Journal of Analytical and Applied Pyrolysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Microstructure and phase evolution in pyrolysed short fibre reinforced polymethylsilsesquioxane-phenolic interpenetrating networks

Ancy Smitha Alex[a], Bhuvaneswari S[b], Sarath Chandran C[a], Jayalatha T[b], Sekkar V[a,*], Gouri C[c,*]

[a] Analytical Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, India
[b] Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, India
[c] Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, India

ARTICLE INFO

Keywords:
Polymethylsilsesquioxane
Phenolic resole
Interpenetrating network
Microstructure

ABSTRACT

Simultaneous interpenetrating networks (IPNs) comprising of polymethylsilsesquioxane (PMSQ) and phenolic resole (PF) systems at various PMSQ to PF ratios (0–75% w/w PF) which formed the matrix resin for 60% w/w short silica fibre reinforced composites (SR-PMSQ-PF) are subjected to a controlled heating regime in argon atmosphere at 1500 °C to investigate the microstructure and phase evolution based on IPN composition. This study aims at giving an insight into thermal, mechanical and chemical stability of silicone-phenolic IPN composites, particularly for high temperature thermal protection applications as in aerospace. The morphology and microstructure of the pyrolysed composites are well characterized using Raman and FTIR spectroscopy, XRD and SEM-EDS and based on this a mechanism for microstructure evolution is proposed. It is inferred that the pyrolysis of SR-PMSQ-PF composites results exclusively in the formation of cristobalite silica. In addition to that, the formation of SiC is also facilitated particularly in nano dimension with increase in phenolic content, by carbothermal reduction of silica derived from PMSQ and silica fibre predominantly through solid-vapour phase reaction along the (111) crystalline plane. The systematic evaluation of microstructure and morphology of pyrolysed SR-PMSQ-PF IPN composites is useful to define specific thermal protection applications for these composites.

1. Introduction

Multicomponent polymeric system with different chemical structure and physical properties inducted in the form of an interpenetrating network (IPN) as a matrix has gained great interest in achieving synergistic property improvements. IPN system comprising of siloxane and phenolic resole (PF) as a thermal protection system (TPS) material is interesting because the thermal insulation properties of siloxane synergized with ablative characteristic of phenolic resin is quite appropriate for designing specific aerospace applications. But, commonly available silanol terminated polydimethyl siloxane (PDMS) is not compatible with phenolic systems and the char yield at high temperatures is almost zero% which is not desirable if the IPNs were to be considered for ablative applications for launch vehicle programmes. Friedrich and Folkers [1] described an IPN system based on phenolic resin combined with oligomeric siloxane leading to a toughened system. However, siloxane-phenolic IPN systems have not been explored extensively. Interestingly, a commercially available siloxane polymer namely polymethylsilsesquioxane (PMSQ) with the empirical formula $(CH_3SiO_{3/2})_n$ is found to mix with phenolic system at molecular levels through solution blending. Further, the char yield at 1000 °C for PMSQ (> 80%) is much higher than the phenolic system [2] and thus makes the PMSQ-PF IPNs ideal candidates for ablative liner applications since the high char residue is helpful in forming an integrated thermal insulation layer protecting the back–up structure [3].

Polymer networks based on PMSQ possess exceptional thermal and weather resistance, non-toxicity and chemical stability because of the rugged siloxane (Si–O–Si) bond [4–8]. However, a major shortcoming associated with cured PMSQ polymer is its brittleness making it unsuitable for structural applications. Of the many means to overcome the deficiencies associated with PMSQ, a very handy approach is to involve it in the form of IPN as well as employing fibre reinforcement. Phenolic (PF) based composites are the most adopted ablative systems. The low cost, ease of processing, superior mechanical strength, excellent wetting property with reinforcements and dimensional stability coupled with robust ablative properties make PF a suitable candidate as an IPN component to modify PMSQ [9,10]. Providing fibre reinforcement by incorporating randomly oriented silica fibres to IPN matrix to form a composite is expected to be further effective in enhancing thermal protection characteristics because silica fibre reinforced PF matrix

---

* Corresponding authors.
E-mail addresses: vsekkar@gmail.com (V. Sekkar), gouri.c.k@gmail.com (C. Gouri).

https://doi.org/10.1016/j.jaap.2017.11.006
Received 30 July 2017; Received in revised form 2 October 2017; Accepted 6 November 2017

Please cite this article as: Alex, A.S., Journal of Analytical and Applied Pyrolysis (2017), http://dx.doi.org/10.1016/j.jaap.2017.11.006

composites are favored in thermal protection structures of numerous vehicle and nozzles of solid rocket motors, due to their better insulating and erosion resistant qualities [11,12].

The synergy of PMSQ and PF resins in the form of a simultaneous IPN matrix at various PMSQ to PF ratios (0–75% w/w PF) for 60% w/w short silica fibre reinforced composites (SR-PMSQ-PF) was evaluated in our earlier study and found to enhance the mechanical and dynamic mechanical properties of brittle PMSQ matrix significantly [9]. The optimum enhancement in properties such as toughness, flexural strength, compressive strength, storage modulus and thermal conductivity was observed at 25% w/w PF loading and is attributed to the complete phase miscibility of the simultaneous IPN formed and its efficient interfacial interaction with fibre reinforcement. When PF concentration reaches 75% w/w, the large domain size of highly crosslinked PF results in phase separated PMSQ-PF system and subsequently, a decrease in the afore-mentioned properties was observed. As far as char residue is considered, TGA results (up to 900 °C in N_2 atmosphere) indicated decrease in char residue with phenolic addition (from 93.6 to 83.7%) for the composite systems [9].

The first and foremost criterion for designing a polymer based TPS material is finding out its capability to be tuned to a wide variety of hyper-thermal environment [10]. A remarkable attempt to use a small scale rocket to screen ablatives was constituted by the Structural Plastics Ablative Rocket (SPAR) [10]. The SPAR motor was designed to be fired with a stagnation temperature controllable from 1100 to 3300 °C, and a chamber pressure controllable from 5 to 50 bar. The decomposition, thermo-mechanical stresses and other material properties of polymeric ablatives are strongly dependent on the type of the hyper-thermal environment and intimately on the heating rate. Thermally induced reactions such as chemical reactions or phase changes taking place in the matrix can govern the ablation process [10]. PMSQ when heated at or beyond 1450 °C, carbothermal reduction takes place leading to the formation of SiC [13–16]. This reaction is highly endothermic and substantial amount of heat is absorbed by this degradation process and thus help in ablative cooling. As far as short silica fibre reinforced PMSQ-PF IPN (SR-PMSQ-PF) composites are concerned, the interpenetration with phenolic resole will increase the chance of carbothermal reduction and *in-situ* formation of SiC. The extent of carbothermal reduction largely depends on the chemical composition of pyrolyzed PMSQ, diffusion coefficient of gaseous species such as SiO and CO formed during the reaction, microstructure and distribution of carbon source and interfacial interactions of PMSQ and carbon source [15]. In addition to carbothermal reduction, high temperature sintering of SR-PMSQ-PF can cause devitrification of silica fibre leading to formation of crystalline polymorphs of silica. SiO derived from the fibre also can take part in carbothermal reduction process.

A comprehensive review by Natali etal on the science and technology of polymeric ablative materials for thermal protection systems evidenced that the nature of the most relevant parameters is thermal, chemical, and mechanical which determines the material to hyper-thermal environment interconnection [10]. Generally ablative evaluation using arc plasma is used to simulate the actual condition encountered by space vehicles. The main drawback of arc jet plasma torches is related to the flow contamination from eroded material inside the chamber; this limitation makes isolating specific free-stream and surface chemistry analysis difficult [10]. However, it is quite interesting to study the microstructure, phase evolution as well as free and bonded carbon content in pyrolysed SR-PMSQ-PF IPN composites with varying IPN composition (0 − 75 % w/w PF), and hence, the composite specimens are subjected to pyrolysis in a controlled temperature condition at 1500 °C. Morphology and microstructure are investigated through SEM, XRD, FTIR and Raman spectroscopy and the results are well correlated and reported here. This study is designed to provide a clear insight into thermal, mechanical and chemical stability of the IPN composites when particularly used for thermal protection applications in specific hyper-thermal environments.

2. Experimental

2.1. Materials

YR 3370, a commercially available PMSQ (Momentive India Limited) with chemical composition $SiO_{1.78}C_{1.22}H_{3.67}$ was employed as the siloxane component in the IPN. Resole type phenol–formaldehyde resin (PF) was synthesized in-house at VSSC, Thiruvananthapuram, India. The viscosity of the resin is 400–600 cps (30 °C). Silica short fibres were procured from Valeth High Tech Composites Pvt. Ltd., Chennai, India. Acetone was received from M/s. Merck India Ltd., Bangalore and was used as the solvent for admixing the polymers.

2.2. Preparation of the composites

PMSQ and PF resin were taken in varying weight ratios, *viz.*: 100/0, 75/25, 50/50 and 25/75. The two polymers taken together in their prescribed weight ratios were dissolved in acetone. After complete dissolution of the polymers, mechanically exfoliated silica short fibres (5 mm length) were dispersed in the solution. Ratio between the weights of polymer mixture and silica fibres was maintained at 40:60 (by wt.). The solvent from the fibre dispersed polymer solution was evaporated by heating slowly at about 60 °C in an air oven. The dried lumps of silica fibre dispersed polymer mixture was ground using a mixer grinder for 5 min and sieved to maintain the fibre length at ultra short range ($\leq 50\,\mu m$). Silica fibre dispersed polymer powder was filled in a SS mould measuring 80 mm x 70 mm x 30 mm and uniaxially compressed using a hot press under a pressure of 15 MPa at 200 °C for 2 h to obtain ultra short fibre reinforced composites with density of 1200 kg/m^3. The resulting composites are designated as SR-PMSQ-0PF, SR-PMSQ-25PF, SR-PMSQ-50PF and SR-PMSQ-75PF, respectively; the number denotes the weight percentage of PF resin in the polymer mix [9]

2.3. Pyrolysis of the composites

To study the various aspects of carbothermal reduction and related microstructure evolution in presence of PF resole, SR-PMSQ-PF (0 − 75) composite specimens were subjected to pyrolysis at 1500 °C under Argon atmosphere using a one-step heating cycle in a tubular furnace at a heating rate of 2 $°C\cdot min^{-1}$ from ambient to 1500 °C and with a dwell time of 1 h at 1500 °C. The samples were allowed to cool to room temperature at the same rate as that of heating for further analyses.

2.4. Characterisation of the composites

The morphology of the pyrolysed composite specimens was analysed using CARL ZEISS-EVO-50 Scanning Electron Microscope operating at 30 kV. Elemental composition of the samples was determined using Energy Dispersive Spectrometer coupled with the equipment. Microstructure evolution and phase identification of the pyrolysed samples were done using XRD, Raman and FTIR spectroscopy. XRD analyses of the composites were carried out using a Bruker D8-Discover X-ray diffractometer operating with a Cu anode (40 kV, 40 mA). Raman spectral studies were conducted on a WITec alpha 300R Confocal Raman microscope equipped with a 50X air objective and 600 grooves/mm grating. FTIR spectrum was recorded using Nicolet iS 50 FTIR spectrometer.

3. Results and discussion

Depending on the phase miscibility based on IPN composition, interfacial interaction between the matrix and fibre reinforcement varies and it leads to alteration in properties of the composite system. Since the polymeric to ceramic conversion largely depends on the interfacial interactions of constituents during pyrolysis of the composite, it is