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Thermal oxidation crosslinking in the blended precursors of organosilicon polymers containing polyvinylsilane with polycarbosilane

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The polymer precursors containing polyvinylsilane (PVS) with polycarbosilane (PCS) in coating form were prepared. As the content of PVS increases, the onset temperature of the precursor oxidation decreases and the surfaces formed after the oxidation become smooth and hard. The role of Si–H bonds in the PCS–PVS systems during the oxidation is quantitatively analysed on the basis of the absorption of the Si–H stretching band in the precursor spectra. In the blended systems, the oxidation of the Si–H groups forms the dense crosslinked polymer layer which limits the oxygen diffusion into the precursor interior.

1. Introduction

The development of processing ceramic materials from polymer precursors has attracted great attention in recent years. In particular, inorganic polymers containing silicon are being actively studied as precursors or ceramics [1–4]. In these organosilicon polymers, polycarbosilane (PCS) derived from polydimethylsilane is well known as the precursor for synthesizing fine siliconcarbide fibres [5–7]. PCS meets the following conditions required for the precursor: ease of manufacture, high yield of pyrolysis and products with amorphous or microcrystalline phase. Recently, we reported on the effect of polyvinylsilane (PVS) addition into PCS in the synthesis of silicon carbide fibres. Since PVS is highly rich in Si–H bonds as compared with PCS, the precursor containing PVS is cross-linked at lower temperature than pure PCS in oxidation atmosphere [8]. The oxidation behaviour of the precursors containing PVS, however, has not been well defined yet. In this study, we prepared the precursor containing a high quantity of PVS into PCS in the casted coating form, and investigated their oxidation crosslinking and the successive pyrolysis processes by infrared (i.r.) spectrum measurement and thermogravimetric–differential thermal analysis (TG–DTA) analysis.

2. Experimental procedure

Material PCS in the form of transparent solid was supplied from Shin-Etsu Chemical Co. Ltd. The number average molecular weight is 2.0×10^3, and melting point is 508 K. PVS in the form of viscous liquid was synthesized by radical polymerization of vinylsilane in an autoclave [9]. The number average molecular weight is 8.5×10^2. Three kinds of the toluene solutions containing 20 wt % of the pure or mixed polymer were prepared and cast on clean glass dishes to form coatings with 300 μm thickness. PVS contents for the whole precursors were 0, 20 and 40 wt %. The cast solutions were dried and oxidized in air at 423, 453 and 483 K with a heating rate of $50\ \mathrm{K\,h^{-1}}$ and a holding time of 1 h.

After the oxidation processes, the polymer coatings formed on the substrates were broken, picked up, and subjected to the i.r. spectra measurements using the KBr pellet method (Perkin Elmer, Fourier transform (FT)-IR1650) and TG–DTA analysis (Rigaku, TG-8110).

3. Results and discussion

Just after drying pure PCS precursor solution forms a turbid coating with many microcracks, while the precursor solutions containing PVS form smooth surfaces with no cracks. The precursor containing 40 wt % of PVS is, however, still soft and viscous. All the samples on glass dishes were heat-treated in air, and the precursors were solidified. Fig. 1 shows the photographs of the precursor coatings formed on the glass dishes after heat treatment at 483 K. The pure PCS precursors form many additional cracks during the oxidation, and the resultant coating is the aggregate of the fragile powders, which could be easily released from the substrate with a steel spatula. The precursor containing 20% of PVS is partially smooth, but large cracks propagate in the precursors. Parts of the coating having cracks can be peeled off from the

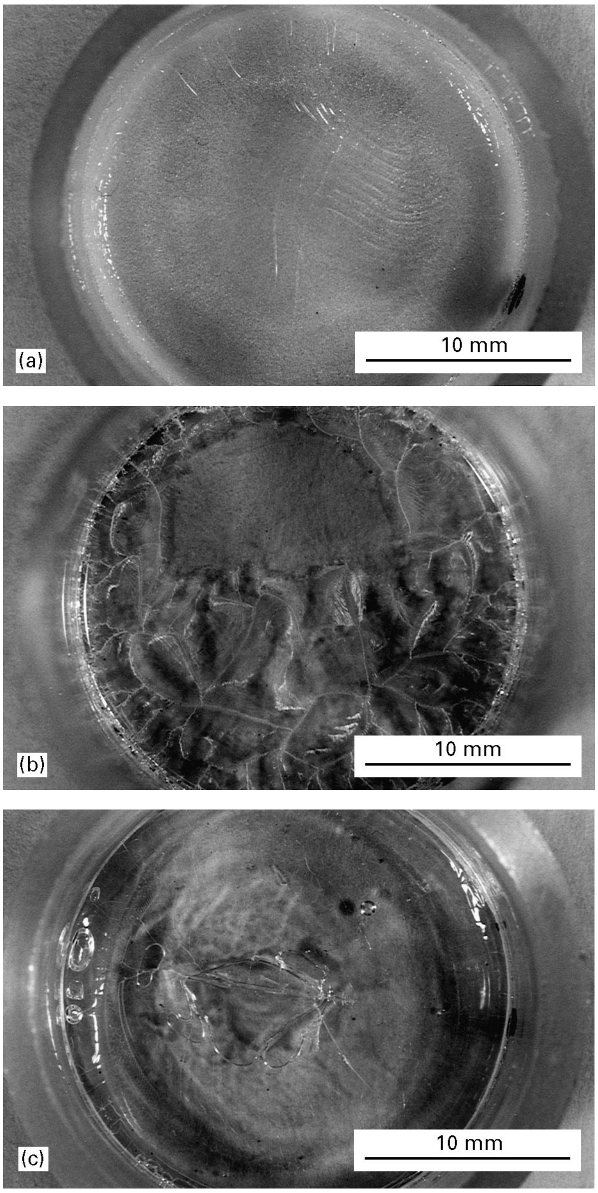

Figure 1 Photographs of the precursor coatings after oxidation at 483 K. (a) Pure PCS; (b) 20% PVS; (c) 40% PVS.

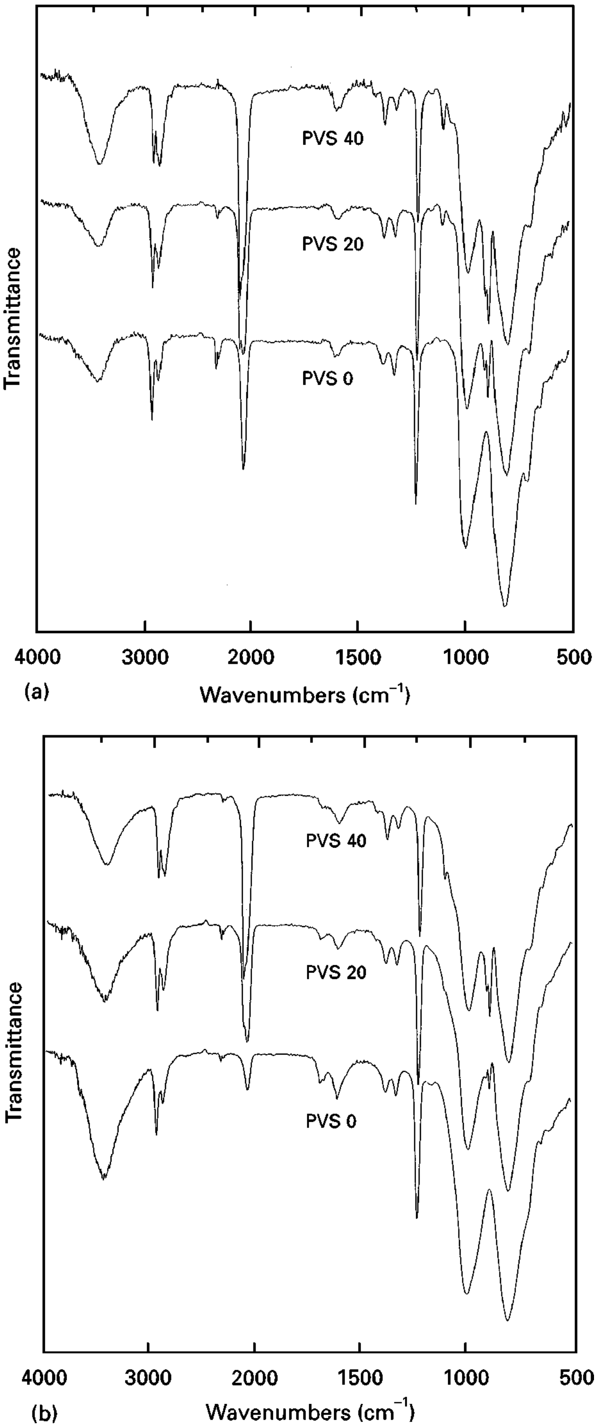

Figure 2 Infrared spectra of the precursors. (a) Original; (b) After the oxidation at 483 K.

substrate. The precursor containing 40% of PVS has less cracks than the precursor containing 20% of PVS. The surface is mostly smooth, and the precursor could be peeled off only with difficulty because of its toughness.

Fig. 2 shows i.r. spectra of the blended precursors before and after the oxidation in air at 483 K. The i.r. spectra of pure PCS precursors before and after the oxidation have been represented [10]. The precursor containing PVS shows new peaks based on the chemical groups of SiH_2 or SiH_3 in PVS structure. The Si–H stretching band in these precursors appears in splitting form in the vicinity of 2100–2200 cm^{-1}. The deformation vibration band of SiH_2 and SiH_3 appears at 890 cm^{-1} which is absent in pure PCS. After the oxidation, the heights of these Si–H peaks decrease, and new peaks of Si–O–Si or Si–O–C band at 1100 cm^{-1} overlap on the original precursor spectra. In Fig. 3, the expanded spectra of Si–H stretching bands are shown. The Si–H absorption bands consist of three components, peak I at about 2110 cm^{-1}, peak II at about 2150 cm^{-1} and a broad tail beyond 2180 cm^{-1}. All spectra were normalized on the highest peak at 810 cm^{-1} as 1.0. Peak I, which appears at the lowest wavenumber, is considered to be the summation of the independent stretching band of Si–H in PCS and the symmetric stretching bands of SiH_2 and SiH_3 in PVS. Peak II, which appears only in the blended precursors at higher wavenumber, would be assigned to the asymmetric stretching bands of SiH_2 and SiH_3 in PVS. After the oxidation, intensities of peak I and peak II decrease but the rate of decrease of peak II seems to be slightly larger than that of peak I. The large decreasing rate of peak II may suggest that

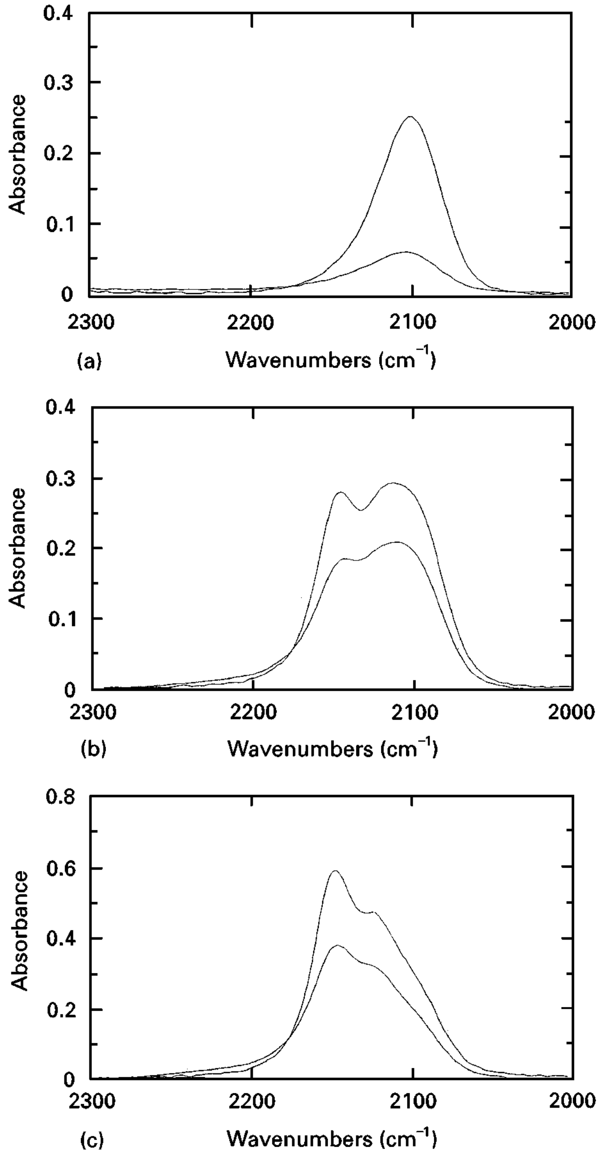

Figure 3 Expanded i.r. spectra of the Si–H stretching band in the original precursors and those after the oxidation at 483 K. (a) Pure PCS; (b) 20% PVS; (c) 40% PVS.

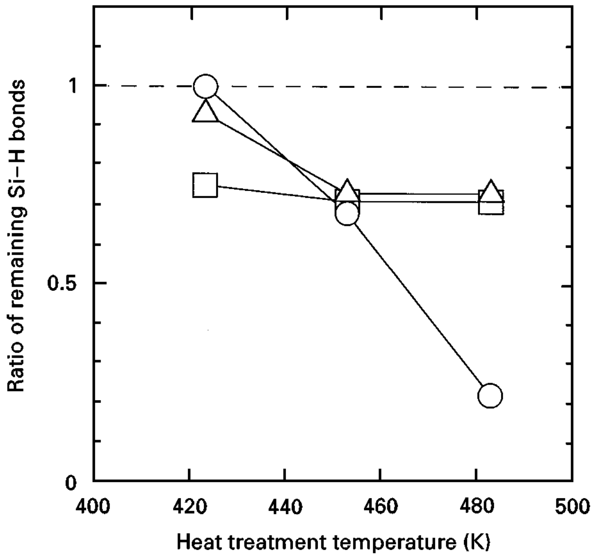

Figure 4 Change in the ratio of the remaining Si–H bonds during the heat treatment in air. (○), Pure PCS; (△), 20% PVS; (□), 40% PVS.

the SiH_2 and SiH_3 groups in PVS prefer to form crosslinks as compared with independent Si–H in PCS. The broad tail beyond 2180 cm^{-1} has not been clearly assigned but would be related to the Si–H bonds near oxidized silicon atoms, because such tails appear only after the oxidation.

The ratios of these three components in the Si–H absorption change during the oxidation. The summation of these components, however, directly corresponds to the number of the whole Si–H bonds in the precursors. Because the shape of the precursor i.r. spectra were not largely influenced with the exception of the absorption bands of Si–H and Si–O–Si (or Si–O–C), we estimated the number of Si–H bonds from the relative area of Si–H absorption bands which have been normalized on the absorption bands at 810 cm^{-1}. This method does not give the absolute number of Si–H bonds, but it is possible to estimate the relative ratio of the remaining Si–H bonds after oxidation in the individual precursors. The calculated results are shown in Fig. 4. Si–H bonds in pure PCS precursor show no change up to 423 K, but begin to decrease at 453 K and reach 0.22 at 483 K. Si–H bonds in the 20% PVS precursor have slightly decreased to 0.93 even at 423 K and reached 0.73 at 453 K. Beyond 453 K, the number of Si–H bands does not change during the heat treatment. In the 40% PVS precursor, the number of Si–H bonds has decreased into 0.75 at 423 K, and becomes almost stable.

Fig. 5 shows the results of TG–DTA analysis of the precursors cured at 483 K. The main weight loss of pure PCS occurs at 950 K with the endothermic reaction which has been assigned to CH_4 evolution from the polymer [10–12], while the main weight losses in the blended precursors occur between 600 and 800 K with the exothermic reaction. Such large weight losses in the blended precursors would come from non-crosslinked polymer chains in the precursors according to the scission and the degradation of PCS and PVS. This temperature region is near the temperature of H_2O evolution at 600 K in oxidation-cured pure PCS [12], but this coincidence would be mere accident, because O–H bonds in blended precursors did not increase to such a large extent during the oxidation. The residual weight after pyrolysis at 1273 K was 83, 70, 66% for pure PCS, 20% PVS and 40% PVS precursors.

These results in i.r. spectra and TG–DTA analysis reveal that the precursor containing PVS is not sufficiently crosslinked by oxygen at 483 K in spite of the hardness in appearance. Such effects of PVS addition can be explained on the basis of compressive polymer layer formation at precursor surfaces by rapid oxidation. The created compressive layer densifies the outer surface and limits subsequent oxygen diffusion into the precursor interior.

The formation of such layers has already been observed in the PCS fibre containing 10% of PVS. In the case of the thin fibres having diameters of 20 μm, the formed layer limits the oxygen diffusion but

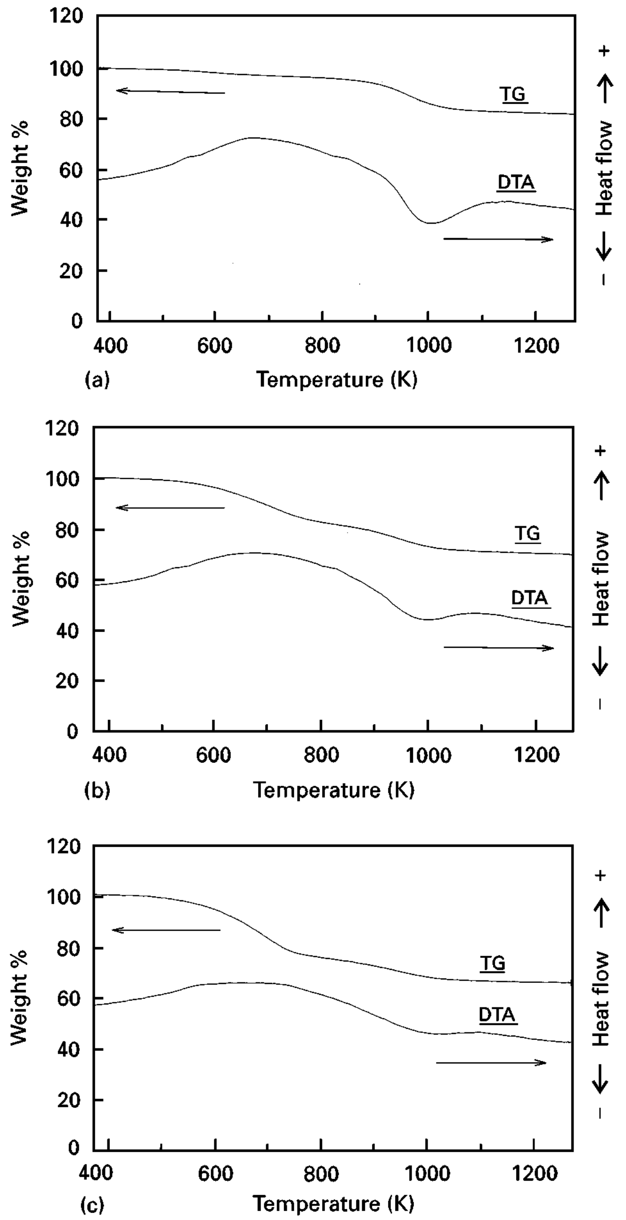

Figure 5 TG–DTA analysis of the precursors in Ar gas flow after the oxidation at 483 K. (a) Pure PCS; (b) 20% PVS; (c) 40% PVS.

provides sufficient support to further ceramization of the fibres [8]. In the form of the thick coatings prepared in this study, such compressive layers make the precursor surface hard and smooth, but do not provide sufficient support for further ceramization. Most of the chains in the precursor are considered to be free of crosslinking even after heat treatment at 483 K.

4. Conclusions

The formation of a compressive skin layer limiting the oxygen diffusion into the precursor interior is confirmed in PCS–PVS blended systems. The addition of PVS makes the precursor more reactive to oxygen, but the crosslinking is not sufficient in the deep part of the coatings, despite the hardness in appearance. The change in the number of Si–H bonds estimated from i.r. spectra reveals that the progress of Si–H oxidation is limited at about 70% of the original bond number in the precursor containing PVS.

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