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Pyrolytic conversion of organopolysiloxanes

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ABSTRACT

This study extends previous work on in-situ generation of nanographene domains in silicon oxycarbide polymer-derived ceramic nanocomposites. The thermal conversion of cross-linked polyhydridomethylsiloxanes (PHMS) has been studied as a function of its initial organic structure and its content. Two cross-linking additives containing vinyl groups, tetramethyl-tetravinyl cyclotetrasiloxane (TMTVS) and divinylbenzene (DVB), have been reacted with the Si—H groups of the PHMS via Pt catalyzed hydrosilylation. These polymers gave a high ceramic yield of 78–85 wt% upon pyrolysis at 1000 °C–1400 °C in inert atmosphere. The use of the aromatic cross-linker (DVB) induces significantly higher carbon content in a controlled fashion into the derived ceramics compared with the TMTVS. The chemistry involved in the in-situ evolution of low-dimensional graphene architectures embedded into silicon oxycarbide network has been studied in detail using thermal gravimetric, mass spectroscopy analyses (TG-MS) and Raman spectroscopy. The presence of aromatic functional groups (DVB) at the polymeric stage leads to graphene generation at lower temperatures than in the case of TMTVS cross-linker. Raman spectroscopy analysis of DVB cross-linked PHMS showed evidence of the beginning of formation of free sp^2 carbon domains from 800 °C. Raman mapping allows obtaining the chemical and the structural distribution of the resulting phases.

1. Introduction

Silicon-based polymers offer a large number of reactions by selecting the appropriate backbone units of the polymeric structure [1]. The most interesting modifications consist of organofunctional groups, either directly incorporated into the polymer backbone or grafted to the Si atoms. These polymers can be used for a broad spectrum of applications, as adhesion promoters for surface coating due to their outstanding water-repellent properties [2,3] and as additive incorporated in organic-based composites. They serve as high temperature elastomeric materials and function as selective membranes [4].

Another emerging field for silicon based polymers is "preceramic polymers", in which the polymers are cross-linked and then thermally converted to silicon-based ceramics by pyrolysis. A large number of thermal conversions of organosiloxanes ceramic precursors have been studied and reported in the literature [1,5,6]. A common feature of polymer-derived ceramic route is the formation of amorphous metastable intermediate phases of SiC_xO_y in which an excess free carbon is embedded. It must be recognized that the thermal conversion of organically modified silicon precursors is the easiest way for preparing ternary and even multinary phases (Si/C/N/O/Al/Mg/B/Zr/Ti/etc.) [7,8]. The excess carbon, which is not directly incorporated into the inorganic Si—O—C networks, results from the thermal decomposition of organic functional groups, incorporated in the polymeric precursor structure. The "free carbon" content depends on the molecular structure of the organic substituent group and its reactivity with neighboring functional groups present in the structure of precursor [9].

The free carbon, recognized for its turbostratic nature, can be either advantageous or detrimental, depending on the application for which the material will be used. In oxidizing atmosphere, carbon is the most vulnerable constituent [10], especially at low temperatures, where protective layer of silica cannot be formed, to inhibit the oxygen diffusion [10,11]. In contrast, in inert atmospheres, the free carbon can be advantageous for the formation of SiC and other metal carbide phases via carbothermal reductions [12,13]. It can also improve the thermal stability, by inhibiting and retarding tran-

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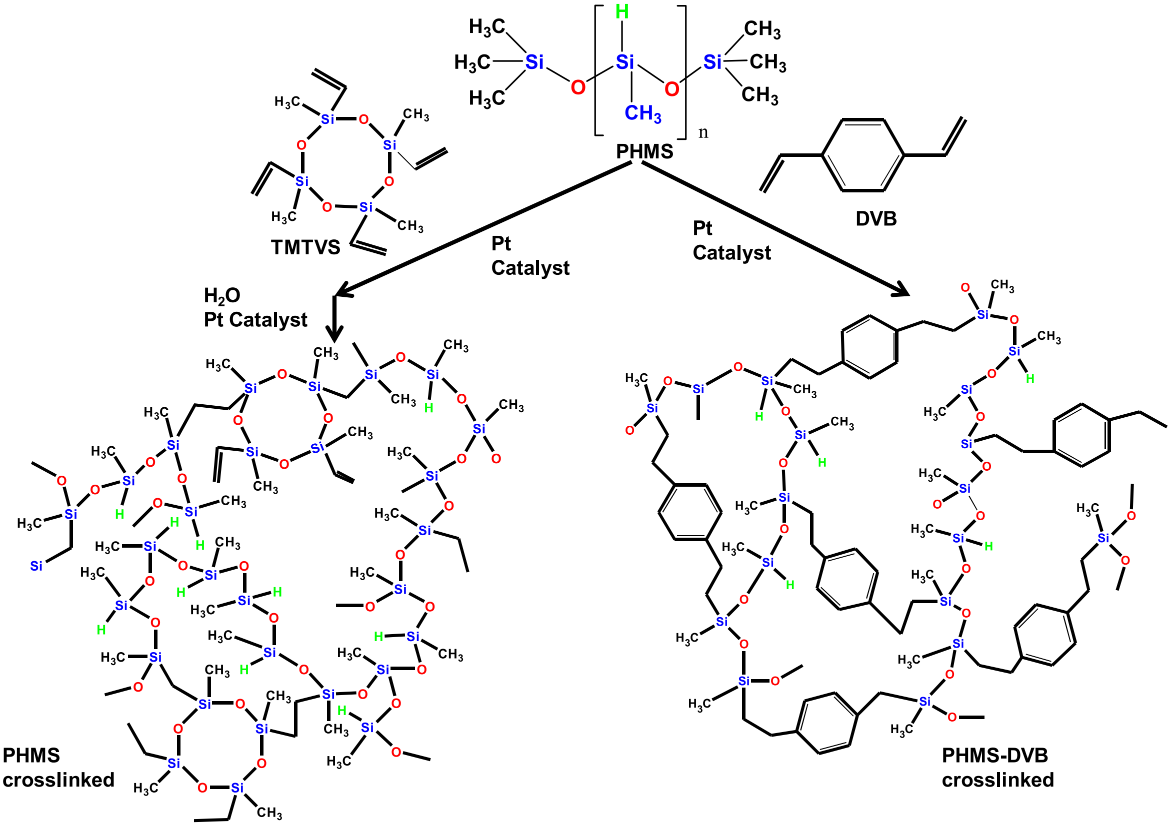

Fig. 1. Schematic representation of the two PHMS-derived polymers.

sitions from the metastable states (oxycarbide phase) to the more stable phases (SiC and SiO_2) [13,14].

A great deal of attention has been directed in the past to lower the free carbon content in polymer derived ceramics. Such attempts were intensive in the case of polycarbosilane precursors for SiC fibers and matrices [15]. This ceramic fiber was intended to be used as reinforcement for thermo-structural composites [16]. It should be noted that the first generation of SiC fibers (Nicalon^{TM}) from polycarbosilanes contained not only an excess carbon, but also SiOC phase. The oxygen incorporation is derived from the oxygen used during the curing step. Advances in chemical synthesis and processing have resulted, indeed, in fibers with reduced free carbon and oxygen content. New generations of stoichiometric SiC fibers (with $Si/C = 1$) with no excess carbon and very low oxygen content are commercially available as Hi-Nicalon [17].

Knowing that the thermal conversion of organic groups to graphene domains is inevitable, the question arises: Can we take advantage of the in-situ formation of these nanodomains inside the SiOC, SiCN or similar matrices as functional materials for specific applications?

A growing interest in carbon-rich silicon oxycarbide materials has been noticed for their potential as anode materials for rechargeable lithium-ion batteries [18,19], or for temperature and pressure sensors [20,21] that can be used in harsh environments. In our previous work, we have also demonstrated that the carbon-rich materials issued from pyrolysis of organopolysiloxanes exhibit a high absorption in terahertz domain [22]. Recently, the high carbon materials discussed in this article have been reported for their extremely high permittivity values, exceeding those of state of the art titanates [23].

Various methods were reported for tailoring chemical compositions of polymer-derived ceramics containing high carbon content. It is mostly done by incorporating phenyl-Si groups into the silicon based polymer [24]. For example, Scheffler et al. and others [25,26] used the advantage of excess carbon to catalytically grow in-situ carbon nanotubes from hydrocarbon species released during the pyrolysis of phenyl containing polysiloxane (Sylres H44). For the preparation of nanoporous SiC-based materials and cross-linking purposes, many researchers incorporated a cross-linking agent containing vinyl groups to initiate the hydrosilylation reaction [27]. The vinyl groups also increase the carbon content of the PDC (polymer-derived ceramic) but not as much as an aromatic group. Blum et al. [28] have deliberately increased the carbon content by incorporating, at molecular level and in a controlled manner, divinyl benzene (DVB) to achieve a highly cross-linked polyhydridomethylsiloxane (PHMS) simultaneously with controlled increase of the carbon content. Their experiments have shown that the ceramic yield of the cross-linked polymers is even higher. A remarkable property of resulting materials is their oxidation stability in-spite of the high carbon content [11,13]. However, volatile species from the pyrolysis of polymers cross-linked with DVB have not yet been studied in detail, which can illuminate differences in the mechanisms of the evolution of the graphenic phase when generated mostly from either methyl or the DVB groups. Previously, Maddocks et al. [29] attempted to analyze by thermogravimetry coupled with mass spectrometry the volatile species of cross-linked polycarbosilane with DVB. Unfortunately, oxygen contamination probably due to a leak in their system does not seem to be reliable. The authors even concluded their article by suggesting that further experiments in an oxygen-free atmosphere are required.

The aim of the present work is to extend previous research on DVB cross-linked PHMS polymers by carefully investigating the gaseous species eliminated during pyrolysis and attempt to eluci-