Oxidatively Stable Thermosets Derived from Thermal Copolymerization of
Acetylene-terminated Imide Monomer with an Acetylenic Monomer Containing
Carborane

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ABSTRACT: One acetylenic monomer (APCB) containing carborane with extremely thermal and thermo-oxidative stability was synthesized and used as the thermal copolymerization component with acetylene-terminated imide monomer (*m*-EFDA) to improve the thermal and thermo-oxidative stability of the polyimide materials. The curing behavior of the blends of imide monomer and APCB was investigated by FT-IR and DSC. Rheometer study showed that the addition of APCB into *m*-EFDA reduced the minimum complex viscosity of *m*-EFDA and lowered the temperature of the minimum viscosity. The thermal and thermo-oxidative stability of the thermoset derived from *m*-EFDA was greatly improved by the addition of APCB based on thermogravimetric analysis. *m*-EFDA with an addition of APCB at a loading level of 50 wt% exhibited a high char yield of 91.5 % at 1000 °C in air and a weight retention of 95.6 % was obtained after aging in air at 400 and 500 °C for 5 h, respectively.

KEYWORDS: carborane; thermo-oxidative stability; thermoset.

1. INTRODUCTION

Addition cure polyimides are being designed for aerospace applications and microelectronics, which require structural performance and durability in high temperature oxidative environments.[1-6] Thermoset polyimides have excellent mechanical, thermal, electrical properties, good chemical resistance.[7-10] However, thermoset polyimides are susceptible to decomposition at elevated temperatures in

oxidative environments. Many studies have been carried out to improve thermal and thermo-oxidative stability of polyimide materials over the recent years, and making the polymer structure organic/inorganic hybrid has been proved to be effective. [5, 11-13] Icosahedral carboranes, carbon-containing polyhedral boron-cluster compound, have special thermal stability because of their stable cage structures and rich boron contents.[14-20] Polymers containing the carborane unit within the backbone exhibit appreciable enhancement in their oxidative stability, and numerous polymers containing carborane cage structures have been reported, such as poly(ether ketone)s, polythiophenyls, polysiloxanes and polysilanes.[21-31] However, study about the modification of polyimides by chemical incorporation of carborane to improve their thermo-oxidative stability is rare. In summary, there are several obstacles in obtaining carborane-containing polyimides. First, the synthesis of diamine monomer containing *o*-carborane or *m*-carborane is difficult due to the deboronation of *o*-carborane and *m*-carborane with amines.[32-34] Though *p*-carborane can withstand the nucleophilic attack by amines, the high cost and limited availability of *p*-carborane severely constrain its application. In addition, the common polar organic solvents such as N,N-dimethylacetamide, N,N-dimethylformamide, N-methylpyrrolidinone and dimethyl sulfoxide lead to cage degradation of *o*-carborane.[35-37] Besides, the cyclizing mixture in chemical cyclisation of polyimides can also cause cage degradation of *o*-carborane.[35] Consequently, carborane-containing polyimides are difficult to synthesized, requiring painstaking synthetic efforts and cannot be obtained by common polymerization methods for polyimides. An effective approach to solve this problem is via copolymerization of imide monomer with reactive monomer containing carborane.

In our previous work, a trimethylsilyl-terminated monomer (CBTMS) containing carborane group was synthesized and thermoset derived from this monomer showed high thermo-oxidative stability.[38] However, products of the cured blends of CBTMS and phenylethynyl-terminated imide oligomers were porous and brittle, which we believe was attributed to the different cross-linking mechanism of

trimethylsilylethynyl and phenylethynyl. Thus, an acetylene-terminated monomer containing carborane was synthesized and used as copolymerization component with an acetylene-terminated imide monomer. In this work, the thermal and thermo-oxidative stability of thermoset derived from this carborane-incorporated monomer was studied in detail, and the thermal and thermo-oxidative stability of polyimide thermoset was effectively improved by thermal copolymerization with this carborane-incorporated monomer. The curing behaviors of the copolymers were studied. Meanwhile, the effect of addition of the acetylene monomer containing carborane on the rheological properties of imide monomer was discussed in detail. In addition, the mechanism of the high oxidation resistance of thermoset derived from this carborane-incorporated monomer was studied in detail.

2. EXPERIMENTAL

2.1. Materials

1,2-bis(4-trimethylsilylethynylphenyl)-carborane (CBTMS) was synthesized according to a previous literature.[38] 3-Ethynylbenzenamine (3-EA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) were purchased from J&K Chemical Co and used without further purification. Potassium carbonate was purchased from Tianjin Damao Chemical Co., Ltd. (China). Acetic anhydride, N-methyl-2-pyrrolidone (NMP) and triethylamine were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (China) and used without further purification.

2.2. Measurements

All NMR spectra were measured on a Bruker AVANCE III 500 spectrometer (500 MHz). Elemental analyses were performed on an elemental analysis Vario EL series. The FT-IR spectra were obtained using a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDITOF-MS) analyses were carried out using a Micromass GC-TOF-CA 156 MALDI-TOF/MS. Thermogravimetric analyses (TGA) of the polymers were performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in nitrogen and air atmosphere at a heating rate of 20 °C min⁻¹ from 30 to

1000 °C. The differential scanning calorimetric (DSC) was measured on Mettler DSC822 DSC under a nitrogen flow (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹ from 25 °C to 300 °C. Melt viscosity measurements were performed on a X dynamic rheometer at a ramp rate of 4 °C min⁻¹ with a fixed strain of 5 % and a fixed angular frequency of 10 rad s⁻¹. Specimen of each resin disks with a diameter of 2.54 cm and a thickness of 1.5 mm were prepared by press-molding the pretreated resin powders at room temperature. Polarized light microscope study was performed on Leica DM2700M. Dynamic mechanical analysis (DMA) of the cured blend sample bar (35×6×2.5 mm³) were carried out with a TA Q800 instrument with a load frequency of 1 Hz and at a heating rate of 5 °C/min from 25 °C to 500 °C under nitrogen. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a D/Max 2400. Scanning electron microscopy (SEM) was performed using a Quanta 450 microscope.

2.3. Synthesis of Acetylenic Monomer Containing Carborane (APCB)

16.4 g (60 mmol) of CBTMS, 25 g (0.18 mol) of potassium carbonate and 400 mL methanol were added to a 500 mL three-necked round bottom flask equipped with a magnetic stirrer. The reaction mixture was magnetically stirred for 2h at room temperature. When the reaction was completed, the reaction was quenched with 300 mL of 10% HCl aqueous solution, and the mixture was extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous Na₂SO₄, followed by vacuum evaporation. The crude product was finally passed through silica gel column chromatography using petroleum ether as eluent to give the pure compound as a white powder (Yield: 95.3%). Purity (HPLC): 99.56%. Found: C, 62.60%; H, 5.76%. Anal. Calcd for C₁₈H₂₀B₁₀: C, 62.76%; H, 5.85%. FT-IR (KBr, cm⁻¹): 3302.2(≡C-H), 2600.6(B-H), 2574.4(B-H), 1503.0(C=C), 1402.7, 842.9, 661.8. ¹H NMR (500 MHz, CDCl₃, Me₄Si): δ 7.38-7.36 (4H, d, Ph), 7.27-7.25 (4H, d, Ph), 3.12 (2H, s, ≡CH). ¹³C NMR (500 MHz, CDCl₃, Me₄Si): δ 132.02, 130.82, 130.48, 124.48, 84.55, 82.04, 79.97. MS (EI-TOF): M⁺ calculated for C₁₈H₂₀B₁₀ 344.2568; found 344.2591.

2.4. Synthesis of Acetylene-terminated Polyimide Monomer (*m*-EFDA)

The acetylene terminated monomer was synthesized according to a published method (Scheme 1).[10] A flame-dried 100 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condensing tube was charged with 3.51 g (30 mmol) of 3-EA and 30 mL NMP. 6.66 g (15 mmol) of 6-FDA resolved in 20 mL NMP was then added and the reaction mixture was stirred at room temperature for 2h. Then acetic anhydride (10 mL) and triethylamine (3 mL) were added one by one with stirring at room temperature for 12h. Then the solution was poured into a large excess amount of deionized water. The precipitate was collected by filtration, washed thoroughly with deionized water for three times, and ethanol for one time. At last, the product was dried under vacuum at 80 °C for 12h to obtain a light yellow powder. (yield: 8.96 g, 93%). Found: C, 65.45%; H, 2.53%; N, 4.30%. Anal. Calcd for $C_{35}H_{16}F_6N_2O_4$: C, 65.43%; H, 2.51%; N, 4.36%. FT-IR (KBr, cm^{-1}): 3260.2($\equiv C-H$), 1780.5($C=O$), 1715.4($C=O$), 1378.8($C-N$). 1H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.06-8.04 (2H, d, Ph), 7.94(2H, S, Ph), 7.90-7.88 (2H, d, Ph), 7.57 (2H, S, Ph), 7.55-7.54 (2H, d, Ph), 7.49-7.46 (2H, t, Ph), 7.44-7.42 (2H, d, Ph), 3.14 (2H, S, $\equiv C-H$). ^{13}C NMR (500 MHz, $CDCl_3$, Me_4Si): δ 165.77, 165.60, 139.26, 135.99, 132.57, 132.26, 132.06, 131.42, 130.00, 129.22, 126.86, 125.43, 124.51, 124.20, 123.45, 122.22, 82.40, 78.54. MS (TOF-LD): M^+ calculated for $C_{35}H_{16}F_6N_2O_4$ 642.1014; found 642.1031.

2.5. Thermal Cure of m-EFDA with APCB

The blends of *m*-EFDA and APCB were prepared with an agate mortar. Acetylene-terminated polyimide monomer (*m*-EFDA) containing 0, 25, 50, 75 wt% of APCB and pure APCB were prepared and denoted as APCB-0, APCB-25, APCB-50, APCB-75 and APCB-100, respectively. Chemical structures of these blends were confirmed by FT-IR, and the FT-IR spectra were shown in Fig S3 (in the supporting information). Two sheets of glass were separated with several coverslips (thinness: 0.2 mm) to keep the two sheets of glass with a fixed gap. Then the two sheets of glass were placed in Muffle furnace and heated to 190 °C. 0.6-0.8 g of sample was placed between the two sheets of glass. Once the sample has melt completely, the sample was stage-cured in air at 210 °C for 2 h, at 240 °C for 2h, at 270 °C for 1h and at 300 °C for

1h. After that, allow the sample to cool to room temperature. Then the cured sample film was obtained by immersing the two sheets of glass in water. The cured film sample with a thinness of 0.2 mm was amorphous film and had an area of about 50 square centimeters.

The cured sample bars for DMA analysis was prepared using a stainless steel mould ($35 \times 6 \times 6 \text{ mm}^3$), and the curing process was similar with preparation of the cured film samples. The mould was heated to 190 or 200 °C to melt the blends, and the blends sample was stage-cured in air at 210 °C for 2 h, at 240 °C for 2h, at 270 °C for 1h and at 300 °C for 1h after the blends has melt completely.

Scheme 1. Synthetic route of APCB and *m*-EFDA

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of APCB and *m*-EFDA

The synthetic route of CBTMS has been reported in our previous paper, which use commercially available decaborane as starting materials.[38] APCB was prepared from CBTMS by eliminating trimethylsilyl groups in the presence of potassium carbonate (Scheme 1). *m*-EFDA was synthesized by the reaction of 3-EA with 6-FDA and subsequently cyclodehydrated by chemical imidization with acetic anhydride and triethylamine according to a published method (Scheme 1).[10] In this work, we chose to use 3-ethynylbenzeneamine instead of 4-ethynylbenzeneamine because imide oligomers end-capped with 4-ethynylbenzeneamine exhibit significantly higher softening temperatures and fail to cure properly, which has been qualified by early work.[39] Chemical structures of APCB and *m*-EFDA were confirmed by FT-IR,

^1H -NMR, ^{13}C -NMR and mass spectrometry.

Figure 1. ^1H -NMR and ^{13}C -NMR spectra of APCB in CDCl_3 .

The ^1H -NMR and ^{13}C -NMR spectra of APCB are shown in Figure 1. A singlet at 3.1 ppm corresponding to the hydrogen atoms of acetylenic group in APCB was showed in the ^1H -NMR, and a broad peak at δ 1.5-3.5 assigned to the protons of B-H in *o*-carborane cage was also observed.[24, 40] APCB exhibited a strong absorption band at 3300 cm^{-1} in the FT-IR spectrum, which was associated with the stretching vibration of acetylenic C-H (Figure S3, in supporting information).[41, 42] In addition, a strong band at 2600 cm^{-1} ascribed to the stretching vibration of B-H on carborane was displayed.[13, 43]

In FT-IR spectrum of *m*-EFDA (Figure S3, in the supporting information), the strong band at 3260 cm^{-1} was associated with the acetylenic C-H stretching vibration, and the absorptions of imide carbonyl groups ($\text{C}=\text{O}$) appeared at 1778 cm^{-1} and 1718 cm^{-1} . The absorption at 1378 cm^{-1} was assigned to C-N stretching vibration of imides rings.[44]

3.2. Curing Behavior of the Blends of *m*-EFDA and APCB

Figure 2. FT-IR spectra of the blends of *m*-EFDA and APCB after thermal curing.

In order to verify the homogeneity of thermosets derived from the blends of APCB and *m*-EFDA, polarized light microscope was performed on the cured film samples. As showed in Fig S4, PLM images of APCB-25, APCB-50 and APCB-75 as well as APCB-0 and APCB-100 were featureless without any sign of inhomogeneity, indicating that APCB and *m*-EFDA were well mixed. The chemical structures of the blends after thermal curing were determined by FT-IR, and the results are shown in Figure 2. The absorption bands of acetylenic C-H stretching vibration at 3300 cm^{-1} and 3260 cm^{-1} corresponding to acetylenic C-H of APCB and *m*-EFDA disappeared after thermal curing process, indicating the curing process was sufficient for accomplishing the curing reaction. The absorption band at 2600 cm^{-1} assigned to the stretching vibration of B-H on carborane cage increased with increasing content of APCB, while the absorptions of imide carbonyl groups decreased as expected.

Figure 3. DSC curves of *m*-EFDA with different content of APCB.

Table 1. DSC data of the blends of *m*-EFDA and APCB

Sample	T_m (°C)	T_i (°C)	T_p (°C)	T_t (°C)	ΔT (°C)
APCB-100	153.8	185.0	202.9	209.8	31.2
APCB-75	145.7	192.0	208.0	214.2	46.3
APCB-50	144.8	195.4	210.5	217.3	50.6
APCB-25	141.1	208.5	216.7	223.1	67.4
APCB-0	207.0	222.8	227.5	233.7	15.8

^a T_m : melting temperature, T_i : initial curing temperature, T_p : peak temperature, T_t : terminal temperature, ΔT : the difference between T_m and T_i .

In addition, the curing behavior of the blends of *m*-EFDA and APCB was investigated by DSC, and the results are shown in Figure 3 and Table 1. The pure *m*-EFDA displayed a melting endothermic peak, centered around 210 °C, followed by the immediate onset of exothermic curing, which peaked in the 220-240 °C range. This data indicated that *m*-EFDA didn't possess a processing window, namely, *m*-EFDA could not be held in a flowable liquid state for any period of time without curing taking place. However, with the addition of APCB, the exothermic peak temperature decreased, and the endothermic peak attributed to the melting point of APCB appeared between 140 and 150 °C. Consequently, the region between T_m (melting temperature) and T_i (initial curing temperature) increased from 15.8 °C to 67.4, 50.6 and 46.3 °C respectively with

the addition of APCB (Table 1), which could be roughly considered as processing window. It was worth mentioning that the difference between T_m and T_i of APCB was only 31.2 °C, suggesting that both of *m*-EFDA and APCB showed a narrower processing window than the blends of them. These results suggested that the processing window of the imide monomer *m*-EFDA was broadened by the addition of APCB.

Figure 4. Complex melt viscosity of the blends of *m*-EFDA and APCB

Table 2. Complex viscosity data of the blends of *m*-EFDA and APCB

Sample	Minimum melt viscosity (Pa s)	Temperature of the minimum viscosity (°C)
APCB-100	0.1	150
APCB-75	0.7	152
APCB-50	0.3	175
APCB-25	27.7	184
APCB-0	24.3	206

3.3. Dynamic Complex Viscosities of the Blends of *m*-EFDA and APCB

The dynamic rheological properties were measured on powder molded discs of *m*-EFDA, the blends and APCB, as shown in Figure 4 and Table 2. *m*-EFDA showed the narrowest processing window with the minimum viscosity of 24.3 Pa·s at 206 °C and followed by an immediate increase in melt viscosity. At a 25 wt% loading level of

APCB, though the minimum viscosity didn't decrease, the temperature of the minimum viscosity decreased from 206 °C to 184 °C. When the loading level of APCB was above 50 wt%, complex viscosity curve exhibited a steep drop at 145 °C, which was attributed to the melt of APCB according to DSC data. As for APCB-50, the complex viscosity of APCB-50 decreased as the temperature increased from 145 °C to 175 °C due to the melt of *m*-EFDA, and APCB-50 showed a minimum complex viscosity of 0.3 Pa·s at 175 °C. The complex melt viscosity of APCB-50 increased rapidly at 180 °C, which was attributed to the crosslinking reaction of ethynyl groups. Unlike APCB-50, the complex viscosity of APCB-75 remained nearly constant from 145 °C to 175 °C, and increased rapidly at 180 °C due to the crosslinking reaction. It was interesting that APCB-50 showed a lower minimum complex viscosity (0.3 Pa·s at 175 °C) than that of APCB-75 (0.7 Pa·s at 152 °C), which we believe was caused by the higher content of trifluoromethyl in APCB-50. The two bulky trifluoromethyl groups in 6-FDA were reported to lower the interchain interaction and thus lower the melt viscosity of polyimide monomer.[45, 46] As expected, the pure APCB (APCB-100) showed the lowest minimum complex viscosity of 0.1 Pa·s at 150 °C. Based on the analysis of dynamic rheological data, the imide monomer with the addition of APCB showed a broader processing window and a lower minimum complex viscosity.

3.4. Dynamic Mechanical Properties of the Thermosets

The DMA curves of the cured sample bars are shown in Figure 5. Regarding the peak temperature in the E'' curves as the T_g, the T_g of the cured sample is summarized in Table 3. Due to the high cross-linking density, the cured samples displayed a high storage modulus and had good retention even above T_g. The cured samples showed T_g values in the range of 431 to 455 °C. With the increase content of APCB, the cured sample showed a higher T_g and a better retention of storage modulus, which was attributed to the absence of flexible trifluoromethyl groups in APCB. APCB-100 exhibited the highest T_g value of 455 °C. However, these thermosets are brittle due to the high cross-linking density, which might restrict their structural applications. Many studies on the polymer toughening have been carried out, such as addition of rigid

particulate fillers, micron-sized soft (elastomeric or thermoplastic) or nanoparticle.[47-49] The toughening of these thermosets is an interesting work to perform.

Figure 5. DMA curves of the cured sample bars.

Table 3. Glass transition temperatures of the cured blends

Sample	APCB-100	APCB-75	APCB-50	APCB-25	APCB-0
$T_g/^\circ\text{C}$	455	446	437	432	431

3.5. XRD Studies

Figure 6. Wide angle X-ray diffraction patterns for the cured blends

The WAXD patterns of the cured blends were performed in the region of $2\theta = 10\text{--}80^\circ$ at room temperature. As shown in Figure 6, all patterns for the cured blends were similar with a broad peak without any crystalline reflection, which revealed their non-crystalline character.

Figure 7. TGA curves of thermosets derived from the blends of *m*-EFDA and APCB under nitrogen

Figure 8. TGA curves of thermosets derived from the blends of *m*-EFDA and APCB under air

Table 4. TGA data of thermosets derived from the blends of *m*-EFDA and APCB in N₂^a

The blends	APCB-100	APCB-75	APCB-50	APCB-25	APCB-0
T ₅ /°C	780.0	566.0	533.8	522.8	521.0
T ₁₀ /°C	>1000	871.4	568.7	541.9	544.6
Char yield	93.8	89.5	84.4	71.7	56.0

(%)

^a T₅: temperature for 5% weight loss; T₁₀: temperature for 10% weight loss.

Table 5. TGA data of thermosets derived from the blends of *m*-EFDA and APCB in air^a

APCB-X	APCB-100	APCB-75	APCB-50	APCB-25	APCB-0
T ₅ /°C	>1000	706.0	534.0	511.7	502.6
T ₁₀ /°C	>1000	>1000	582.1	522.6	527.1
Char yield (%)	95.2	91.5	84.2	27.2	0

^a T₅: temperature for 5% weight loss; T₁₀: temperature for 10% weight loss.

3.6. Thermal Stability of the Cured Blends of *m*-EFDA and APCB

One important aspect of this study is the influence of incorporation of APCB on the thermal and thermo-oxidative stability of *m*-EFDA. Thermogravimetric analysis (TGA) was performed on a piece of the cured film sample with a heating rate of 20 °C min⁻¹ in N₂ and air, and the results are shown in Figure 7 and Figure 8. The weight loss temperatures of 5% and 10% (T₅ and T₁₀) for cured blends and the char yield at 1000 °C are summarized in Table 4 and Table 5. As shown in Figure 7 and Figure 8, APCB-100 was the most thermally and thermo-oxidatively stable with a high char yield of 93.8% and 95.2% at 1000 °C in nitrogen and air, respectively.

The thermoset derived from the imide monomer of *m*-EFDA (APCB-0) exhibited a high thermal stability with T₅ at 521 °C and 502 °C in nitrogen and air, respectively. However, APCB-0 showed a dramatic weight loss from 550 °C to 700 °C, especially in air. As expected, the blends with a higher loading level of APCB showed a better thermal and thermo-oxidative stability, as shown in Figure 7 and Figure 8. In spite of an improved thermo-oxidative stability compared with pure imide monomer, APCB-25 showed a great weight loss at 550 °C, especially in air. With an APCB content of 50 wt%, APCB-50 exhibited outstanding oxidative stability with a char yield of 84.4 % and 84.2 % at 1000 °C in nitrogen and air, which was much better than common

polyimide materials. When compared APCB-50 with APCB-100, a weight loss of about 10 % was observed between 500 and 550 °C, which was attributed to the thermal degradation of imide structures in APCB-50. As expected, APCB-75 exhibited a better thermal and thermo-oxidative resistance compared with APCB-50 with a char yield of 89.5 % and 91.5 % at 1000 °C in nitrogen and air, respectively. Based on these results, at least 50 wt% content of APCB was needed to maintain the excellent thermal and thermo-oxidative stability of the imide monomer.

3.7. Long-term Thermo-oxidative Stability study of APCB-50 and APCB-100

Figure 9. Aging study of APCB-0 and APCB-50 under air at 400 °C and 500 °C for 5h, respectively.

In order to investigate the long-term thermo-oxidative stability of APCB-50, oxidative aging study was performed on the APCB-50 and APCB-0, and the result is shown in Figure 9. Aging study was conducted by heating the sample at 400 °C and 500 °C for 5 hours under air atmosphere. APCB-50 exhibited outstanding oxidative performance during the entire heat exposure. After aging at 400 °C and 500 °C for 5 hours, APCB-50 changed from orange-red transparent film into black film and it remained its original shape, while APCB-0 was almost burnt out. **Based on TGA data, APCB-50 after aging at 400 °C for 5h produced a weight gain of 5.5 %, which was attributed to oxidation of boron upon exposure to oxidizing atmospheres at elevated temperatures. [50]** A weight loss of about 10 % was displayed with the aging temperature of APCB-50 rising to 500

°C, while the weight of APCB-50 maintained almost constant at the end stage of aging study and a weight retention of 95.6 % was finally obtained after aging study. APCB-0 showed a steady weight loss at the aging temperature of 400 °C and gave a char yield of 94.3 % after aging at 400 °C for 5h. However, a dramatic weight loss appeared when the aging temperature rising to 500 °C and APCB-0 was quickly burnt out at 500 °C. Based on the analysis above, we concluded that long-term thermo-oxidative stability of m-EFDA could be greatly improved by addition of APCB.

Figure 10. Aging study of APCB-100, under air at 400, 500, 600 and 700 °C for 5h, respectively.

Figure 11. Photos of APCB-100 film before and after aging study: a. before aging study; b. after aging study.

In order to investigate the long-term thermo-oxidative stability of APCB-100 and the mechanism of the high oxidation resistance of APCB-100, oxidative aging study of APCB-100 was also performed (TGA data is shown in Figure 10). Aging study of APCB-100 was conducted by heating the sample at 400, 500, 600 and 700 °C for 5

hours in sequence under air atmosphere. APCB-100 exhibited a uniform shrinkage of 10 ± 1 % during the aging study, though the shape of the sample was maintained well, as shown in Figure 11. According to TGA data, aging at 400 °C for 5h produced a weight gain of 3.9 %, and then the weight was almost constant after aging at 500, 600 and 700 °C for 5h, respectively. A weight retention of 103.5 % was finally obtained after oxidative aging study.

To understand the mechanism of the high oxidation resistance of APCB-100, the thermoset film after oxidative aging study was further investigated through SEM, FT-IR and XPS. Surface of the thermoset film after oxidative aging study remained flat and smooth, as shown in Figure 12a. However, many microscale cracks were displayed at high magnification on the surface of the film after ablation. The microscale cracks were formed from escaping of CO or CO₂ generated from oxidation of carbon in matrix.[51, 52] Figure 12c and Figure 12d showed the fracture surface of the film after aging study, which revealed the film after aging study was composed of a protective layer with a thickness of about 10 μm (Figure 12d) and a dense matrix. The matrix of thermoset without any cracks and pores proved by SEM micrographs (Figure 12d) was well protected, suggesting that the protective layer formed from oxidation of *o*-carborane could effectively prevent the permeation of oxygen into the matrix.

As shown in Fig S5, absorption at 1400 cm⁻¹ in FT-IR spectrum of the protective layer was attributed to stretching vibrations of B-O.[53-55] The bonds at 1191 cm⁻¹ and 3163 cm⁻¹ were assigned to the characteristic absorptions of B-OH deformation vibration and BO-H stretching vibration, which was formed from hydrolysis reaction of B₂O₃. [53, 56] XPS could provide chemical bonding information of the material surface. XPS spectra of the protective layer of the sample after aging study showed the protective layer contained carbon, boron and oxygen, as shown in Figure 13. The peak at 284.7 eV was corresponded to C-C bonds in the high-resolution core spectrum for C 1s, while the peak at 286.9 eV was assigned to C-O bonds.[57-60] The binding energy for the B 1s was 189.4 eV assigned to B-H bond [57, 58], indicating that the presence of the carborane cluster in the protective layer of the sample. The peaks at 195.1 eV and 191.6

eV corresponding to B_2O_3 and B-O confirmed the presence of B_2O_3 in the protective layer.[61] Additionally, the binding energy for the O 1s is 533.0 eV assigned to B-O bonds in B_2O_3 . [57, 62] The peak at 535.1 eV was attributed to $-COOH$. [63] Based on the analysis above, the superior thermo-oxidative stability of APCB-100 could be attributed to the presence of passivation layer formed during thermal ablation, which was agreed with previous literatures. [50, 64-66]

Figure 12. SEM micrographs of the thermoset film after oxidative aging study: a. surface of the film at low magnification; b. surface of the film at high magnification; c. and d. fracture surface of the film.

Figure 13. XPS spectra of the surface of the film sample APCB-100 after aging study.

4. CONCLUSIONS

In order to improve the thermal and thermo-oxidative stability of the polyimide materials, one novel acetylenic monomer (APCB) containing carborane with extremely thermal and thermo-oxidative stability was synthesized and used as the thermal copolymerization component with acetylene-terminated imide monomer (*m*-EFDA). The curing behavior of the blends of imide monomer and APCB was investigated by FT-IR and DSC. The imide monomer *m*-EFDA with addition of APCB showed a broader processing window and a lower minimum complex viscosity according to the dynamic rheological study, suggesting that the processability of the acetylene-terminated imide monomer was significantly improved by the addition of APCB. Due to the high cross-linking density, the cured samples displayed a high T_g values in the range of 431 to 455 °C according to DMA analysis. Thermal properties of the cured blends were studied by thermogravimetric analysis (TGA). The blends with more content of APCB showed a better thermal and thermo-oxidative stability, and at least 50 wt% content of APCB was needed to maintain the excellent thermal and thermo-oxidative stability of the imide monomer. Additionally, APCB-50 and APCB-100 exhibited excellent long-term thermo-oxidative stability confirmed by oxidative aging study. The excellent long-term thermo-oxidative stability of APCB-100 was attributed to the presence of a protective layer formed from oxidation of *o*-carborane, which was proved by SEM, XPS and FT-IR. APCB was synthesized by four-step reaction in our lab and was not commercially viable. In spite of the high cost of APCB, APCB has a potential for heat resistant coating for conventional thermosetting polyimides due to the excellent thermal properties of the thermoset derived from it.

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