CHARACTERISATION OF POLYSILANES BY THERMAL ANALYSIS METHODS

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Polysilanes have been synthesised as potential precursors for silicon carbide fibres. One criti-
cal property of these precursors is the ceramic yield obtained on pyrolysis. This is determined by
TG and typical curves are shown. A second important property is the suitability for spinning a fine,
flexible fibre. The characterisation of 'spinnability' is subjective but one of the aims of this work
has been to define more precisely the temperature at which to attempt spinning. This has involved
the use of TMA and DSC.

Keywords: DSC, precusors, polysilanes, TG, TMA

Introduction

Much work is currently being carried out to investigate novel routes for the
production of ceramic materials, especially in areas where conventional fabrica-
tion methods are not possible, for instance in the production of silicon carbide
fibres. One route to producing these fibres is by pyrolysis of a suitable polymeric
precursor.

The production of silicon carbide fibres via a polymeric precursor requires
that several criteria be met. First a silane or carbosilane polymer must be prepared
by a viable route, i.e. one which provides a suitable yield of the required precur-
sor material. It is then necessary that this polymer can be readily spun into con-
tinuous fibres and that the fibre itself should be easy to handle. The fibre must
then be cured in some way to prevent melting when further heating is applied.
The next stage of the process is to pyrolyse the fibre to produce silicon carbide.
This means that the yield on pyrolysis should be sufficiently high to ensure that a
continuous fibre remains after the heat treatment.

A simplified way of looking at the route is as follows:

Polymer synthesis → Separation of suitable fraction → Melt spinning → Curing → Pyrolysis.

The behaviour of these precursors in different temperature regions is therefore important and the aim of the work described is to characterise more fully their thermal properties, including the softening and degradation processes.

Experimental

Most of the polysilanes were produced by the alkali dechlorination of various combinations of chlorinated silane monomers. Syntheses were carried out in an argon atmosphere using xylene and sodium, or THF and potassium, as solvent and alkali metal, respectively. This reaction usually produces three types of polymer: insoluble solid, soluble solid and soluble liquid. The following discussion refers only to the solid fractions as the liquid form is not suitable for conversion into a ceramic material.

Thermogravimetry was carried out on a Stanton Redcroft TG 672 using a heating rate of 20 deg·min^{-1} in a nitrogen atmosphere. TMA and DSC were obtained on Du Pont 943 TMA and 910 DSC respectively. TMA was carried out in air (as
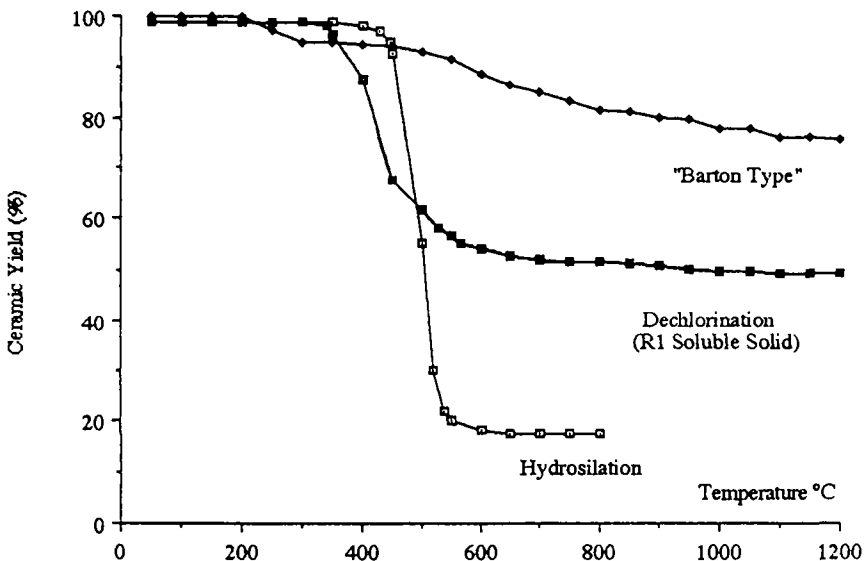
Fig. 1 Ceramic yields of different potential precursors

spinning was not in a controlled atmosphere) at a heating rate of 5 deg·min^{-1} and DSC carried out in nitrogen at 10 deg·min^{-1}.

Determination of ceramic yield

Although most of the polysilanes were produced via an alkali metal dechlorination route [1, 2], there are other ways to produce potential silicon carbide precursor materials. The various polysilanes and polycarbosilanes produced exhibit different properties, depending on the degree of crosslinking within the product. For example, a linear polymer which contains very little crosslinking will usually be spun with relative ease but will give a poor ceramic yield on pyrolysis. The converse is generally true for a highly crosslinked polymer.

The wide variation in ceramic yield determined from TG curves obtained using potential precursors prepared in different ways is illustrated in Fig. 1. The dechlorination reaction is that described above, producing a polymer with a − Si− Si− backbone; the hydrosilation method produces a polycarbosilane with a − Si− CH$_2$CH$_2$− Si− CH$_2$CH$_2$− backbone and the 'Barton' type polymer [3] has a − Si− C≡ C− backbone. From Fig. 1 it is seen that an extremely high ceramic
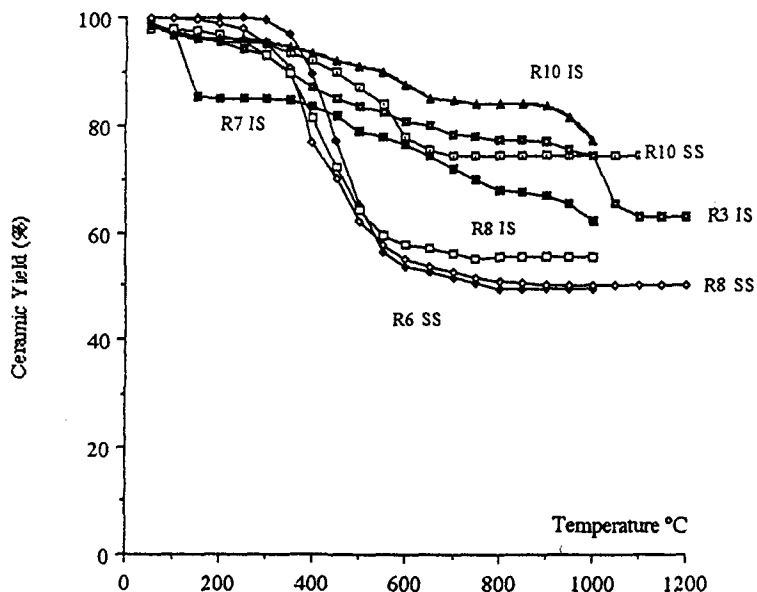

Fig. 2 Ceramic yields of various polysilanes

yield can be obtained from the 'Barton' type polymer. However, attempts to melt spin this type of polymer produced a very poor fibre.

To illustrate the differences in ceramic yield which can be observed, even from polysilanes prepared by the same method, plots obtained from the products of various syntheses are shown in Fig. 2 (IS represents an insoluble solid and SS a soluble one). Hence, the dechlorination route can give a polysilane product of varying ceramic yield but, as discussed previously, a good ceramic yield and suitability for fibre spinning are diametrically opposed. The choice of a polymeric precursor therefore requires the best compromise between these two properties.

Determination of spinning temperature

When a suitable copolymer, i.e. one with an adequate ceramic yield, has been prepared, the next stage in the production of a silicon carbide fibre is to spin the fibre. This is carried out using a specially designed spinning rig as illustrated in Fig. 3. Polymer granules are placed in a 'hopper', a ram is placed above and the polymer is forced down the cylinder and on to the heater block. As the polymer melts it is forced through the block and then through the spinneret. The emerging fibre is then pulled downwards and fed onto a set of collecting drums. It is therefore very important to be able to characterise the melting/softening behaviour of the polymer to enable this process to be carried out successfully.
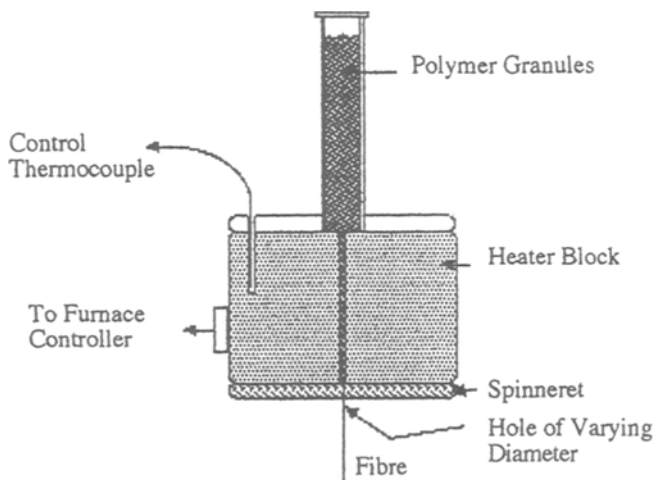

Fig. 3 Fibre spinning rig

Previous trials on spinning polycarbosilane fibres have used a melting point obtained from traditional melting point determination, which is rather subjective, especially if no clear melting point is seen. However, it can be used to give an estimate of the spinning temperature, although it is a temperature range that is determined in practice. In an attempt to understand the requirements of the spinning process more fully, thermal methods have been applied to both well characterised polymers and to soluble and insoluble polysilanes.
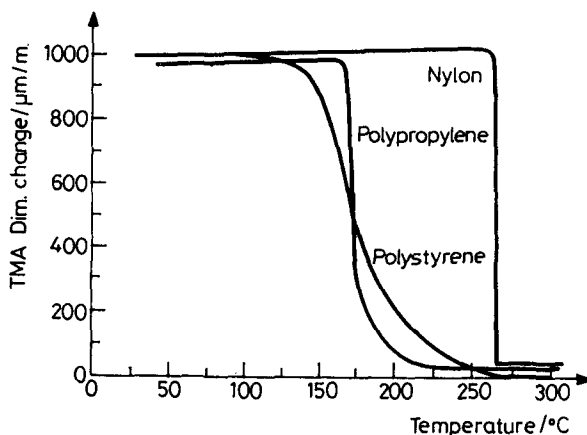

Fig. 4 TMA plots for polypropylene, polystyrene and nylon

Thermomechanical analysis (TMA) was used to determine the melting behaviour of the sample as the temperature was raised. Initially a TMA run was carried out on polypropylene, the results of which are shown in Fig. 4. This material has a 'melt flow index' value of 230°C quoted on the container and experience had shown that this was a suitable temperature at which to spin fibres. The TMA curve shows that softening first started to occur at ~160°C and that melting was complete at 230°C, i.e. at the previously established spinning temperature.

TMA runs were also carried out on two other 'standard' polymers: Nylon 66 and polystyrene (Fig. 4). From these it is seen that the softening temperatures of polystyrene and polypropylene were quite similar, although polystyrene started to melt earlier but finished later, i.e. it melted over a larger temperature range. It is interesting to note that the supplier of the polystyrene quoted a softening value of 95°C, i.e. the start of melting and not the end as is the case for polypropylene. The plot for Nylon 66 was different as the range over which melting occurred was very sharp as is typical for a crystalline polymer. By comparison with the polypropylene data, spinning temperatures of 275° and 265°C were chosen for the

polystyrene and Nylon 66 respectively. Both polymers were spun using these temperatures as starting figures, with different amounts of success.

The polystyrene was actually spun successfully at 280°C, except that the fibre emerged from the spinneret very rapidly and it was difficult to collect it on a drum. The fibre was very fine, flexible and readily spun.

The nylon presented more of a problem. The temperature had to be raised from 265° to 285°C before any polymer was extruded. At this temperature a fibre was produced although as for polystyrene it was difficult to wind on to a collecting drum due to the speed at which it emerged. The resulting fibre was strong, flexible and produced in a large amount.

In view of these results, especially for nylon for which a very specific melting temperature was obtained from TMA but had to be exceeded by ~20°C in spinning, the temperature gradient across the actual heater assembly was measured. A thermocouple was attached to the top of the block and the temperature controller of the spinning rig increased in 50°C intervals. The temperature at the top was noted immediately the control thermocouple reached the set point and then again after five minutes. At the highest temperature used a dwell time of 30 minutes was allowed. The whole procedure was repeated with the thermocouple attached to the bottom of the spinneret. The results are shown in Table 1.

Table 1 Variation of temperature across the spinning rig heater block

Set temperature	Top-0 min temperature	Top-5 min temperature	Bottom-0 min temperature	Bottom-5 min temperature
50	40.7	46.4	42.4	47.0
100	87.9	92.5	89.9	93.5
150	136.7	139.4	138.3	140.5
200	182.3	184.4	184.8	186.7
250	226.3	228.1	230.9	231.7
300	270.0	271.0 *	275.0	275.8 *

* After 30 minutes there was no change from the 5 min readings

It can be seen from Table 1 that there is a significant temperature difference across the heater block, e.g. up to 29° at 300°C. Therefore, under certain circumstances the spinning temperature set on the spinning rig needs to be raised by a suitable amount as was the case for nylon. If the temperature range over which melting occurs is wide then this effect appears to be less important, as a difference of a few degrees between the set and the actual temperature has less effect on the state of the polymer, since it is still virtually molten despite the lower temperature.

Using 'standard' polymers has therefore allowed us to make a comparison between the actual spinning behaviour and the TMA data, which show that both the shape of the curve and the temperature at which melting has fully occurred are important. This information was then applied to polysilanes and typical curves are shown in Fig. 5. In these examples the curves all show a gentle slope and not the sharp drop as for nylon. Also included are examples of TMA curves of insoluble polysilanes and, although some softening was seen, complete melting did not occur. This was also observed for R10 which was isolated as a soluble solid fraction but was later found to have become insoluble on ageing, which was also reflected in the high ceramic yield of this polymer (Fig. 2). For the soluble polymers the point where the melting just finishes was used as the spinning temperature, as suggested by the work decribed above.
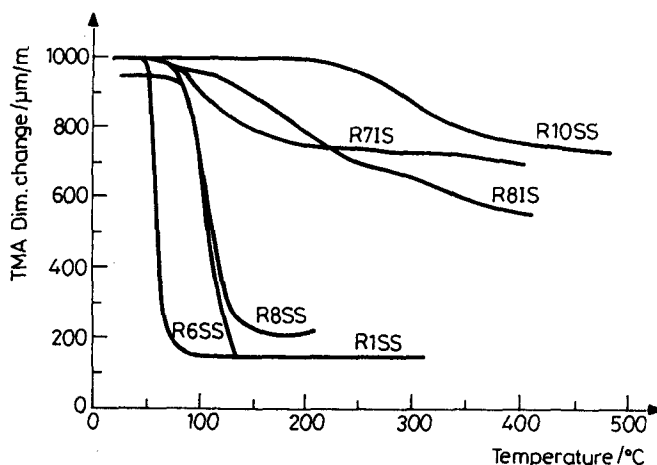

Fig. 5 TMA plots for various polysilanes

For polysilane R1SS spinning was attempted at 135°C and at this temperature a fibre could indeed be spun. Several metres were spun but the fibres were very brittle and, although they could be coiled onto a collecting drum, they shattered when touched.

For polysilane R6SS a spinning temperature of 105°C was used and, although a fibre was produced, it was quite different to that produced from the other polysilanes. As the fibre was extruded through the spinneret it was very viscous and showed considerable swelling and tended to fold back on to the spinneret. As it emerged it appeared quite elastic in nature, i.e. it could be pulled back straight. Once it had cooled, the fibre was very rigid and extremely brittle. However, if the temperature was raised further there was no observable change in the nature of

the polymer, indicating that the optimum temperature had indeed been selected. No attempt was made to spin R8SS as insufficient polymer was produced.

The spinning temperature selected on the basis of the TMA data (after accounting for the temperature differential where necessary) is obviously suitable and appears to correspond with the manufacturer's instructions [4] calling for a temperature where the polymer is just extruded. These instructions also note that a temperature several degrees above the nominal melting point is needed, but the use of Table 1 combined with the TMA data is more specific.
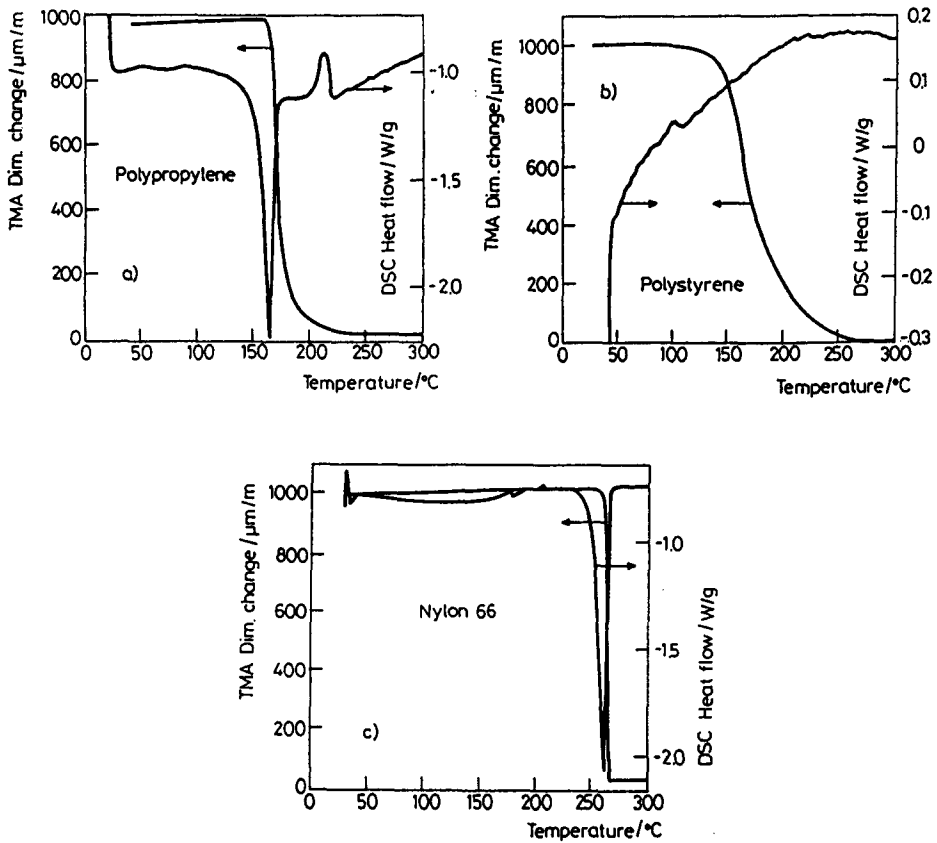
Fig.6 Comparison of TMA and DSC plots for polypropylene, polystyrene and nylon

Use of differential scanning calorimetry

Since DSC is often used to determine melting points, further characterisation of the various polymers was carried out using this technique to determine its use-
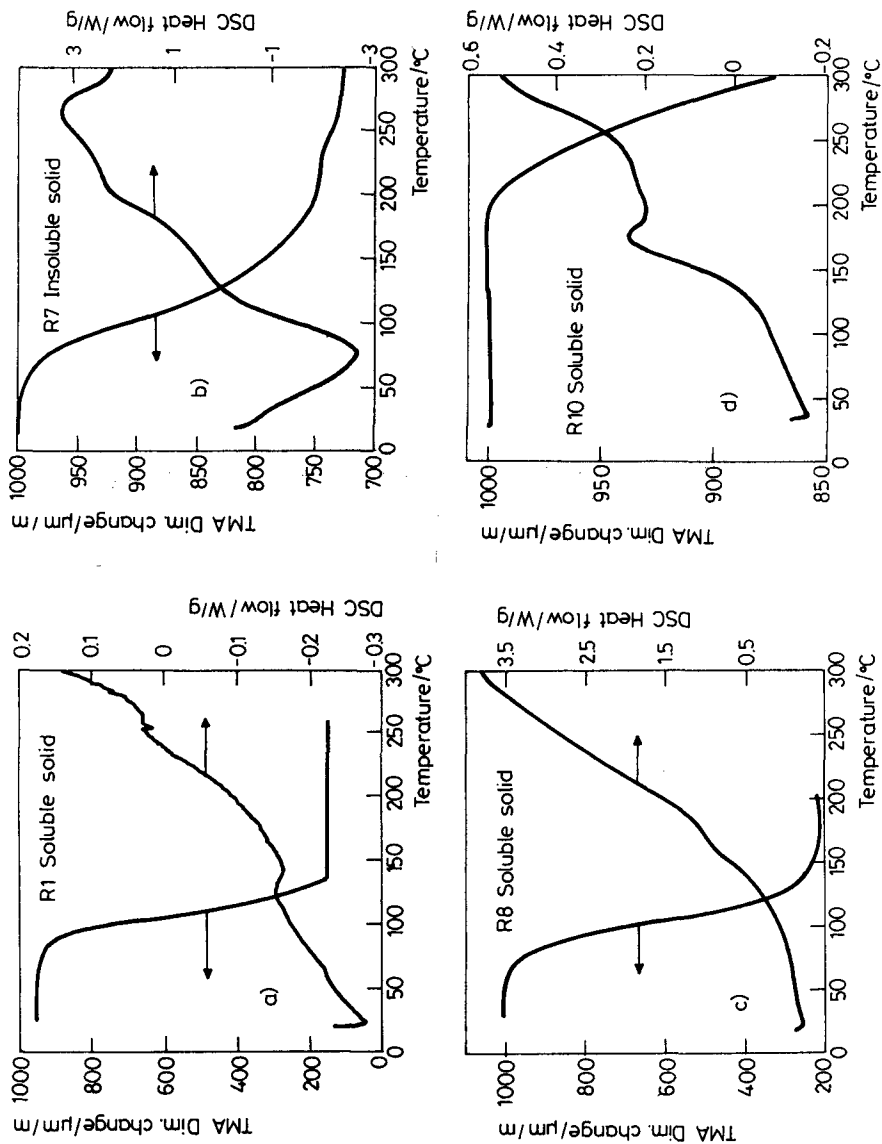
Fig. 7 Comparison of TMA and DSC traces for various polysilanes

fulness as applied to this particular species of polymer. DSC traces were obtained from all the polymers previously discussed and comparison with the TMA data made. The DSC traces obtained from Nylon 66 and polypropylene (Fig. 6) showed endothermic peaks at temperatures similar to those where melting is complete as shown by TMA plots. The DSC trace for polystyrene also shown in Fig. 6 does not exhibit an endothermic peak corresponding to the TMA melting point; this behaviour is consistent with an amorphous polymer.

Examples of the DSC traces obtained from polysilanes are shown in Fig. 7. In each of these plots there is some evidence of a glass transition, most noticeably for sample R10SS. However these peaks are generally ill defined and do not correspond closely to the spinning temperature determined by TMA. Therefore, although DSC is suitable for determining a melting temperature for some polymeric materials, it is not an appropriate method for these polysilanes.

Conclusions

Thermogravimetric analysis is of great value in assessing the potential ceramic yield of a polymeric precursor. New polymers produced can be readily characterised in this manner to determine their suitability as a precursor material.

The use of thermomechanical analysis is shown to be very promising in the determination of a spinning temperature for a polymer and in characterising its potential spinning behaviour. TMA is shown to be preferable to differential scanning calorimetry in this regard for the polysilanes of interest in this study.

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References

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Zusammenfassung — Polysilane wurden als potentielle Präkursoren für Siliziumkarbidfasern synthetisiert. Ein kritisches Merkmal dieser Präkursoren ist die Keramikausbeute bei der Pyrolyse. Dies wird mittels TG ermittelt und typische Kurvenverläufe sind angeführt. Die zweite wichtige Eigenschaft ist die Eignung zum Spinnen einer feinen, flexiblen Faser. Die Eigenschaft "Spinnbarkeit" ist subjektiv und eine der Zielsetzungen dieser Arbeit bestand in einer präziseren Definition der Temperatur, bei der das Spinnen versucht wird. Dabei werden TMA und DSC eingesetzt.