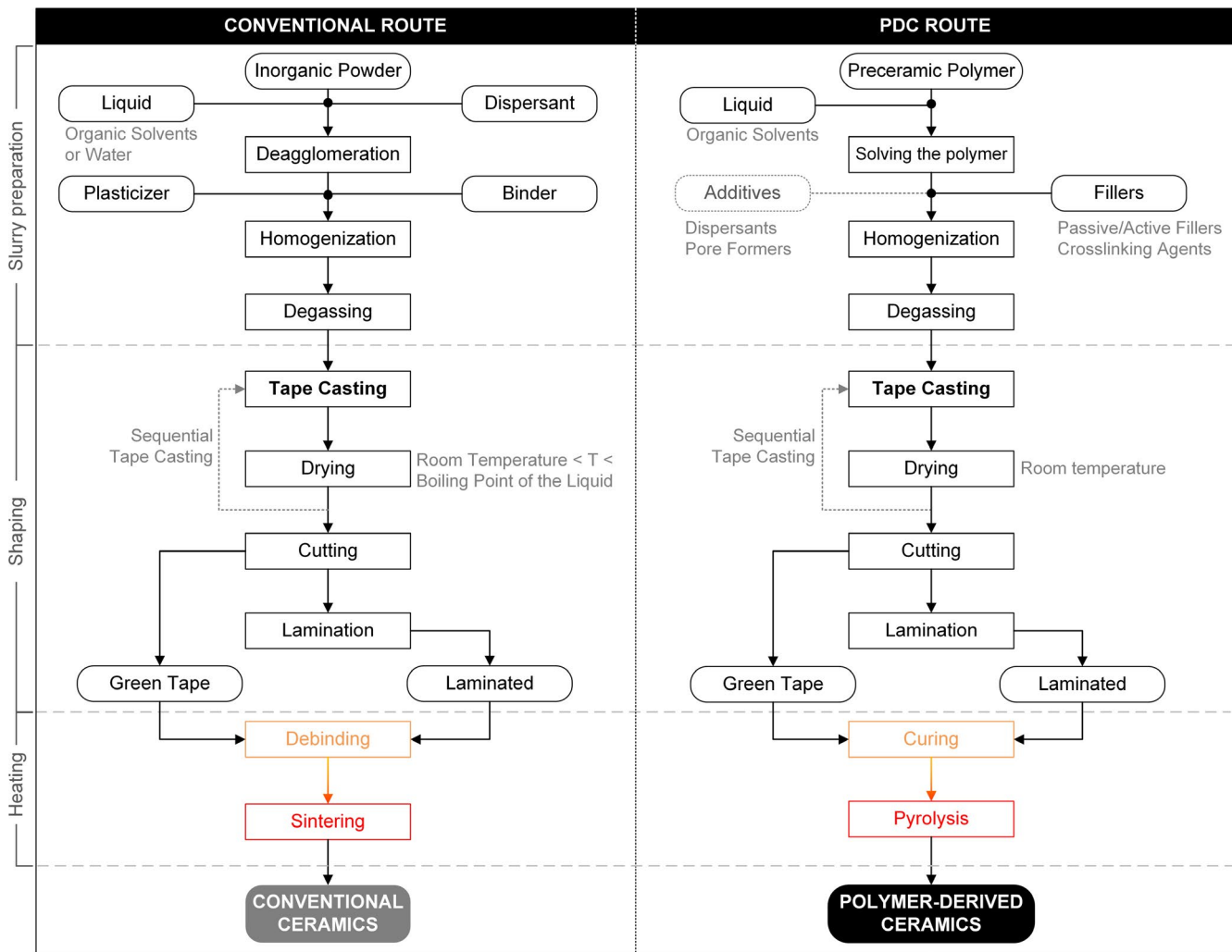
FIGURE 13 Flowchart of tape casting-based shaping leading to either conventional or polymer-derived ceramics

effect of catalysts and/or temperature and/or pressure, it suffers a complex transformation, which leads to extreme changes in the viscoelastic (also known as "viscoplastic") behavior (Figure 14).[110]

During a single processing step (eg, cross-linking), a preceramic polymer resin (ie, liquid) may turn into a "solid" given the proper conditions (catalyst/filler concentration, temperature, time). In this way, the rheological properties are to be measured dynamically and expressed rather as a complex combination of elasticity and viscosity, related to the so-called elastic and viscous moduli, G' and G'', respectively. Thus, dynamic tests must be carried out for PCPs, at controllable oscillatory frequency and temperatures, in order to establish the time evolution of the elastic and viscous moduli, as a function of the catalyst and filler concentration (Figure 15).[111]

Indeed, due to the high degree of control on the physical and rheological properties of PCPs, the PDC route allows polymer shaping before, after, or even during the cross-linking or curing step to produce a large variation of shapes and sizes. This in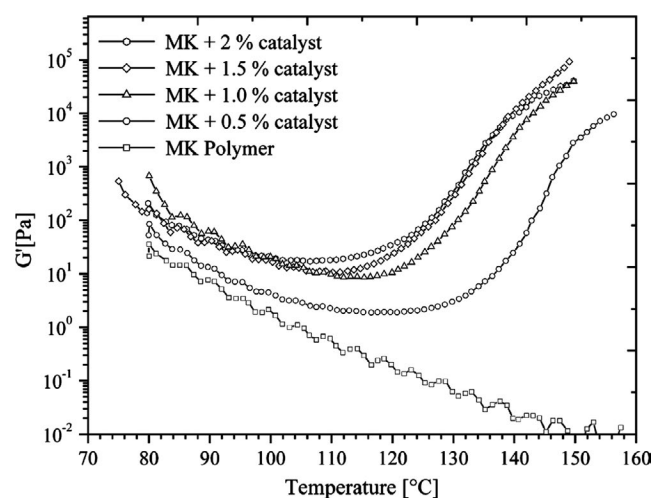cludes thin ceramic parts or multilayered laminates, such as those obtained from tape casting, as well as fibers, coatings, or dense monoliths.[107]

Another even harder challenge is adjusting the rheology of a polymer with a large amount of nanosized powders,[116] which are typically required to produce a near net shape PDC within a desired composition. Because of the decrease in flow ability of the polymer containing the nanoparticles, suitable precursors and processing conditions need to be carefully selected, depending on the forming technology employed.[38]
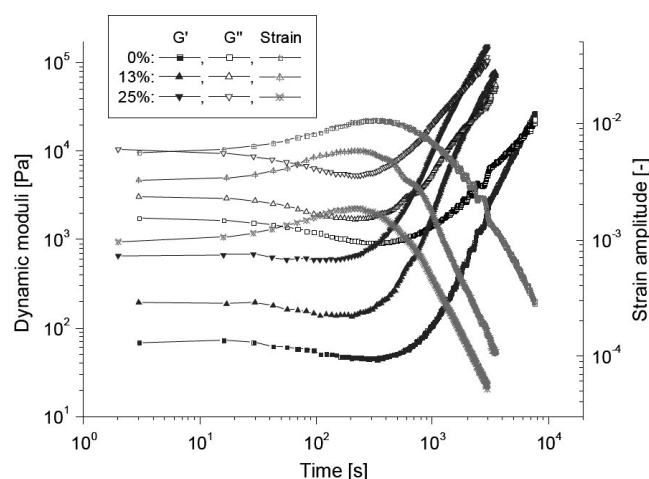
It is important to point out that in preparing the slurry or slip, the order in which the organics are added is almost as critical as the materials themselves.[1] The main objective of dispersion milling is breaking up agglomerates before adding plasticizers and binders. In the same way, PCPs must be first properly dissolved in a solvent to form a dispersion medium for particulate fillers and/or pore formers. To this suspension, catalyst(s) for cross-linking are added and homogenized. Commonly, a degassing step under vacuum follows to release air bubbles and prevent defects after shaping.

TABLE 3 Main processing parameters for manufacturing polymer-derived ceramics from cast tapes

Processing parameters	Conventional route	PDC Route
Ceramic Raw Material	Ceramic powders, such as alumina, zirconia, silicon carbide, or aluminum nitride	Preceramic polymers, such as polysiloxanes or polysilazanes, with passive or active fillers
Mandatory additives	Dispersants, binders, plasticizers	cross-linking agents
Other additives	Antifoaming, releasing agents	Dispersants, pore formers
Mixing/Milling	Powders are mixed, generally in a ball mill, to liquid + dispersant, for breaking up agglomerates; binders and plasticizers are added homogenized	PCPs (solid or liquid) are dissolved, with the aid of different equipment, in a solvent; fillers, cross-linkers, and others are added and homogenized
Degassing	Under vacuum	
Tape Casting/Drying	Casting with a doctor blade followed by drying at temperatures between room temperature and boiling point of solvent	Casting with a doctor blade followed by drying and eventually cross-linking at room temperature or low temperature during shaping
Cutting/Lamination	Cutting into desired shapes, and eventually lamination by sequential casting or thermopressing	
Thermal Treatments	Debinding at middle temperatures and sintering at high temperatures are needed	cross-linking at low temperatures (as low as room temperature) and pyrolysis at high temperatures are needed; eventually crystallization at higher temperatures are accomplished; composite materials may be produced with partial pyrolysis of precursors
Ceramic Products	Dense parts with a residual porosity and controlled shrinkage; or less often, macroporous parts; all kinds of oxide and nonoxide ceramics may be fabricated	Near net shape parts with the use of active/passive fillers, or controlled porosity with the aid of pore formers; mostly silicon-based ceramics are fabricated (SiC, SiOC, SiOCN, etc.)

FIGURE 14 Evolution of elastic modulus ($G`$) with temperature as function of catalyst concentration of a PCP (polysilsesquioxane, MK).[110] (reproduced with permission)

FIGURE 15 Dynamic moduli and strain amplitude as function of time for a PCP (MK + 1wt% catalyst) as function of the filler concentration at 85°C.[111]

A typical tape casting machine is comprised by a doctor blade, a casting surface, a drying chamber, and a carrier with adjustable speed. An industrial tape caster could be more properly referred to as a casting and drying equipment, since the largest part is the dryer itself, usually with a controlled atmosphere saturated with the solvent. In the case of the PDC route, it might serve as an environment for cross-linking the cast tapes at controlled temperature and atmosphere.

According to another recent approach, a PCP cast slurry can be solidified by immersion precipitation in a nonsolvent (deionized water, in this case), which is a technique commonly used for casting polymeric membranes, known as phase inversion.[117]

In the sequence, the dried tapes may proceed directly to thermal treatments, particularly when intended to be used as porous thin membranes, or can be submitted to a sequential casting to render higher thickness. Alternatively, laminates

may be manufactured, either for conventional or for PDC-based ceramic parts.

Finally, in the conventional route, the green parts are submitted to a burnout step, also known as debinding, for eliminating the organic components before sintering, normally at temperatures from 300 to 600°C and long times (18 hours or more) to prevent delamination or warping of the pieces.[1] A debinding cycle is usually built in the overall sintering time-temperature curve. Atmosphere is normally oxidizing for binder burnout and oxide ceramics sintering, but vacuum, neutral (Ar, N_2), or even reducing atmosphere are sometimes applied, for instance for carbides or nitrides. Sintering may occur at temperatures as low as 900°C for glass-ceramics,[118] or as high as 1850°C for silicon nitride.[103,119]

On the other hand, thermal-induced decomposition of ceramic polymer precursors offers the possibility of near net shape manufacturing at lower temperatures (500 to 1500°C), when compared to the powder sintering route.[54] Ceramic materials with a wide range of compositions can prepared from PCPs, such as SiC, SiOC, SiCN, Si_3N_4, among others, being some of these compositions possible exclusively to be obtained by the PDC route.[31]

8 | CONCLUSIONS AND OUTLOOK

Tape casting has been applied in the last two decades to produce PDCs from PCPs, such as polysiloxanes and polysilazanes. This review recalls the efforts to adapt the conventional tape casting technology to permit using PCPs for manufacturing diverse ceramic and composite products with unique compositions and properties.

In the traditional approach, organic additives are needed to achieve rheological and mechanical suitable behavior, respectively, for casting a stable suspension and handling a robust green tape or laminate. Due to their organic nature, after proper shaping, they should be burnout at intermediate temperatures, and the green body must be submitted to final densification through sintering at higher temperatures.

Alternatively, the use of PCPs as feedstock for tape casting allows tailoring both slurry viscosity and green tape strength in order to design an adequate processing window. Besides PCPs, solvents and catalysts are needed, as well as fillers (passive and/or active), to render a proper combination of shrinkage rate and residual porosity after heat treatments.

Thermal treatments to yield PDCs from tape cast PCPs include cross-linking (from 120 to 270°C) and pyrolysis (from 600 to 1600°C), normally at lower temperatures than those needed for sintering ceramics, particularly nonoxides, such as carbides or nitrides. Moreover, partial pyrolysis may lead to hybrid or composite products with unusual and synergistic combination of properties, such as hydrophilic/hydrophobic character and open porosity.

Importantly, some technological gaps were detected, for example related to the lack of rheological characterization of viscoelastic PCP systems toward optimization of tape casting parameters. In addition, as far as we know, no specific investigation was carried out to clarify the role of microstructure evolution on the mechanical behavior of tapes or laminates, particularly after drying or curing/cross-linking and before pyrolysis. Even for pyrolyzed tapes and laminates, the relationship between the formulation of raw materials and properties of final products is also not straightforward, due to the huge variation in chemical compositions and processing conditions employed. However, for porous PDCs obtained from tape cast PCPs, the major influence on mechanical strength might be correlated to the temperature of pyrolysis and to the amount of pore formers, which lead respectively to a lower or higher porosity.

Finally, the fields of application of PDC tapes or laminates are relatively open. The PDC route offers the possibility of tailoring porosity in final products, by the proper adjustment with fillers and/or pore formers and/or heat treatments at mild conditions. Thus, the fabrication of porous membranes or filters based on carbides and nitrides, for example, for use in aggressive or high-temperature media, is foreseen as a promising technological way to go for PDC-based tape casting.

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