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1 Introduction

Silicon carbide (SiC) fibres are widely employed in industry as reinforcements for advanced ceramic-matrix composites (CMCs), due to their high resistance to oxidation and corrosion, high specific strength/modulus, low density, *etc.*¹⁻⁶ They are generally derived from polycarbosilane (PCS), the precursor to SiC, *via* melt spinning, curing, and high-temperature pyrolysis. Therefore, given their importance as a raw material, the relationship between the molecular structure, molecular weight distribution, and spinnability of PCS is an important issue affecting the preparation of high-performance SiC fibres.

PCS is a polymer with a certain molecular weight distribution. In early studies,^{6,7} PCS was studied as a whole. It was thought that the number average molecular weight (M_n) and softening point of PCS increased with the preparation temperature or time, while the molecular weight distribution changed from a single peak to a double peak. When the preparation temperature or time was further increased, a peak corresponding to super-high-molecular-weight molecules appeared. This component proved detrimental to the spinnability. The evolution of the molecular weight distribution indicated that PCS is made up of many molecules, each having a different M_n . Therefore, the relationship between the molecular composition and spinning performance of PCS has become the focus of

Evolution of molecular composition of polycarbosilane and its effect on spinnability[†]

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The molecular composition of polycarbosilane (PCS) and its evolution in the synthesis process, as well as the contribution of each component to the spinnability of PCS, were explored by combining distillation separation with gel permeation chromatogram peak-splitting. The results show that PCS is composed of four kinds of molecules with different structures, namely M_L , M_M , M_H , and M_{SH} (number-average molecular weights of 531, 1207, 2731, and 10 977, respectively). In the synthesis process, PCS changed from containing two components to three components, and finally to four components. The PCS can be spun when it is composed of M_L , M_M , and M_H , but is not suitable for spinning when it is composed of M_H and M_H , but is not suitable for spinning the amount of M_H and restricting M_L to within a certain range can enhance the spinnability of PCS. The underlying mechanism is controlled by the linear structure of M_H and its low melting point by there being an appropriate M_L content, which ensures melting, de-foaming, and stability in spinning. The final optimum ratio is found to be an M_H content of 30–45%, an M_M content of 30–51%, and an M_L content of 18–25%.

researchers' attention. Based on the solvent-extraction method or chromatographic-column grading method,8 PCS was divided into multiple components according to the experimental conditions. As the M_n increased, so too did the degree of branching, while the Si-H content decreased. Those components with an initial melting point of less than 200 °C can be spun, while the other components proved difficult or even impossible to spin. In the above studies, the PCS was separated by adjusting the solvent ratio or the elution time. The results were influenced by the experimental conditions and did not reflect the actual molecular composition of the PCS. Therefore, the relationship between the spinnability and the molecular composition of the PCS was not accurately investigated. In other studies,9,10 based on the evolution of the molecular weight distribution of the PCS, the PCS was divided into high-, medium-, and low-molecular-weight components by drawing lines across the gel permeation chromatograph (GPC). With the condensation reaction carried out, the branching and ring structure of molecules increase, and the ratio of high molecular weight components is increasing too. Only PCS containing less high-molecular-weight component and more low-molecularweight component has good spinnability. In the above research, the relationship between molecular weight distribution and spinnability of PCS was initially revealed, but the PCS was divided into different components empirically, then different researchers give different standards. Therefore, the conclusion are quite different and may be inaccurate.

The spinnability of the PCS is closely related to its structure and molecular composition. Therefore, it is very important to accurately determine the molecular composition of the PCS, as

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well as study the relationship between the composition, structure and spinnability of the PCS when preparing highperformance SiC fibres. To overcome the above problems, in the present study we used, for the first time, distillation separation combined with GPC chromatographic analysis, to test and analyse a number of samples. The molecular composition of the PCS and the evolution of the synthesis process were studied systematically. The influence of the mechanism on the spinning performance was discussed.

2 Experimental

2.1 Raw materials and reagents

Polydimethylsilane (PDMS) (purity > 98%) was obtained from Shenzhen Gujia Chemicals Co., Ltd., while xylene (purity > 99%) was sourced from Tianjin Hengxing Chemical Reagent Co., Ltd.

2.2 PCS synthesis and separation

PDMS was placed in a three-neck flask fitted with a condenser and receiving trap, for pyrolysis at 400 $^{\circ}$ C in a protective N₂ atmosphere. Liquid polysilane (LPS) was obtained after the resulting solution was cooled and filtered.^{6,9,10}

The obtained LPS was placed in a three-neck flask fitted with a quartz reactor tube, a condenser, and a receiving trap. The LPS was then heated to 450 °C in a protective N₂ atmosphere. This temperature was maintained for a few hours, after which the solution was cooled to room temperature to obtain pre-PCS. The pre-PCS was dissolved in xylene, filtered, and vacuum-distilled at 350 °C for 10 min. Finally, the reactor was cooled to room temperature to obtain PCS.

The PCS was placed in a tilted test tube, heated to a temperature of <450 °C in a sand bath under N_2 protection, distilled under reduced pressure for some time, and then cooled to room temperature to obtain the different components of PCS.

2.3 Spinnability of PCS

Approximately 10 g of PCS was placed in a single-hole meltspinning apparatus, heated to 140–160 °C above the initial melting point for 2 h to allow it to de-foam, and then cooled to the spinning temperature. The spinning pressure was set to 0.2– 0.3 MPa and the spinning speed to 240–294 m min⁻¹. With continuous spinning time (*t*) as the criterion of spinnability: t >30 min, spinnability is excellent; 15 min < t < 30 min, spinnability is good; 5 min < t < 15 min, spinnability is moderate; t <5 min, spinnability is poor. Meanwhile, as the spun PCS fibre becomes finer, the spinnability of the raw PCS is said to be better.¹⁰

2.4 Analysis and characterisation

The softening points of the samples were measured using a Shanghai Precision Scientific Instrument WRS-2A microprocessor melting-point apparatus, with a heating rate of $2 \,^{\circ}\text{C} \,^{\min^{-1}}$. The M_{n} and distribution of the molecular weights of the samples were measured using a Wyatt Technology DAWN HELEOS-II high-performance gel permeation chromatograph (GPC), with an s-Styragel column, and tetrahydrofuran (THF) as the solvent and eluent. The rate of elution was 1 mL min⁻¹. A three-dimensional (3D) super-depth digital microscope (VHX-500, Keyence, Japan) was used to capture photos of fibers and to calculate the average diameter of 50 fibers.

3 Results and discussion

3.1 Composition of PCS

The PCS used for the commercial preparation of SiC fibre was fabricated using a PDMS pyrolysis rearrangement transformation method.¹¹ This method is simple and can be easily applied to mass-production. The M_n of the PCS and its structure are closely related to its synthesis conditions. PCS (hereinafter referred to as PCS-10) with the same molecular weight distribution and softening point as PCS used for the commercial preparation of SiC fibre was synthesised in the laboratory according to the above process and reacted at 450 °C for 10 h. The softening point was found to be 216–241 °C. The M_n was 1758. The GPC curve exhibited a "bimodal" distribution, as shown in Fig. 1.

Due to the different synthesis conditions of the samples, when using the line-drawing method described in the literature, only one boundary can be drawn, at an elution time of about 13.2 min, thus dividing the PCS-10 into two parts.¹¹ However, there is an obvious bulge in the figure at about t = 15.5 min, indicating that there should actually be three regions of concentration for the PCS-10. Since the PCS synthesis reaction is a free radical reaction, the intermolecular reaction combination in the reaction process is random. Therefore, the distribution of each component should be a normal distribution. According to the above speculation, the XPSPEAK software was used to divide the GPC curve for the PCS-10 into three normal distributions of the molecular peaks shown in Fig. 1. The fitted curve for the three peaks exactly matches the original GPC curve, indicating that the PCS-10 is indeed composed of three kinds of molecule, with different $M_{\rm n}$ and structures. The peak values corresponding to each component were 15.3, 14.0, and 12.4 min, while the M_n were 531, 1207, and 2731, respectively. According to the $M_{\rm n}$, from low to high, the molecules corresponding to the three peaks were recorded as ML, MM, and M_H, respectively. The mass ratio of each component was obtained by integrating the area as $M_L: M_M: M_H$ 0.19:0.37:0.45.



Fig. 1 GPC curve and fitting curves for PCS-10.



Fig. 2 GPC curves of PCS synthesised under different conditions. (a) LPS; (b) LPCS; (c) PCS-2; (d) PCS-6; (e) PCS-8; (f) PCS-10; (g) PCS-16; (h) PCS-24.

Table 1 Properties of PCS synthesised under different conditions

| Samples | Reaction temperature (°C) | Reaction time (h) | Melt point (°C) | $M_{ m n}$ | Polydispersity index |
|---------|---------------------------------|-------------------------|-----------------------|------------|-------------------------|
| LPCS | 42.0 | 4 | <20 | 552 | 16 |
| PCS-2 | 450 | 2 | 104-124 | 1008 | 2.7 |
| PCS-6 | 450 | 6 | 158-175 | 1505 | 2.6 |
| PCS-8 | 450 | 8 | 180-200 | 1679 | 2.9 |
| PCS-10 | 450 | 10 | 216-241 | 1758 | 3.4 |
| PCS-16 | 450 | 16 | 256-287 | 2275 | 4.1 |
| PCS-24 | 450 | 24 | >300 | 2661 | 5.3 |

In the PDMS pyrolysis rearrangement conversion processes, the first reaction involved the pyrolysis of the Si–Si bond in the PDMS and the rearrangement of the Si–Si bond to form a Si–C bond. When the Si–C bond becomes the main chain structure, the reactant converts to low-molecular-weight PCS. Then, PCS with a certain degree of polymerisation is attained by the rapid increase in the M_n by dehydrogenation and demethane condensation at 420–460 °C. PCS with good spinnability, which can be used as a precursor for the preparation of continuous SiC fibres, is the product of a particular condition in this process. The whole reaction process could be shown by the products obtained at 450 °C but with different holding times. Under different conditions, the molecular weight distribution of the reaction product changes as shown in Fig. 2. The properties of the products synthesised under different conditions are listed in Table 1. The PCS-*x* in the picture refers to the preparation condition of the sample is *x* h at 450 °C.

The LPS forms a low-molecular-weight polycarbosilane LPCS with a "unimodal" distribution with $M_{\rm n}$ of 552 and softening point lower than room temperature through a structural rearrangement reaction (Fig. 2b). A new peak appears on the lefthand side in a further reaction, becoming a bimodaldistribution PCS with Mn of 1008, softening point of 104-124 °C, and polydispersity index of 1.6 (Fig. 2c). With the prolongation of the reaction time from 4 h to 10 h, the $M_{\rm n}$ increases from 1008 to 1758, the soft point increases from 104-124 °C to 216-241 °C, and the polydispersity index increases from 1.6 to 3.4, with an increase in the high-molecular-weight peaks (Fig. 2c-f). As the reaction goes on further, the $M_{\rm n}$ increases from 1758 to 2661, the soft point increases from 216-241 °C to a temperature beyond the measurement range (300 $^{\circ}$ C) and the polydispersity index increases from 3.4 to 5.2, with significant bulging on the left, but overall, they continued to exhibit a "bimodal" distribution (Fig. 2f-h). The GPC curve of the above PCS was also subjected to the same peak-splitting processing. The result is shown in Fig. 3.

Although the PCSs with different reaction degrees produce different GPC curves, the fitting curves obtained from the peaksplitting are in good agreement with the original curves, indicating that such peak processing is reasonable. It can also be seen that the original "unimodal" LPCS contains two peaks



Fig. 3 GPC curves and fitting results of PCS synthesised under different conditions.

 Table 2
 Peak positions in GPC curves of PCS synthesised under different conditions

| | Elution time (min) | | | | | | |
|---------|--------------------|----------------|----------------|-------------------|--|--|--|
| Samples | $M_{\rm L}$ | M _M | M _H | M_{SH} | | | |
| LPCS | 15.7 | 14.2 | _ | _ | | | |
| PCS-2 | 15.3 | 13.7 | 12.4 | — | | | |
| PCS-6 | 15.6 | 14.1 | 12.5 | _ | | | |
| PCS-8 | 15.7 | 14.2 | 12.5 | — | | | |
| PCS-10 | 15.3 | 14.0 | 12.4 | — | | | |
| PCS-16 | 15.1 | 13.8 | 12.0 | 10.9 | | | |
| PCS-24 | 15.1 | 13.8 | 12.0 | 10.9 | | | |

while the original "bimodal" distribution of PCS-2, PCS-6, PCS-8, and PCS-10 contains three peaks. Meanwhile, PCS-16 and PCS-24 exhibit a "bimodal + bulge" distribution, which means another new peak with an ultrahigh molecular weight (M_{SH}) at t = 10.9 min on the high-molecular-weight side is produced, that is, it actually has four peaks. The peak positions corresponding to each peak formed after these PCSs were fractionated are listed in Table 2.

As shown in the table, a low-molecular-weight peak M_L and middle-molecular-weight peak M_M appeared at 15.4 min and 14.0 min in each group of samples. With the increase in the reaction time, the higher-reacting PCS component produced a high-molecular-weight peak at 12.3 min M_H , and an ultra-high molecular PCS component in the vicinity of 10.9 min. Considering that all peaks occur at 15.4 ± 0.3 , 14.0 ± 0.3 , 12.3 ± 0.3 , 9.7, the peaks appearing at same position can be regarded as being of the same molecular type. This indicates that, during the high-temperature polycondensation to form PCS, specific molecular weight groups of different molecules will be formed. Specifically, the LPCS transformed by LPS contains both M_L and M_M molecules, while PCS-2, PCS-6, PCS-8, and PCS-10 contain the same M_L , M_M , and emerging M_H molecules. The higher-molecular-weight PCS-16 and PCS-24 contain M_L , M_M , M_H , and new M_{SH} molecules.

3.2 Evolution of PCS components

As shown in Fig. 2, in the synthesis of PCS, as the reaction proceeds, the molecular weight distribution of the product changes significantly. On the surface, it changes from "unimodal" to "double peak". After the peak-splitting treatment, the M_L and M_M molecules are actually produced first, followed by a polycondensation reaction between the two components to derive the third component which further reacts to generate the fourth component. The ratio of each component in the reaction at 450 °C at different times was quantitatively analysed, and the change in the mass fraction is shown in Fig. 4 (the initial sample was LPCS).

As the reaction time is prolonged, among the low-, medium-, and high-molecular-weight components, ML decreases rapidly and M_M decreases slightly and then decreases slowly. Corresponding to the rapid decrease in the M_L content, the M_H content increases rapidly, reaching its highest value at about 16 h. The reaction from the beginning of the reaction to about 16 h constitutes the first stage of the reaction. The LPCS formed by the rearrangement of the LPS contains only two components, that is, M_L and M_M, with contents of 64.1% and 37.9%, respectively. At this time, the M_L is the main component. However, when the LPCS reacted at 450 °C, the M_L content began to decrease. After reacting for 2 h, a new peak appeared at around 12.4 min, indicating that the reaction had produced a new component, M_H. With the prolongation of the reaction time, the M_L content decreased while M_H increased significantly and M_M decreased slowly. In the reaction, over about 2-10 h, the three components exhibited a "three pillars" trend. Once the reaction had run for about 16 h, the M_H no longer increased, marking the completion of the first stage of the reaction. In the first stage, the M_L and M_M are the main reactants, in which M_M has both formation and consumption processes. After 16 h, the reaction enters the second stage. The main characteristic of this phase is that the M_L, M_M, and M_H contents all decrease as the reaction time increases, and another new component, M_{SH}, appears on the GPC chart. In this case, the resulting PCS is characterised by the original three components being replaced by four components, namely, ML, MM, MH, and MSH.

During the transition from the high-temperature polycondensation of LPCS to PCS, the evolution of the 2-3-4 components in the two stages of M_n increase is related to the reaction mechanism of the high-temperature polycondensation reaction. After the Si–Si rearrangement reaction is completed at 400–420 °C, the dehydrogenation and demethanisation reactions occur mainly at higher temperatures (440–460 °C):



Fig. 4 Change in cumulative ratio of PCS with reaction time.



| Table 3 | Peak positions | and M_n for PCS | obtained under | different of | distillation condition | S |
|---------|----------------|-------------------|----------------|--------------|------------------------|---|
|---------|----------------|-------------------|----------------|--------------|------------------------|---|

| | Distillation condition | | Distillation results | | Peak fitting results | |
|-----------------|------------------------|----------|----------------------|----------------|----------------------|----------------|
| Samples | Temperature (°C) | Time (h) | Peak position (min) | M _n | Peak position (min) | M _n |
| 'M _L | 360 | 2 | 15.7 | 393 | 15.6 | 531 |
| 'M _M | 420 | 2 | 14.3 | 1009 | 14.1 | 1207 |
| 'M _H | 440 | 5 | 12.8 | 2378 | 12.5 | 2731 |



This polycondensation reaction between molecules will inevitably bring about a rapid increase in the M_n , and eventually form a complex structure with PCS of a certain M_n . The hightemperature polycondensation process involves four different molecular weight components, namely, M_L , M_M , M_H , and M_{SH} , with the corresponding peak M_n being 531, 1207, 2731, and 10 977. This variation points to the reactivity of the components varying from strong to weak in the order of $M_L > M_M > M_H >$ M_{SH} . As the peak value for a component falls, so too does its reaction activity. It thus takes more time or a greater amount of content to promote the reaction. Given the M_n values, it can be speculated that an intermolecular polycondensation reaction occurred between the main components, as follows:

First stage:

$$\begin{array}{ll} 2M_L \rightarrow & M_M \\ M_L + & M_M \rightarrow & M_H \\ 2M_M \rightarrow & M_H \end{array}$$

Second stage:

$$M_L + M_M + M_H + \dots \rightarrow M_{SH}$$

In the first stage, the polycondensation mainly occurs between two low-molecular-weight components, one lowmolecular-weight component and one middle-molecularweight component, or two middle-molecular-weight components. In the second stage, as more molecules become involved in the response, the polycondensation reaction occurs between multiple molecules. As mentioned above, since the reaction first forms two types of molecules, M_L and M_M , having a specific M_n , and then, in a subsequent reaction, forms M_H and M_{SH} molecules of a specific M_n according to a certain rule, there are no disorderly or diverse molecule species. Based on this evolution of M_n growth, the reaction conditions can be adjusted to control the composition of the product, resulting in a product with an appropriate structure and M_n .

3.3 Relationship between components and spinnability

The above study shows that PCS with good spinnability is composed of M_L, M_M, M_H. Therefore, these three components and their impact on spinnability need to be studied. In addition, the above-mentioned peak-splitting processing is very good for dividing good-spinnability PCS into three components with a normal distribution, but this is done through image processing, and whether these three components actually exist in PCS remains questionable. There is, therefore, a need for experimental separation to prove this. To isolate the PCS components, several researchers previously used solvent extraction or chromatographic column fractionation.8,9 However, it is difficult to accurately separate the components by means of solvent extraction, which is accompanied by some molecular weight tailing in the separated components. The column separation method is inefficient and can only produce small amounts of samples, which cannot be used to test their spinnability. In the present study, a distillation unit, designed and built in-house, was used to perform the vacuum distillation of PCS-6 under different conditions. By controlling the distillation temperature, the three components with low, medium, and high $M_{\rm n}$ (denoted 'M_L, 'M_M, and 'M_H) were separated from the PCS-6. The vacuum distillation conditions and the properties of the three obtained fractions are listed in Table 3, in which ${}^\prime M_L$ and ${}^\prime M_M$ correspond to the fractions obtained from the distillation, and 'M_H to the fraction remaining after the

Table 4 Spinnability of M_L, M_M, and M_H

| Samples | Melt point (°C) | De-foaming temperature (°C) | Optimum spinning temperature (°C) | Average continuous spinning time (min) | Diameter (µm) |
|----------------|--------------------|--------------------------------|--------------------------------------|--|------------------|
| $M_{\rm L}$ | <30 | 150 | _ | 0 | _ |
| M _M | 152-168 | 330 | 268 | 16 | 16.2 |
| $M_{\rm H}$ | >300 | 410 | — | <2 | _ |

Table 5 Melt point, composition ratio, and spinnability of PCS

| | Cumulative ratio (%) | | | | | | |
|----------|----------------------|----------------|----------------|-----------------|--|------------------|--------------|
| Samples | M _L | M _M | M _H | M _{SH} | Average continuous spinning time (min) | Diameter (μm) | Spinnability |
| LPCS | 64.1 | 37.9 | 0 | 0 | _ | | None |
| PCS-2 | 40.0 | 47.9 | 12.1 | 0 | 25 | 17.6 | Good |
| PCS-6 | 24.6 | 43.5 | 31.9 | 0 | >30 | 15.6 | Excellent |
| PCS-8 | 22.4 | 42.7 | 34.9 | 0 | >30 | 13.7 | Excellent |
| PCS-10 | 18.7 | 36.5 | 44.8 | 0 | >30 | 13.5 | Excellent |
| PCS-10-2 | 10.2 | 39.0 | 47.8 | 0 | 7 | 16.4 | Good |
| PCS-16 | 8.7 | 32.5 | 55.9 | 3.0 | 17 | 14.8 | Good |
| PCS-24 | 6.3 | 31.4 | 46.5 | 15.8 | <1 | _ | None |

distillation. For comparison, the corresponding peak-splitting results for M_L , M_M , and M_H , obtained from the PCS-6, are also listed in the table. The GPC for ' M_L , ' M_M , and ' M_H is shown in Fig. 5.

Although the peak shape of the three components separated from PCS-6 by vacuum distillation is not completely normal, and there is still some tailing in M_H , the overall composition is a single peak, which is better than the result attained when using solvent extraction. The peak positions of the three fractions were 12.8, 14.3 and 15.7 min, respectively, corresponding to and closely approximating to the 12.5, 14.1, and 15.6 min of the PCS-6 peak-splitting value, and the corresponding M_n deviation was not large. The three samples are equivalent to the M_L , M_M , and M_H components (' M_L , ' M_M , and ' M_H are expressed as M_L , M_M , and M_H in the following discussion). This also shows that the above-mentioned results of the peak-splitting are correct, demonstrating that the above three components are present in the PCS.

As mentioned above, during the synthesis of the PCS, the intermolecular polycondensation reaction takes place during the conversion of the components from M_L to M_M and from M_M to $M_{\rm H}$. In addition to causing a doubling of the $M_{\rm n}$ of the components, this also causes changes in the molecular structure (ESI, Fig. S1-S4, Tables S1 and S2[†]). In particular, the occurrence of intramolecular cyclisation and a branched structure will significantly change the molecular structure and thus affect the spinnability of the product. As the linearity of the molecule increases, the rheology improves, as does the spinnability. The linearity increases with the increase in the length of the molecular chain and decreases with any increase in the ring and branching structures. In the transformation of the components, the existing molecular chain, and the ring and branching structures increase, which will have some impact on the spinnability of the PCS. To determine the spinnability of the

three components, they were individually placed in a singlehole melt spinning apparatus, which was used to conduct spinning at a constant spinning pressure of 0.3 MPa and a takeup rate of 267 m min⁻¹. The results are listed in Table 4.

The M_L has a low M_n , and a softening point that is lower than room temperature, such that it is a viscous liquid at room temperature. When spun at room temperature, the sample drips after being extruded from the spinneret and cannot be formed into fibres. The spinnability of the MM component is better than that of M_L. Continuous spinning can be achieved at an appropriate de-foaming temperature and spinning temperature, but the spinnability is still inferior to that of commercial PCS (PCS-10). M_H has a higher M_n than M_M , so may have a better spinnability. However, due to its high softening point, defoaming in the melting cylinder at 410 °C for 2 h will still fail to completely de-foam the sample, such that when the melt is spun from the spinneret, the extrusion will be intermittent, failing to produce a continuous fibre. Increasing the de-foaming temperature will cause further polycondensation, resulting in increased viscosity, and thus the failure of the spinning.

The above results indicate that the spinnability of PCS is not determined by a single component, but that it is a combined effect of all the components. An analysis of the evolution process in the last section of the PCS reveals that two components, three components, and four components, as well as three kinds of PCS, were formed during the reaction. To verify the contribution and influence of each component on the spinning, spinning experiments were undertaken with these three types of PCS, as shown in Table 5 (spinning conditions and pictures of fibers were shown respectively in the Table S3 and Fig. S5 in ESI†). PCS-10-2 sample obtained after 30 min re-vacuum of PCS-10.

The effect of the four components on the spinnability of the PCS is shown in the table: LPCS containing only the M_L and M_M

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components incurs the same problem as M_L in the spinning process because M_L is the main component. The sample drips after being extruded from the spinneret and cannot be formed into fibres. PCS-2 to PCS-10, all containing M_L , M_M , and M_H , exhibited good or excellent spinnability, and as the value of M_H increased, the diameter of the spun fibre decreased from 17.6 to 13.5 µm. As the M_H content of the PCS increased, its spinnability further improved, indicating that, among the three PCS components, the M_H structure is the most suitable for spinning, and makes the largest contribution to the spinnability. When the higher M_n M_{SH} components in the PCS formed a fourcomponent system, the spinnability gradually decreased in order, from PCS-16 to PCS-24.

Obviously, the spinnability of the PCS depends on its composition. The $M_{\rm n}$, structure and content of each component have different impacts on the spinnability of the PCS. The M_n and structure of M_H are suitable and are key to determining the spinnability of PCS. Although M_H is not suitable for melt-spinning by itself, it exhibits excellent spinnability when combined with M_L and M_M. When M_{SH} is added, however, since M_{SH} is a polymolecular polycondensation reaction product with a M_n that is four times greater than that of M_H, the structure contains more cyclised, branched, and even crosslinked structures, thus adversely affecting the spinnability of PCS. Of the three components of PCS, M_L exhibits no spinnability but is nevertheless an indispensable component. The M_L content in PCS-10 (which has good spinnability) was reduced by about 8%, thus adversely affecting the spinnability of the PCS. Although the drastic reduction in the M_L content from PCS-2 to PCS-10 does not significantly affect the spinnability, there is clearly a limit to the effect on the spinnability when the M_L content is below this limit. The presence of M_L lowers the softening point of the PCS and can also act as a lubricant at the spinning temperature, which avoids the selfpolymerisation of the samples, ensures good de-foaming, and reduces the dependence of the PCS viscosity on the temperature, making the viscosity temperature curve smoother and the spinning process more stable.

The above studies show that a "unimodal" type of LPCS containing both M_L and M_M components is not suitable as a raw material for spinning due to its M_n and low softening point; the "bimodal + bulge" four-component PCS exhibits poor spinnability due to the presence of the M_{SH} component. Only the three-component PCS offers excellent spinnability. In the three-component (M_L , M_M , and M_H) PCS, the M_H provides a linear structure that realises the spinnability and which is a major contributor to the spinnability, while M_L ensures uniform melting, de-foaming, and stable spinning. In the synthesis of spinning-grade PCS, the M_H content must be increased as much as possible and the required M_L content should be maintained to ensure a reasonable ratio of the three components. The optimal ratio, determined by experiment, was 30–45% M_H , 30–51% M_M , and 18–25% M_L .

4 Conclusions

In the present study, the molecular composition of PCS, the evolution of the synthesis process, and the influence of each

component on the spinnability were systematically studied by combining distillation separation with GPC peak-split. The results showed that, during the synthesis of PCS, LPCS contains two components, M_L and M_M. Because of further hightemperature pyrolysis, two new components, M_H and M_{SH}, were produced. The product composition evolves from two components, through three components, to four components. PCS with good spinnability has average M_{L} , M_{M} , and $M_{H} M_{p}$ of 531, 1207, and 2731. The spinnability of the PCS does not depend on a single component but on the combined effect of the individual components. The M_H polymer component provides a linear structure and makes the greatest contribution to the spinnability. The M_L ensures the uniform melting and defoaming, as well as the stable spinning of the PCS. To produce PCS with good spinnability, the content of the M_H polymer component should be maximised while an appropriate amount of the M_L should be incorporated. Results of experiments proved that the optimum content ratios were 30-45% M_H, 30-51% M_M, and 18-25% M_L.

Conflicts of interest

There are no conflicts to declare.

Abbreviations

| M_L | Low-molecular-weights component |
|----------------|--|
| M _M | Middle-molecular-weights component |
| M_{H} | High-molecular-weights component |
| M_{SH} | Super-high-average-molecular-weights component |
| CMC | Ceramic-matrix composite |
| GPC | Gel permeation chromatogram |
| PCS | Polycarbosilane |
| SiC | Silicon carbide |
| THF | Tetrahydrofuran |
| PDMS | Polydimethylsilane |
| LPS | Liquid polysilane |

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