

Preparation and Properties of Novel Hybrid Resins Based on Acetylene-Functional Benzoxazine and Polyvinylsilazane

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ABSTRACT: A series of addition-curable hybrid resins for resin matrix of advanced composites are prepared by thermal prepolymerization between acetylene-functional benzoxazine(BZ) and polyvinylsilazane(PSN) with various weight ratios. Processing capability of BZ-PSN resin is investigated by measuring viscosity. Cure behavior is investigated by differential scanning calorimetry (DSC) and Fourier transform infrared (FT-IR) spectra. Thermal property of cured BZ-PSN resin is investigated by Thermogravimetric analysis (TGA) and Dynamic mechanical analysis (DMA). BZ-PSN resin shows a low viscosity of 40–180 mPa·s between 60 and 90°C, and maintains the low viscosity for 6 h, indicating that the resin is suitable for resin transfer molding (RTM) process to fabricate composites. DSC results show that BZ-PSN resin can be cured completely at about 250°C without adding any other curing additives. FT-IR shows the reaction between BZ and PSN take place. TGA shows that thermal stability of cured BZ-PSN resin is increased with the content of polyvinylsilazane increasing both in nitrogen and in air. DMA shows cured hybrid resins have excellent thermal properties. The excellent processability and thermal properties suggest that BZ-PSN resin is a promising candidate for resin matrix of advanced composites. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3794–3799, 2013

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INTRODUCTION

Recently polybenzoxazine has been developed as a novel thermosetting phenolic resin. Polybenzoxazine has excellent mechanical performance, flame retardance properties. It also possesses fascinating characteristics, such as molecular design flexibility, low water absorption, high char yield, release of no byproducts during curing, especially low volumetric change upon curing.^{1–3} However, the thermal stability needs to be enhanced further to widen their application. One effective approach to improve the thermal performance of polybenzoxazine is to introduce cross-linkable units into the structure of the benzoxazine, such as ethynyl groups,^{4–7} nitrile groups,^{7,8} propargyl groups⁹ and allyl groups^{10,11} to stabilize the Mannich Bridge during thermal degradation. Another effective method is to introduce the inorganic component into the organic polybenzoxazine.^{12–20} For example, Ardhyananta et al.¹⁷ reported the preparation of Polybenzoxazine(6,6'-(1-methylethylidene)-bis-(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine,Ba)/polydimethylsiloxane(PDMS) hybrids by sol-gel method. The inorganic component, PDMS, led to enhance the thermal stability of polybenzoxazine to higher temperature obviously. In N₂, the 5% weight loss temperature and char yield

at 850°C of cured PBa/PDMS with 13 wt % PDMS were increased to 339°C, 46%, and the 5% weight loss temperature and char yield at 850°C of cured PBa were 302°C, 31%, respectively. The introduction of the inorganic component does enhance the thermal stability of polybenzoxazine.

As a kind of polymeric precursor for ceramic, polyvinylsilazane (PSN), prepared in our laboratory as reported,^{21–23} which contains Si inorganic component and produces a thermally robust organic–inorganic hybrid material with a Si–N backbone and organic side groups above 400°C through solidification and pyrolysis, may also enhance the thermal stability of polybenzoxazine.

In this article, we first report a novel addition-curable hybrid resin prepared by thermal prepolymerization between benzoxazine with ethynyl group and PSN. The preparation, processing capability, cure behavior, and thermal properties of the hybrid resin were studied systematically.

EXPERIMENTAL

Materials

3-aminophenylacetylene (A.R., Beijing Chemical Reagents Corporation, China) was freshly distilled before used. Phenol

Table I. Viscosity Values of BZ-PSN Resins at 90°C for 6 h

Resin	BZ-5%PSN	BZ-10%PSN	BZ-15%PSN	BZ-20%PSN	BZ-25%PSN	BZ-30%PSN
Viscosity/cP	20-27	30-34	35-38	40-41	42-43	45-48

(A.R., Beijing Yili Chemicals Factory, China), para-formaldehyde (A.R., Beijing Chemical Reagents Corporation, China), sodium hydroxide (A.R., Beijing Chemical Reagents Corporation, China), toluene (A.R., Beijing Chemical Reagents Corporation, China) were used as received.

Measurements

Viscosity-temperature relationship study was performed from 25 to 220°C at a heating rate of 4°C min⁻¹ using TA instrument (AR-2000 rheometer) with a 25-mm diameter and viscosity-time relationship was determined using NDJ-79 rotating viscometer. DSC was carried out with a Mettler Toledo DSC 822° over the range from 25 to 350°C at a heating rate of 10°C min⁻¹ under nitrogen. FT-IR spectra were recorded with Bruker Tensor 27 using KBr disks. TGA was carried out from room temperature to 900°C with a Netzsch STA409PC at a heating rate of 10°C min⁻¹ in nitrogen and air. DMA was performed from 30 to 400°C in a nitrogen atmosphere using dynamic mechanical analysis Netzsch 242c at a heating rate 5°C min⁻¹.

Synthesis of Benzoxazine and Polyvinylsilazane

The [3-phenylacetylene-3,4-dihydro-2H-1,3-benzoxazine(BZ)] monomer was synthesized by a solvent procedure.²⁴ 1 mol 3-aminophenylacetylene was added to the mixture of 2 mol para-formaldehyde and 200 mL toluene in a 500 mL three-necked flask equipped with thermometer, condenser and mechanical agitator. This mixture was stirred for 5 min at room temperature before adding 1 mol phenol. The temperature was raised gradually up to 90°C and kept stirring at 90°C for 2 h. The solution was allowed to cool to room temperature and washed with 3 N sodium hydroxide solution several times until the aqueous base layer was colorless. The solution was washed distilled water until it achieved a pH of 7, and then it was dried with anhydrous sodium sul-

fate, followed by evaporation of toluene under vacuum to afford pale yellow powder (187 g, 80% yield).

Analysis: Calcd. for BZ (C₁₆H₁₃NO), % : C, 81.70; H, 5.53; N, 5.96; O, 6.81;

Found: C, 81.74; H, 5.54; N, 6.27; O, 6.45.

Polyvinylsilazane (PSN) $\left[\text{NH}(\text{CH}_3)\text{Si}(\text{CH}_2\text{CH}_2) \right]_x \left[\text{NHSi}(\text{CH}_3)\text{NH} \right]_y$ was prepared as reported.²¹⁻²³ The number average molecular weight (M_n) of PSN is 843, with a polydispersity distribution index of 2.4.

Preparation of BZ-PSN Hybrid Resins

The following is the general procedure used for the preparation of the hybrid resin containing 20 wt% PSN (noted as BZ-20% PSN). In a 100 mL three-necked flask, 16 g BZ was melted and mechanically stirred at 90°C. To this melt, 4 g PSN was added. The mixture was mechanically stirred for 4 h to achieve well dispersion of PSN in BZ. At last, a homogenous liquid hybrid resin was obtained. All the other hybrid resins were similarly prepared containing 5, 10, 15, 25, and 30 wt % PSN (noted as BZ-5%PSN, BZ-10%PSN, BZ-15%PSN, BZ-25%PSN, BZ-30%PSN, respectively).

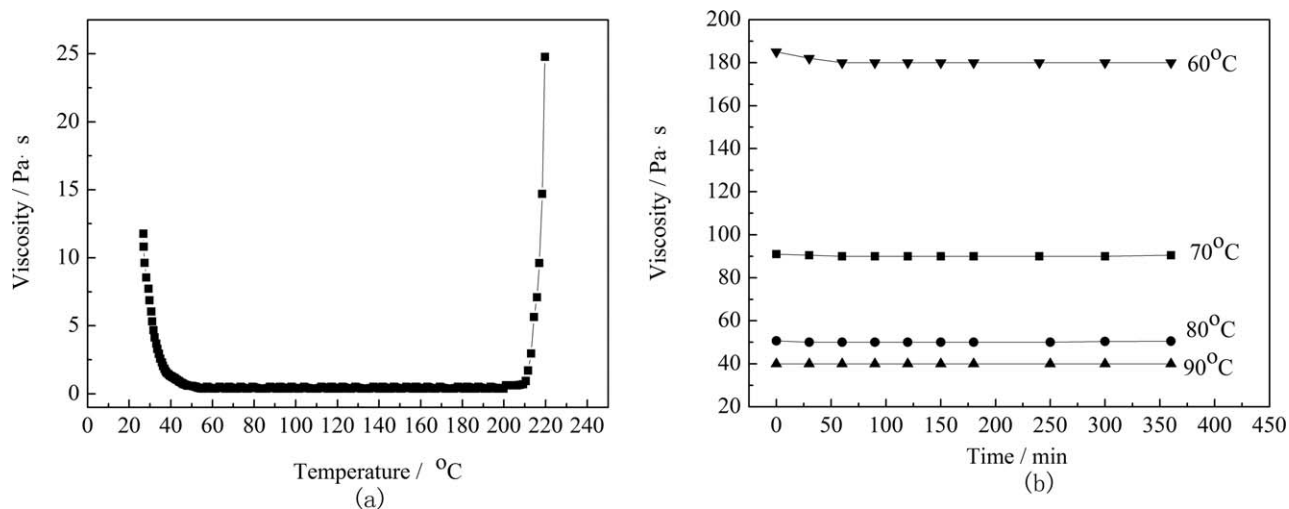
Thermal Cure of BZ-PSN Hybrid Resins

All hybrid resins were free cast in stainless steel molds that were pretreated by dichlorodimethylsilane release agent. The resins were thermally cured by heating in an electric oven in argon atmosphere, and the curing cycle was (180°C/2 h → 200°C/2 h → 220°C/2 h → 250°C/4 h).

RESULTS AND DISCUSSION

Processing Capability of BZ-PSN Resin

Viscosity of the resin is an important factor for processing capability, especially for RTM.²⁵ Table I is the viscosity values of BZ-PSN

**Figure 1.** Viscosity of BZ-20%PSN resin: (a) Viscosity-temperature plot; (b) Viscosity-time plot at 60, 70, 80, and 90°C.

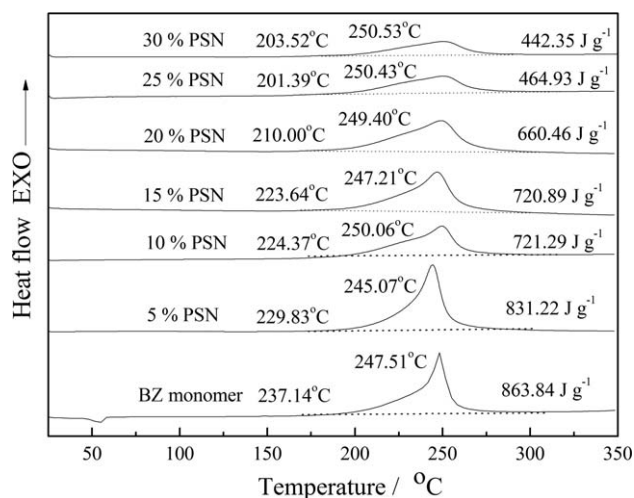


Figure 2. DSC curves of BZ monomer and the BZ-PSN resins with various weight ratios.

resins at 90°C for 6 h. As can be seen in Table I, all BZ-PSN resins had low viscosity.

BZ-20%PSN resin was taken as an example. Temperature dependency of viscosity of the resin was shown in Figure 1(a). It can be seen that viscosity of BZ-20%PSN resin at room temperature is about 12 Pa s, and decreased dramatically with increasing the temperature from room temperature to 60°C. At the temperature above 60°C, the viscosity of the resin was below 180 mPa s and maintained the low viscosity until 200°C. The resin viscosity increased rapidly at the temperature above 200°C due to the curing reaction of the BZ-20%PSN resin. The result showed the BZ-20%PSN resin had a wide processing window. Besides, time dependency of viscosity of BZ-20%PSN resin at 60, 70, 80, and 90°C was given in Figure 1(b). As shown in Figure 1(b), the low viscosity of BZ-PSN can be maintained as long as 6 h, which indicated that the resin was suitable for RTM process to fabricate composites even at low temperature.

Cure Behavior of the BZ-PSN Resin

For BZ monomer and the hybrid resins with various weight ratios of PSN, DSC was used to study the cure behavior of the resins as shown in Figure 2. For BZ monomer, it shows an initial endothermic transition at about 54°C due to the melting of the monomer and a sharper exothermic peak starting at 237.14°C with a maximum of 247.51°C. This exotherm is due to the ring-opening of the cyclic benzoxazine and the crosslink reaction of acetylene. For all BZ-PSN resins with various weight ratios, only a single exotherm peak was observed. However, the onset temperature of the exotherm shifted to lower temperature. Figure 2 shows the effect of the weight ratio on the cure behavior of BZ-PSN resins, indicating catalytic effect of PSN on the ring-opening polymerization of benzoxazine.²⁶ In addition, cure exothermic enthalpy of all BZ-PSN resins are obviously lower than that of BZ monomer due to the inclusion of PSN. Therefore, it can be concluded that BZ-PSN resins possessed better cure processability than BZ monomer, which is advantageous to fabricate composites with high quality.

And also the completion of curing of BZ-PSN resin was confirmed by DSC analysis. Figure 3 is the DSC of the BZ-20%PSN

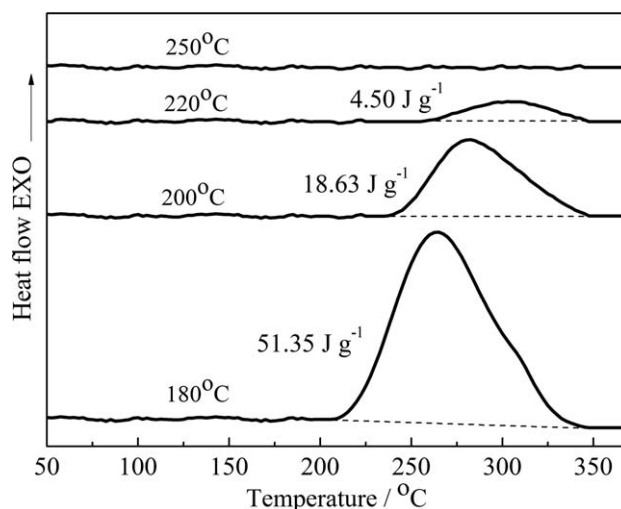


Figure 3. DSC curves of BZ-20%PSN resin after different cure temperature.

resin after each cure stage. As shown in Figure 3, the exotherm gradually decreased with the increase in cure temperature and almost disappeared after curing at 250°C for 4 h.

The possible cure reaction mechanism between BZ and PSN was studied by FT-IR spectra. Figure 4 shows the FT-IR spectra of BZ, BZ-20%PSN and PSN cured after 250°C. For the cured PSN, the characteristic absorptions of structure appeared at 1261 and 1169 cm^{-1} due to the stretching of Si—CH₃ and Si—NH—Si, respectively. Both absorptions are also appeared for the cured BZ-PSN hybrid resin. It is an interesting result that there is a new peak appeared at 1093 cm^{-1} due to the O—Si—O for the cured BZ-PSN hybrid resin,¹⁷ suggesting that the reaction between BZ and PSN took place.

Figure 5 shows the possible cure reaction process between BZ and PSN. The reaction mechanism may be that phenolic hydroxyl group derived from ring-opening polymerization of benzoxazine monomer reacted with Si—NH—Si of PSN. And the Si—O—Si may be beneficial to improve the thermal property of cured BZ-PSN resin.

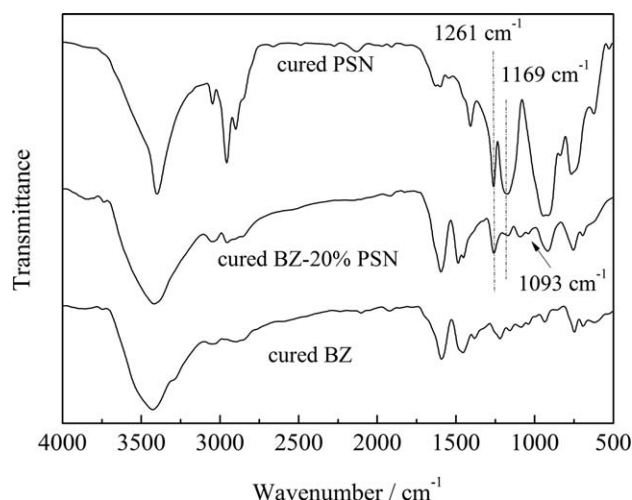


Figure 4. FT-IR spectra of resin cured after 250°C.

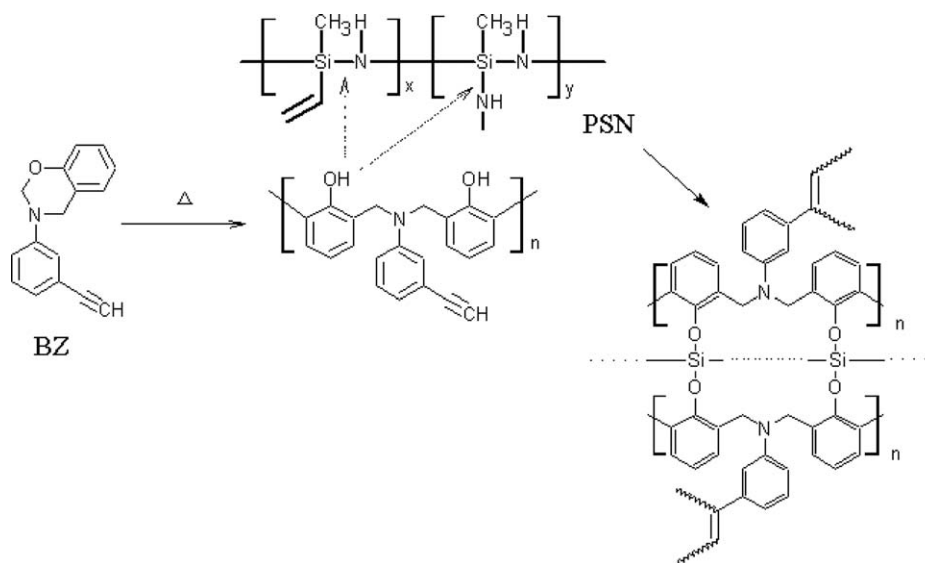


Figure 5. Possible cure reaction process between BZ and PSN.

Thermal Property of Cured BZ-PSN Resin

Heat-resistant property of cured resin was evaluated by DMA. Figure 6 shows DMA curves of representative cured resin, including cured BZ, BZ-25%PSN and BZ-30%PSN resin.

The initial decrease temperature of storage modulus (T_i) can reflect heat-resistant property of cured resins. As shown in Figure 6, T_i of cured BZ-25%PSN resin moved to lower temperature comparing to cured BZ resin, which showed heat-resistant property of cured BZ-25%PSN resin decreased. T_g s of all cured BZ-PSN resins are tabulated in Table II. T_g s showed a decreasing tendency with increase in PSN content, but all the values are higher than 250°C, revealing that cured BZ-PSN possesses excellent heat-resistant property.

Table III lists glass transition temperature (T_g) of all cured BZ-PSN resins from $\tan \delta$ curves. It can be seen that cured BZ-30%PSN resin showed two relaxation processes. The relaxation corresponding to $\tan \delta$ peak temperature 175.1°C is Si-N molecular segment relaxation of PSN. The relaxation corresponding to $\tan \delta$ peak temperature 280°C reflects networks from ethenyl crosslink reaction of PSN.²² However, T_g of other cured BZ-PSN resins are about 350°C as tabulated in Table III, revealing that cured BZ-PSN resins show excellent heat-resistant property. And also the height and width of $\tan \delta$ peak was associated with crosslink density.¹⁹ As shown in Figure 6, the height of $\tan \delta$ peak decreased and the width of $\tan \delta$ peak broadened with the increase in the

content of PSN. Decrease in height and increase in width of $\tan \delta$ peak revealed a decrease in segmental mobility and increase in crosslinking density. The increased crosslink density may be beneficial to improve thermal stability of cured BZ-PSN.

Thermal stability of cured BZ-PSN resins was investigated by TGA in nitrogen. The TGA and DTG curves of cured resins were presented in Figure 7, and typical parameters were summarized in Table IV.

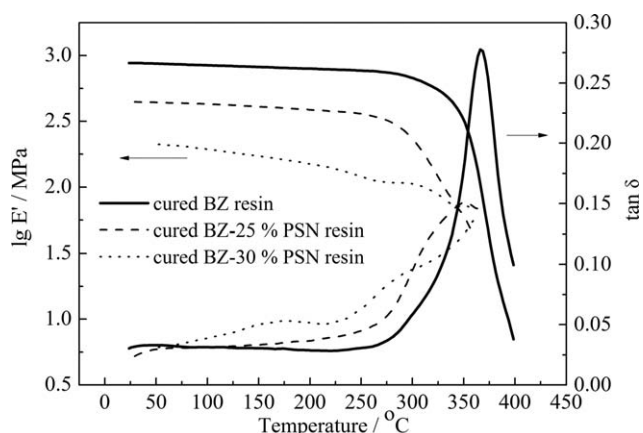


Figure 6. DMA curves of the cured BZ, BZ-25%PSN, and BZ-30%PSN resin.

Table II. Initial Decrease Temperature (T_i) of Storage Modulus of Cured BZ and BZ-PSN Resins

Resin	BZ	BZ-5%PSN	BZ-10%PSN	BZ-15%PSN	BZ-20%PSN	BZ-25%PSN	BZ-30%PSN
T_i (°C)	339.1	326.8	309.3	305.8	303	275.8	270

Table III. Glass Transition Temperature of Cured BZ and BZ-PSN Resins

Resin	BZ	BZ-5%PSN	BZ-10%PSN	BZ-15%PSN	BZ-20%PSN	BZ-25%PSN	BZ-30%PSN
T_g (°C)	366.8	359.4	348.3	347.3	356.8	351.6	175.1280

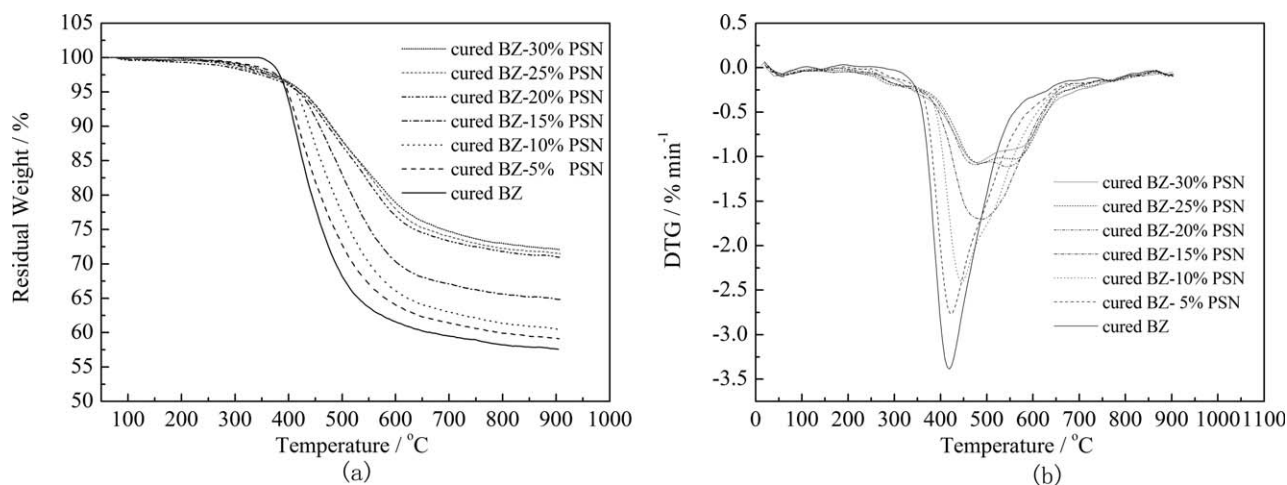


Figure 7. TGA curves of cured BZ resin and BZ-PSN resins in nitrogen: (a) Residual weight–temperature curves; (b) Derivative thermo gravimetric curves (DTG).

Table IV. Typical Parameters of TGA and DTG Curves for Cured BZ and BZ-PSN Resins

Resin	5% weight loss temperature (°C)	Maximum weight loss temperature (°C)	Maximum weight loss rate (% min ⁻¹)	Char yield at 900°C (%)
BZ	395.3	417.2	-3.42	57.64
BZ-5%PSN	399.1	418.3	-2.79	59.16
BZ-10%PSN	414.3	441.2	-2.47	60.52
BZ-15%PSN	418.4	476.4	-1.72	64.90
BZ-20%PSN	419.5	471.6	-1.18	70.91
BZ-25%PSN	431.0	477.9	-1.09	71.55
BZ-30%PSN	425.9	470.0	-1.08	72.17

As shown in Figure 7(a), cured BZ-PSN resin decomposes slower than cured BZ resin. Table I shows that 5% weight loss temperature ($T_d^{5\%}$) and the char yield of cured BZ-PSN resin in nitrogen gave an increase tendency relative to cured BZ resin with the content of PSN increasing. For example, $T_d^{5\%}$ of cured BZ-25% resin is 431.0°C, and the char yield is 71.55% at 900°C, increasing by 35.7°C and 13.91% than that of cured BZ resin, respectively.

As shown in Figure 7(b), DTG peaks of cured BZ-PSN resins were broader than that of cured BZ resin, and the maximum loss rate of cured BZ-PSN resins were slower than that of cured BZ resin. For example, the maximum decomposition rate of the cured BZ-25% resin is $-1.09\% \text{ min}^{-1}$, comparing to that of cured BZ resin $-3.42\% \text{ min}^{-1}$.

All of above results revealed that BZ-PSN had excellent thermal stability.

The thermo-oxidative stability of cured BZ-PSN resin was evaluated by TG testing in air atmosphere, and the results were shown in Figure 8. The cured BZ-PSN resins showed a delayed decomposition behavior comparing to cured BZ resin and the char residues was increased with increase of the PSN content. For example, $T_d^{5\%}$ and the char yield at 900°C of cured BZ-30% resin is 434.0°C and 21.5%, increasing by 17°C and 17.9% than

that of cured BZ-5%PSN resin, respectively. It revealed that cured BZ-PSN resin possesses excellent thermo-oxidative stability.

CONCLUSIONS

Novel hybrid resins based on acetylene-functional benzoxazine and polyvinylsilazane were prepared. BZ-PSN resins possess

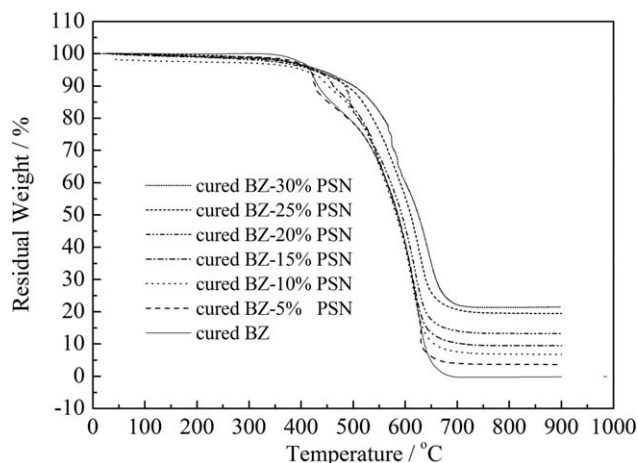


Figure 8. TGA curves of cured BZ and BZ-PSN resins in air.

excellent processing capability, suitable for RTM process to fabricate composites. The resin can be cured completely at about 250°C. Cured BZ-PSN resins possess excellent heat-resistant property, thermal and thermo-oxidative stability. BZ-PSN resin would be a promising candidate for matrices of advanced composites.

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