



Design of carbon fiber reinforced boron nitride matrix composites by vacuum-assisted polyborazylene transfer molding and pyrolysis

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Abstract

In the present study, the vacuum-assisted polyborazylene transfer molding (VAPTM) followed by pyrolysis at 1450 °C under nitrogen was successfully applied to prepare C/BN composites with a relative density of 94.7%, and an open porosity of 5.1 vol%. Rheology measurements combined with TG experiments and measurement of the weight gain of the composites after each polymer impregnation pyrolysis (PIP) cycles allowed fixing elaboration parameters (10 PIP cycles using two types of polyborazylene) to generate C/BN composites as high temperature vacuum compatible materials which demonstrate potentialities for vacuum technology and space applications. Scanning electron micrographs of composites demonstrated that the BN matrix appropriately filled the space between the fibers with a low fiber-matrix bonding which affects the compressive modulus. The thermal diffusivity and electrical conductivity of the BN matrix have been measured and showed that carbon fibers have poor effects on the intrinsic properties of BN.

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1. Introduction

The *Polymer-Derived Ceramics* (PDCs) route is an attractive means for the production of advanced ceramics and offers significant advantages over traditional ceramic processing techniques.^{1–4} Among these advantages, this chemical route allows controlling the ceramic composition at an atomic scale during the synthesis of the preceramic polymers (=ceramic precursor), tailoring the material structure from amorphous

to crystalline, and processing materials in particular shapes that are difficult, or even impossible to obtain following more conventional routes.

Fiber-reinforced ceramic matrix composites (FRCMCs)^{5–9} are examples among others that demonstrate the interest of molecular precursor-based processes including the Chemical Vapor Impregnation (CVI) and in particular the PDCs route (both usually combined for these materials) to process materials in particular shapes that cannot be produced in other ways. Nevertheless, the use of preceramic polymers to manufacture FRCMCs is a more attractive way in comparison to the CVI route that needs a very long manufacturing time, sophisticated equipment and is therefore very expensive.

The preparation of FRCMCs *via* the PDCs route is usually termed as the PIP (*Polymer Impregnation Pyrolysis*) process. Such a process requires specific preceramic polymer properties (liquid, fusible and/or soluble and relatively high ceramic yield) to be implemented and it includes three stages: (1) impregnation of fiber preforms with preceramic polymers which can be

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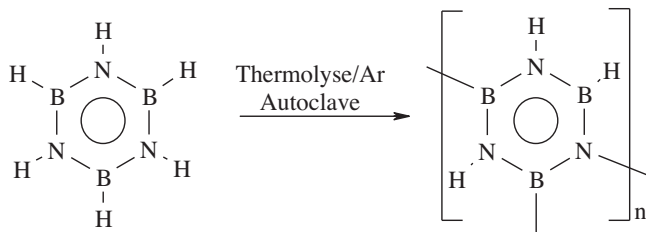


Fig. 1. Borazine and its thermolysis generating the polyborazylene.

assisted by vacuum, *i.e.*, vacuum-assisted resin transfer molding (VARTM), (2) crosslinking of the polymer matrix, and (3) pyrolysis of the crosslinked polymer matrix in an inert and/or reactive atmosphere to generate the desired ceramic matrix. Several PIP cycles are required to densify composites due to both the density increase and the volume shrinkage imposed by the polymer-to-ceramic conversion. Depending on the fiber volume content and the ceramic yield of the considered preceramic polymer, between five and ten PIP cycles are required to obtain porosities less than 10 vol%.

FRCMCs have gained substantial interest for high temperature applications in high-performance space and military domains, such as heat shields, aircraft exhaust flaps and rocket nozzles because of their damage tolerance behavior, high temperature resistance and high strength. This is particularly the case for carbon fiber reinforced carbon and silicon carbide matrices (C/C and C/SiC) composites that are probably the most suitable candidates for many high-temperature applications under harsh environment as fusion power reactor, aerospace and aircraft components.^{10,11}

Here, we focus on a particular class of FRCMCs, *i.e.*, carbon fiber reinforced boron nitride composites (C/BN).

In the development of materials which can be used at high temperatures, the interest for hexagonal boron nitride we labeled BN grew during the past decades in relation with its thermostructural stability and chemical durability. BN is a synthetic compound that shows similarities in its crystal structure with graphite providing anisotropic properties. It was therefore widely developed as nanotubes^{12,13} and fibers^{14–16} to propose alternatives to carbon analogs.

As general properties, BN displays high-temperature stability, good lubricating properties and oxidation resistance up to 850 °C. Furthermore, it proposed a good thermal conductivity and it represents an electrical insulator. In addition, it is non-reactive toward molten metals such as aluminum, iron, copper and hot silicon which reinforces its potential for high temperature applications.¹⁷ BN derived from preceramic polymers has been intensively investigated.^{18–27} The studies mainly concerned the design of the molecular architecture of preceramic polymers with a particular focus on polymer-derived BN fibers.

In the family of BN precursors, it appeared that borazine (Fig. 1), a colorless liquid, has considerable interest as molecular candidate.

It represents a single BN source of both nitrogen and boron elements with the correct B/N ratio (1/1) and geometry (planar six numbered ring) in comparison to BN. Borazine exhibits high reactivity and volatility at room temperature, which makes of it

an excellent precursor for gas phase processing route such as CVD to prepare BN nanotubes²⁸ or spray-pyrolysis to prepare BN nanopowders and derived nanostructures.^{29–31} However, for PIP processing, it has to be thermally stabilized, *i.e.*, thermolyzed at low temperature, prior to its conversion into BN. This leads to the intermediate polyborazylene (Fig. 1) that is built by condensation reactions of BH and NH units as well as probable ring-opening mechanisms.^{18–22,32–35}

Through the study of the thermolysis of borazine, we recently demonstrated the possibility to control the physical state of polyborazylene from liquid (45–55 °C) state to solid state (≥ 60 °C) by adjusting the temperature of thermolysis.^{33–35} Liquid polyborazylene from condensation of borazine at 45 °C labeled **PB45** could be successfully dip-coated to prepare coatings on metallic (titanium, aluminum and copper) substrates.³³ A RT stable polyborazylene obtained by thermolysis of borazine at 50 °C we labeled **PB50** was used to prepare highly ordered BN nanotube arrays and BN foams with hierarchical porosity by using templating processes.³⁴ The most appropriate polyborazylene candidate to prepare highly dense monolithic BN ceramics as well as micro-/mesoporous powders is a polyborazylene prepared by self-condensation of borazine at 60 °C we labeled **PB60**.³⁵ As structural materials, monolithic BN ceramics suffer from one important reliability issue, namely the inability to tolerate stress levels. To increase the work of fracture or the toughness of monolithic BN, incorporation of carbon or ceramic fibres in the BN phase is one of the toughening solutions. As matrix in FRCMCs, polyborazylene-derived BN could also be particularly attractive in applications in which high temperature resistance, excellent radiated thermal property and low thermal resistance combined with thermal conductivity and electrical insulation are required. C/BN composites as thermally conducting but electrically insulating components could offer a heat management solution for electrical/electronic components in aerospace applications as well as for heat exchangers where the high thermal conductivity achieved allows efficient heat dissipation.

Kim et al.²¹ reported for the first time in 1993 the preparation of C/BN composites through one or two step impregnation of a liquid polyborazylene into a mold containing the carbon fiber layups. After impregnation within the porous structure of the carbon fiber layups, the C/polyborazylene composite was heated up to 60–70 °C before to be pressed at 400 °C. Finally, samples were pyrolyzed in the temperature range 1200–1500 °C to generate C/BN composites. Then, the same group published several papers in which they focused on the characterization of C/BN composites, *i.e.*, thermal stability^{21,36} and mechanical properties (friction and wear properties^{37,38}). Authors demonstrated the high interest of these materials but very few details were given on the preparation process. No other groups investigated the preparation of polymer-derived C/BN composites since that time.

In the present study, we provide a detailed investigation of the preparation of C/BN composites through (1) a rheological study of tailored polyborazylens selected among those prepared at 45 (**PB45**), 50 (**PB50**) and 60 °C (**PB60**) for the vacuum assisted polyborazylene transfer molding (VAPTM) and (2) the study of

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