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Boron nitride thin fibres obtained from a new copolymer borazine–tri(methylamino)borazine precursor

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Abstract

Boron nitride thin fibres have been obtained using the melt drawn technique from a new molecular precursor prepared by reacting borazine $(HBNH)_3$ with trimethylamino-borazine $(CH_3NHBNH)_3$, (MAB). Borazine reacted very slowly with MAB at room temperature but this reaction was very enhanced when heated. Polymers have been prepared with different borazine/MAB ratio and several reaction temperatures and times. According to the precursor properties required for the melt drawing technique, the best results were obtained with copolymer prepared with a borazine/MAB molar ratio of 90/10 heated at 75 °C for 36 h. Its glass transition was 22.5 °C and no decomposition occurred up to 100 °C. The ceramic yield was 78%, however the ceramisation, even under an ammonia atmosphere, was very slow up to 300 °C. Using a spinning machine, a mother fibre was easily extruded at 85 °C under a 40 daN pressure with a diameter of about 200 μm but its mechanical properties were too low to allow stretching of this crude fibre to lower its diameter down to 20 μm without a lot of breaks. After a chemical and thermal treatment up to 1800 °C, samples of BN fibres have been obtained. If the diameter from the crude fibres was thin enough, short samples of a thin ceramic BN fibre have been obtained, but if the diameter of the crude fibre was to important, the ceramisation yield to catastrophic defects on the surface of the fibre. Theses results were related to the low glass transition of the copolymer and to the poor reactivity of the crude fibre during the preceramisation treatment as showed by TGA. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron nitride; Precursor; Fibre

1. Introduction

Boron nitride composites appeared as very promising ceramic compounds especially for spatial and high temperature applications. The iso-electronic nature of the carbon–carbon and boron–nitrogen bond has given new outlook to the preparation of BN/BN composites, similar to C/C composites, but with two important specific properties: an improved stability at high temperature and a low dielectric constant, that render BN/BN composites very attractive for high technology applications [1–3]. The most important problem for this project was to obtain high performance BN fibres exhibiting mechanical properties comparable to those of the PAN carbon fibres and industrially available. In the last 20 years, several routes have been explored starting from very different precursors. Using boron oxide or borate derivatives which were first spun then treated with ammonia through a high temperature nitruration [4,5], an industrial production of very thin BN fibres have been obtained but the stability of the fibres properties were very poor. The most promising results have been obtained by thermolysis of polymeric fibres prepared using the melt-drawn technique from molecular precursors [6–14]. This technique required special properties of the polymers used as precursor in order to obtain crude fibres exhibiting a constant diameter of about 20 μm in a great length and without defect. The

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physical properties of the polymer have to be very constant during all the extrusion to allow the stretching of the crude fibres and their wounding around a spool to obtain regular fibres. Among the precursors which have given high performance boron nitride fibres, most of them have been obtained from borazines but the dehydropolymerisation of pure borazine, $H_3B_3N_3H_3$ yielded to non-spinnable polymers without chemical modification [14]. Usually an amine was added to the borazine to enhance the spinning properties of the precursor but this addition lower the ceramic yield of the polymer. An other family of fibre precursor was issued from aminoborazine (AB) through a thermal [8] or chemical polymerisation [11]. Convenient polymers have been prepared and several patents claimed the knowledge to obtain long thin fibres. In this work, using the reaction of borazine and AB new copolymers have been prepared with reological properties allowing their spinning with a melt-drawn apparatus yielding to BN fibres when ceramised. Unfortunately, even using the most easily processible polymer, the extruded fibres exhibit poor stretching properties and fine crude fibres were difficult to obtain in long run (about 1 m) so no mechanical properties could be measured. If the crude fibres were not thin enough, during the ceramisation the gas evolved induced many defects on the surface leading to catastrophic properties and porous materials. The ceramisation heating program and the reductive gas used seemed not appropriated to allow a good fibre/gas exchange specially with thick fibres. However, the copolymerisation borazine–AB seemed to be a new way to get spinnable copolymers with a ceramic yield higher than the classical trimethylamino-borazine $(CH_3NHBNH)_3$, (MAB) issued polymer.

2. Results and discussion

2.1. Study of the borazine/AB reaction

To be converted into boron nitride, the most promising precursor leading to the highest ceramic yield was issued from the borazine ($H_3B_3N_3H_3$). Unfortunately the obtained polyborazylenes were known to be unable to be melt-spun into fibres with out chemical additives which lower the ceramic yield [12]. The behaviour of the amino group supported by the boron atoms of the AB $(RNHBNH)_3$, were known to present a reactivity comparable to the chemical behaviour of amines. To enhance the spinning properties of polyborazylene, the addition of (AB) have been realised and the copolymerisation of borazine and (AB) have been studied. To get high ceramic yield polymers; the (AB) chosen was MAB $(CH_3NHBNH)_3$. To get a panel of the possibilities given by this copolymerisation and modify the physical properties of copolymers, several borazine/AB ratio have been used. The two reactants were prepared according to published methods [14–20]. The study of the reaction was followed using ^{15}N-NMR (with a ^{15}N non-enriched borazine). When (MAB) was mixed with borazine, a new ^{15}N signal appeared to high field attributed to a NH_2 group with a chemical shift of -368 ppm. The spectrum recorded at the beginning of the copolymerisation was given in the (Fig. 1). The low field multiplet was attributed to non-equivalent NH groups of the BN cycles in the copolymer. The admitted scheme when a secondary amine was reacted with borazine was a simple bonding yielding to a $N(CH_3)_2$ addition on the boron atom with the evolving of an hydrogen atom [21,22]. The behaviour of the aminogroup of (AB) was usually considered as reacting like a secondary amine yielding to a polymerisation as described in (Scheme 1). Effectively, only hydrogen could be characterised during the reaction. However, the presence of the NH_2 group involve a more complex reaction than expected. In fact, the more probable reaction occurring after the first step addition of the amino group of (AB) on the borazine molecule could only be explained by a total reorganisation of the cycles (Scheme 2), a scrambling of the NH and BH groups of the borazine structure as described in the ammonia initiated polymerisation of the borazine [17].

The reaction of reorganisation schematised by (Scheme 2) led to condensation of the borazinic cycles but no evidence of the anthracenic like structure of the copolymer could have been determined using NMR because, out of the NH_2 group appearing during the synthesis, the chemical shifts of the atoms of boron, nitrogen and carbon were very small and the ^{11}B signal were too broad to distinguish non-equivalent sites.

When (AB) had been completely reacted, the NH_2 signal and disappeared after a heating of 15 h at 75 °C, the spectrum obtained is given on Fig. 2. If the heating of the copolymer was carried on for a longer time, the

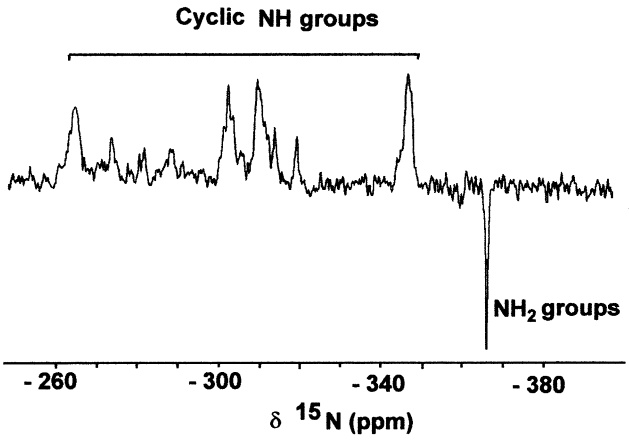
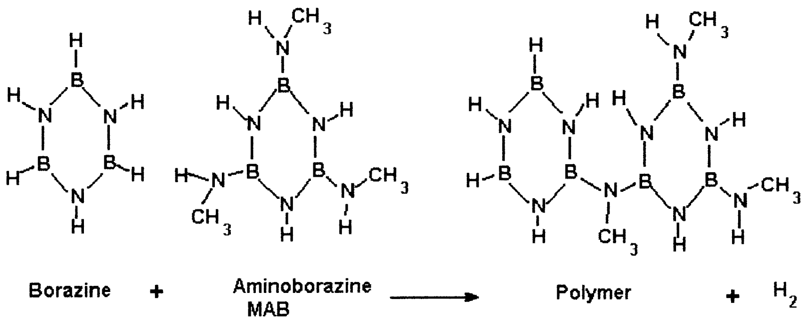
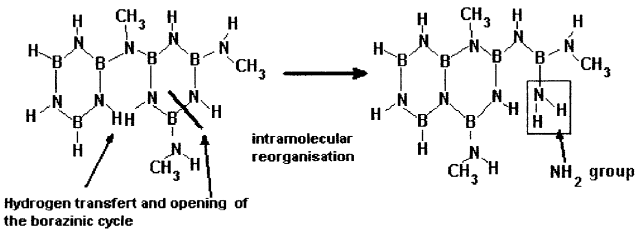


Fig. 1. ^{15}N-NMR spectrum of the copolymer at the beginning of the reaction.



Scheme 1. Reaction of copolymerisation borazine/MAB.



Scheme 2. Reorganisation of the polymer after the addition reaction.

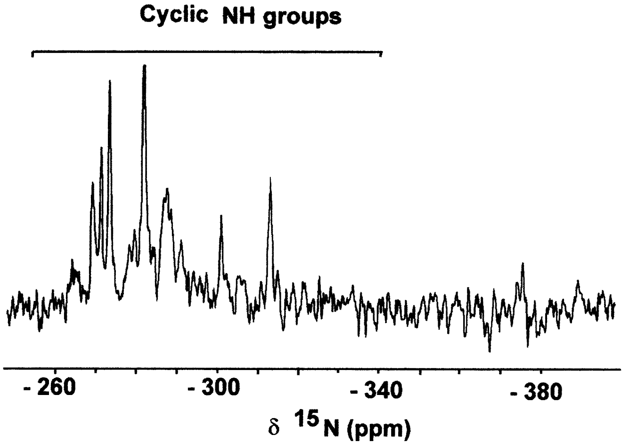


Fig. 2. ^{15}N-NMR spectrum at the end of the co-polymerisation reaction.

copolymer became more hard and the number of the low field signals increased corresponding to the cross-linking of the polyborazylene through the classical mechanism.

2.2. Determination of the experimental conditions of the synthesis of the copolymer

The most representative results are given in (Table 1). In a first study, the spinning properties of the obtained copolymers were tested using a Kofler hot plate placed in a dry box under an argon atmosphere.

This screening of the composition and thermal treatment during the copolymer synthesis had shown that the best copolymer to be used in a melt drawing technique were: a high borazine/(AB) ratio of 90/10% and a medium temperature treatment, performed for a time long enough.

The increasing of the reaction time increased the softening temperature of the copolymer. A balance had to be made between a high spinning temperature characteristic of a more crosslinked polymer leading to good mechanical properties to the spanned crude fibres and the extrusion temperature which should be as low as possible to avoid the polymerisation of the precursor during the spinning. The results were summarised in (Table 2). The sample 3 seemed to have the most promising properties and the synthesis of 8 g of polymer had been achieved.

2.3. Properties of the copolymers

Several parameters were very important to determine the ability of a copolymer to be converted into fibres. Thermal properties were measured using DSC, leading to the thermal behaviour and the range of the spinning temperature, and TGA under controlled atmosphere leading to the ceramic yield and reactivity of the fibres during the transformation of the polymer into BN.

2.3.1. DSC measurements

The thermal behaviour of the copolymer was determined by DSC and two important information could be pointed out: the glass transition temperature, Tg, which was characteristic of the possibilities of handling the crude fibres and the temperature of decomposition, which was the upper limit of the extrusion temperature. The thermogramm is given in the (Fig. 3). The glass transition began at −1.2 °C and lasted up to 38.4 °C with the mid point at 22.5 °C. This value was characteristic of a low crosslinking of the copolymer. Moreover, the important range of temperature between the beginning and the end of Tg, about 40 °C, was generally interpreted as large molar mass dispersion in the copolymer which could render the stretching of the crude fibres difficult due to the polymer heterogeneity. At a temperature of 100 °C, irregular thermal effects took place leading to the explosion of the crucible. This

Table 1
Copolymerisation conditions and properties of the obtained copolymers

Borazine/MAB molar ratio	Temperature (°C)	Reaction time (h)	Polymer aspect	Spinning properties
90/10	25	15	Liquid	
90/10	75	15	Soft glass	Thread at 80 °C
90/10	75	48	Glass	Powder 110 °C
90/10	110	1	Glass and liquid	Thread at 160 °C
90/10	150	2	Liquid	
75/25	75	15	Glass	Thread at 100 °C
50/50	75	15	Rubber	Powder 180 °C
50/50	75	15	Rubber	Powder 180 °C

explosion was due to the hydrogen exhaust when the polymerisation was carried on again. From these results, the spinning window could be considered from 45 to 90 °C.

2.3.2. TGA measurements

The ceramic yield of the copolymer was 78% using the common preceramisation program described in the experimental part. However, the TGA curve showed clearly a poor reactivity of the copolymer towards the reducing atmosphere used. If the weight loss was steep at the beginning of the heating, it slowed down when reaching 100 °C leading to a plateau up to 300 °C. Then the weight loss increased again and slowed down at 700 °C. This very slow reaction when the main part of the fibres would be still under a polymeric form, could involved a lot of defects. The thermogramm is given in (Fig. 4).

The residue in the crucible was characterised as turbostratic boron nitride, with a d value of 3.73 Å and a correlation length of about Lc = 1.2 nm. The IR spectrum clearly showed the classic BN bands at 1378 and 781 cm^{-1}. However, the presence of NH groups at $v = 3450$ cm^{-1} and CN bond at $v = 1120$ cm^{-1} pointed out that the thermolysis was not achieved.

2.4. Spinning and ceramisation

2.4.1. Spinning conditions and prepared crude fibres

The copolymer had been spun in a special machine specially devoted to fibre production from other polymers. It was an extrusion machine in which the polymer was put into the inoxidable chamber of a furnace fitted at its bottom with a 200 μm die plate. The extrusion of the crude fibre was obtained using a monitored advance of a piston, pressing on the polymer in order to obtain a stable flow of polymer trough the die plate hole. The temperature of the furnace could be raised slowly until a first crude mother fibre was extruded. The diameter of this fibre was about 200 μm. This thick fibre was wound on a graphite spool whose rotation speed could be controlled in order to stretch the fibre to lower its diameter to facilitate the ceramisation. The machine was placed under a dry nitrogen atmosphere during all the spinning. The first fibre was obtained at 65 °C under a pressure of 40 daN but the fibre quantity was to small to allow a winding on the graphite spool. The temperature was raised slowly up to 85 °C, the piston advance could be stabilised at 0.5 mm min^{-1}. In spite of very stables extrusion conditions, the crude fibre diameter (Fig. 5a) was regular but its was very difficult to wind it around the spool. When stretched, the diameter of the fibre became not very regular but several bundles of less than 20 μm crude fibres had been obtained (Fig. 5b). The mechanical resistance of this thin fibre was very low and the wound thread broke in several places on the spool before the preceramisation treatment. If the temperature was raised up to 95 °C, the copolymer become too liquid and drops were formed in place of a crude fibre. This results could be related to the low value of the Tg of the copolymer and the spinning window temperature determined using DSC.

When the temperature of the extrusion was to high, the polymerisation reaction was carried out again and the crude fibres presented a lot defects on the surface caused by the hydrogen evolving.

Table 2
Influence of the reaction time on the spinning properties of the copolymer

Experiment no.	Borazine/MAB molar ratio	Temperature (°C)	Reaction time (h)	Spinning temperature (°C)
1	90/10	75	15	60
2	90/10	75	24	65
3	90/10	75	36	70
4	90/10	75	48	No thread

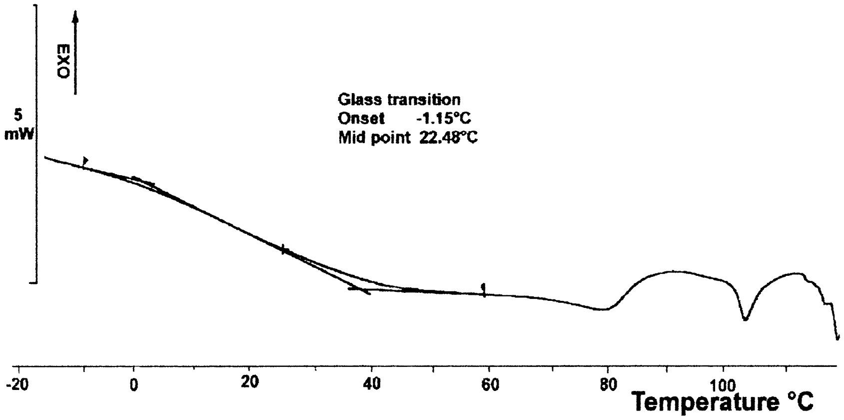


Fig. 3. DSC of the copolymer.

2.4.2. *Ceramic fibres and main defects*

The transformation of the polymer fibres into ceramic fibres was realised as described in Section 3. No morphological analysis had been done when changing of furnace during the thermal treatment. The fibres which were on the spool at the beginning of the preceramisation were broken during the treatment and only remained strands of the fibres. This small amount of fibres of various diameter were gathered in a graphite crucible and ceramised up to 1800 °C. An example of BN fibre is given in Figures (Fig. 6a–c). If the crude fibre was very thin, less than 10 μm, short but good looking fibres are obtained (Fig. 6a). If the diameter of the crude fibre was to broad (about 25 mm), irregular fibres were obtained showing long cracks on their surface (Fig. 6b). The last sample (Fig. 6c) has been obtained from a very thick fibre. The ceramisation was first realised on the surface of the fibre but the gas exchanges through the ceramic skin were too difficult to allow to ammonia to permeate into the fibre. The ceramisation was not performed under the fibre skin and the centre of the fibre stayed a polymer up to a high temperature. When the temperature reached more than 200 °C, the thermolysis of the polymer led to an important gas evolving, the preceramic thin skin exploded with large hole on the fibre surface and which involved poor mechanic properties.

The XRD spectrum recorded on the fibres was consistent with the usual values obtained from polyborazylene thermolysed [23]. For the 002 diffraction corresponding to the *c* axis between the hexagon plans, $d = 3.5_{55}$ Å was measured with a correlation length value of Lc = 14.3 nm. However, the difference between the 100 and 101 rays was not possible and an average value of $d = 2.17$ Å was obtained with a correlation length along the hexagon plan of La = 41.3 nm. This values were characteristic of a good organisation of the boron nitride. The IR spectrum only showed the two bands characteristic of BN at $\nu = 1373$ and 785 cm^{-1}.

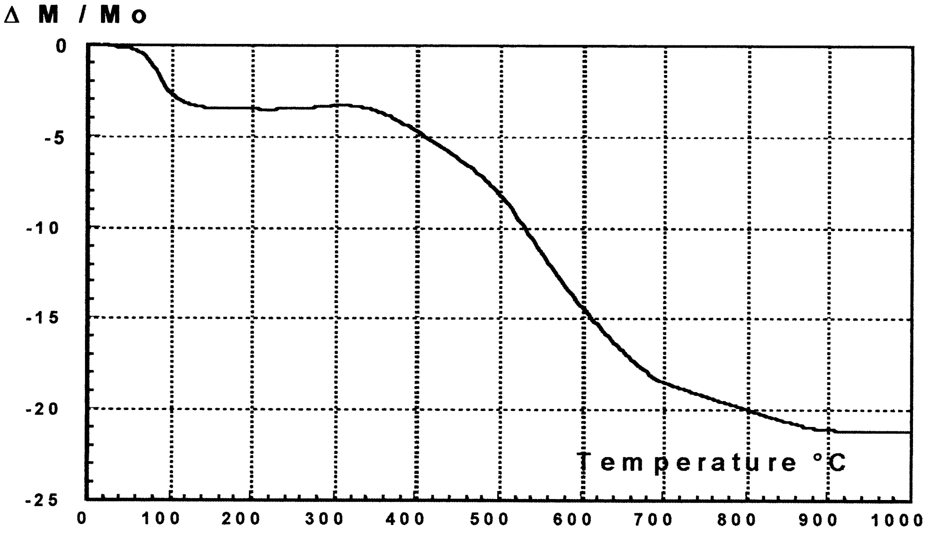


Fig. 4. TGA of a thin powder of polymer.

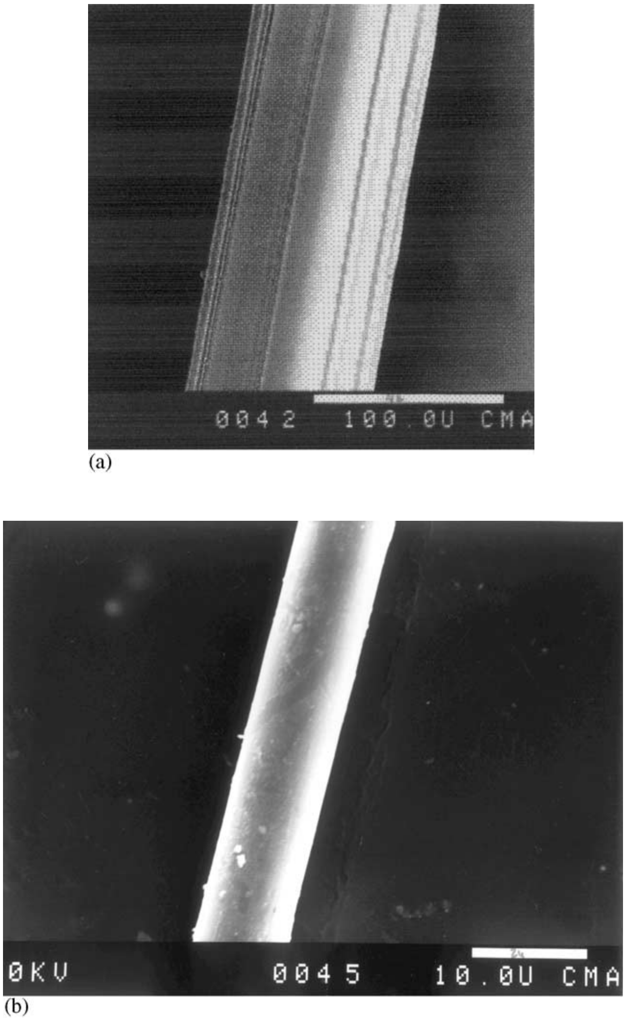


Fig. 5. (a and b) Fibres of copolymer spanned at 85 °C unstretched and stretched.

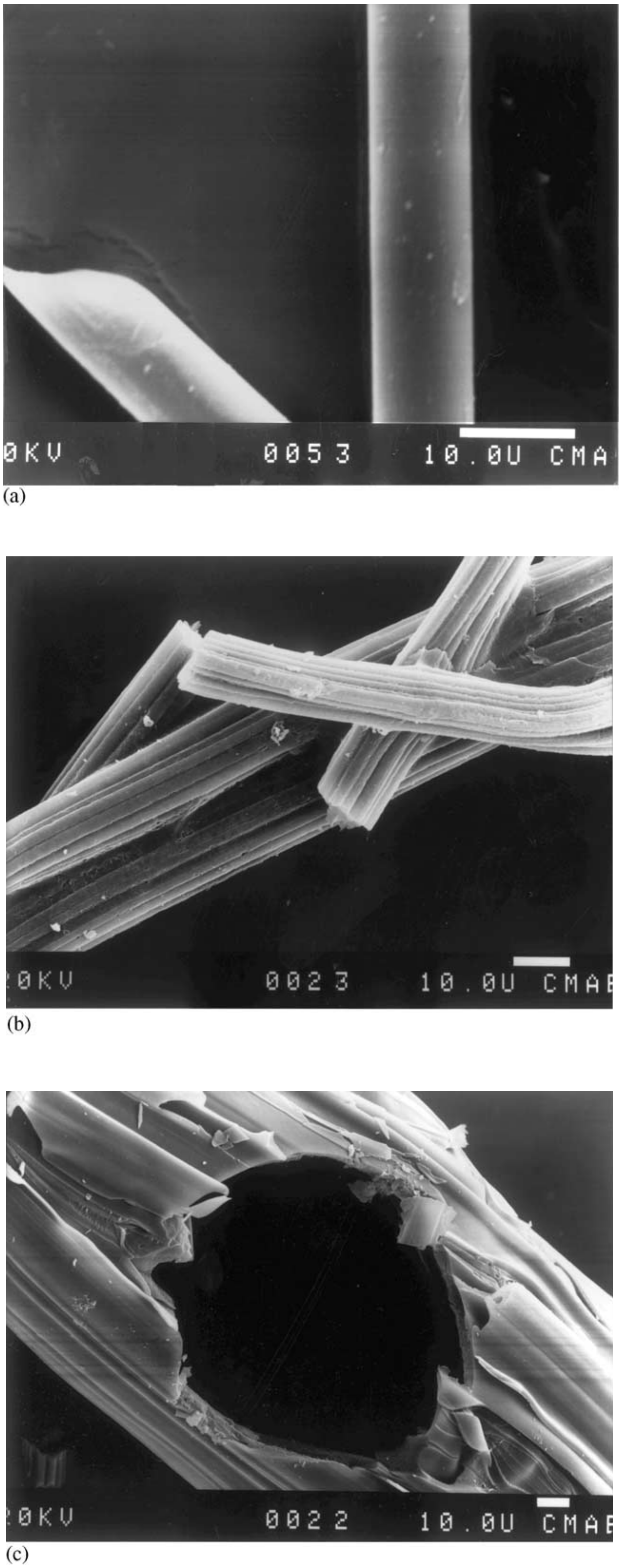


Fig. 6. (a–c) Fibres ceramised at 1800 °C.

3. Experimental

3.1. Starting materials

All experiments were performed in an atmosphere of pure Ar using standard vacuum-line, Schlenk techniques and an efficient dry box with solvents purified using standard methods [24]. The starting materials, NH_4CO_3 and KBH_4 (Aldrich ACS) for the synthesis of NH_3BH_3 were used as received. The trichloroborazine (TCB) was prepared from BCl_3 (Alphagaz) and NH_4Cl (Aldrich ACS). Ammonium chloride was dried under vacuum at 130 °C for 12 h before the synthesis. Methylamine (Fluka, 97%) was used as supplied without further purification.

3.2. Characterisation

^{11}B-, ^{1}H-, ^{13}C- and ^{15}N-NMR spectra were recorded on a Bruker AM 300 (CRMPO Rennes) respectively at 96.26 MHz (external reference Et_2OBF_3 non-decoupled, with positive value down field), 300 (reference Me_4Si), 75 (reference Me_4Si, total decoupling) and 30 MHz (reference CH_3NO_2, using a Dept 135 sequence were

NH and NH_3 correspond to positive signals and NH_2 as negative one, tertiary nitrogen atom do not lead to any resonance because they are not bounded to proton). The chemical shifts were explained in ppm and proton and carbon spectra were obtained from C_6D_6 solutions. The following abbreviations are used: d, doublet; s, singlet; t, triplet; q, quadruplet; br, broad. The IR spectra were recorded on a FTIR Nicolet Magna 550 spectrophotometer in KBr pellets. The ceramic yield was determined using a TGA B70 apparatus and the study was performed under ammonia up to 600 °C and then under nitrogen up to 1000 °C with a 2 °C $\min^{-1}$ heating rate. DCS analysis were ran on a TA 8000 Mettler-Toledo under an Ar atmosphere. SEM images were obtained from a JEOL 55 CF (CMEABG Lyon). X-ray powder diffraction (XRD) were obtained with Cu$-$K$_\alpha$ radiation using a Philips PW 3710/3020 diffractometer equipped with a monochromator.

3.3. Preparation of the studied compounds

3.3.1. Synthesis and characterisation of borazine

The borazine was prepared using a two steps classical method. In a first step, NH_3BH_3 was prepared from NH_4CO_3 and KBH_4 through an exchange reaction performed in THF [15,17]. IR (cm^{-1}): ν 3315 (NH); 2350 (BH); 1375 (BN str.); 785 (BN bend). ^{1}H-NMR (ppm): δ 1.47 (q, 3H, $^1J_{\mathrm{HB}} = 94$ Hz (BH_3); 4.07 (br t, 3H, $^1J_{\mathrm{H^{14}N}} = 34$ Hz (NH_3). ^{11}B-NMR (ppm): δ -22.4 (q, $^1J_{\mathrm{BH}} = 94$ Hz). ^{15}N-NMR (ppm): δ -373.6 (q, $^1J_{\mathrm{NH}} = 70$ Hz). The amine borane NH_3BH_3 was the pyrolysed in glyme as described in the literature [16,17]. It was purified by low pressure distillation leading to pure monomer. IR (cm^{-1}): ν 3460 (NH); 2496 (BH); 1425 (BN str.); 745 (BN bend). ^{1}H-NMR (ppm): δ 4.53 (q, 3H, $^1J_{\mathrm{HB}} = 133$ Hz (BH); 5.54 (t, 3H, $^1J_{\mathrm{H^{14}N}} = 54$ Hz (NH). ^{11}B-NMR (ppm): δ 30.4 (d, $^1J_{\mathrm{BH}} = 133$ Hz). ^{15} N-NMR (ppm): δ -265.8 (q, $^1J_{\mathrm{NH}} = 67$ Hz).

3.3.2. Synthesis and characterisation of the MAB

MAB was prepared from TCB and methyl amine CH_3NH_2. TCB was commercially unavailable so it was prepared in the laboratory using the standard method using the reaction between BCl_3 and NH_4Cl in $C_6H_5CH_3$ [18]. To a suspension of NH_4Cl in refluxing $C_6H_5CH_3$, BCl_3 was slowly added, the addition rate was rule by the reflux of BCl_3. After the reaction, TCB was recovered from $C_6H_5CH_3$ with a 60% yield from BCl_3. IR (cm^{-1}): ν 3450, 3416 (NH); 1438 (BN stretch); 1031 (NH); 743 (BCl); 704 (BN bend). ^{1}H-NMR (ppm): δ 5.29 (t, br, (NH). ^{11}B-NMR (ppm): δ 29.7 (s). TCB was reacted with $MeNH_2$ at low temperature in a ratio 1/8 leading to the formation of MAB and CH_3NH_3Cl which was separated by filtration. MAB was recovered by evaporation of $C_6H_5CH_3$ [21,22]. IR (cm^{-1}): ν 3446, 3250 (NH); 2922, 2830 (CH); 1514 (CH); 1420 (BN stretch.); 1194 (NC); 1029 (NH); 715 (BN bend). ^{1}H-NMR (ppm): δ 1.50 (s, br, 1H, (BN*H*CH_3); 2.5 (s, br, 3H, (NHC*H*$_3$)), 2.66 (s, br, 1H (NH cycle)). ^{11}B-NMR (ppm): δ 25.9 (s, br). ^{14} N-NMR (ppm): δ -377.4 (s, br, 1N (*N*HCH_3)); -321.9 (s, br, 1N (*N*H cycle). ^{13}C-NMR (ppm): δ 27.5 (s, br (NH*C*H$_3$).

3.3.3. Synthesis and characterisation of the copolymer

The reaction of copolymerisation was performed in a Schlenk vessel under controlled atmosphere. The MAB, a waxy compound, and the borazine, clear liquid, were mixed together under a vigorous magnetic stirring. As soon as the mixing has been done, a gas evolved characterised as mainly hydrogen. After 36 h, the copolymer was allowed to cold down to room temperature (r.t.) and then the product was kept at -20 °C to avoid a chemical evolution. The copolymer was very waxy and the stirring was not very efficient after few hours. IR (cm^{-1}): ν 3447, 3250 (NH); 2934 (CH); 2483 (BH); 1445 (CH); 1404 (BN stretch.); 1101 (NC); 1029 (NH); 700–650 (BN bend). ^{11}B-NMR (ppm): δ 31.2 (d, br (BH)), 27.1 (s, br (BN_3)), -17.5 (q, br (BH_3)). ^{14}N-NMR (ppm): δ -254, -251, -253, -257, -266, -276, -286 (B_2NH). ^{13}C-NMR (ppm): δ 27.5 (s, br (NH*C*H$_3$), 34.1 (s, $-$*N*CH$_3-$).

3.4. Preceramisation and ceramisation conditions

The crude polymer fibres were transformed into ceramic fibres by a two steps thermal and chemical treatment using two different apparatus. First, a preceramisation; was performed from r.t. up to 1000 °C in a classic ovens fitted with a silica tube, this operation was run under reactive ammonia flow (1 l h^{-1}) up to 600 °C and then under nitrogen flow. Ammonia was used to strip the organic parts of the copolymer, as showed in previous work [25]. The heating rates used were 1° min^{-1} up to 600 °C and then 5° min^{-1} up to 1000 °C. Then the fibres were transferred into a high temperature oven where the were heated up to 1800 °C with a heating rate of 10° min^{-1} under a nitrogen atmosphere.

4. Conclusion

A new route to BN ceramic fibres has been demonstrated through the use of a melt spinnable copolymer based borazine backbone. The addition of a small amount of AB to borazine followed by an appropriated chemical treatment, yielded to a new precursor exhibiting the required physical properties to be easily extruded and spanned into thin polymer fibres. The ceramic yield of this copolymer was kept high by the low AB addition which was proved to be sufficient to improved the reological properties of polyborazylene. The crude fibres extruded were hardly drawn to lower their diameter down to 10 μ required. The ceramic fibres obtained seemed to have good crystallographic properties but the ceramisation protocol issued from polyaminoborazines ceramisation appeared clearly ill-adapted and led to the fibres breaking and created important defects. However, the copolymer prepared have showed excellent extrusion properties and a more homogeneous and crosslinked product characterised by a Tg value of about 70 °C would lead to polymer fibres more easy to handle. The ceramisation program used has also to be modified to take in account the difficult gas/solid exchanges during this essential part of the preparation. However, this problem could be related to an excellent non-porous preceramic skin of the fibres. This type of copolymer could be an alternative to polyaminoborarzine polymers for boron nitride fibres industrial fabrication.

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