Thermal properties of a series of tetra-functional quinoxaline-based benzoxazine/monofunctional benzoxazine blends

Tiantian Feng1,2,*, Yanxia Li1, Xiumei Zhang1, Yuhua Cao1, Lin Li1

1Faculty of Mechanical and Electrical Engineering, Guangdong Baiyun University, Guangzhou, Guangdong, China
2Research Institute of Composite Materials, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, Heilongjiang, China

* *email: TT.Feng@baiyunu.edu.cn; phone number: 020-36095280-9223

Abstract: In this article, a series of tetra-functional quinoxaline-based benzoxazine/monofunctional benzoxazine (P-a) blending resins were prepared. Differential scanning calorimeter (DSC), dynamic mechanical analyzer (DMA) and thermogravimetric analysis (TGA) were utilized to study the curing behavior of blends and heat resistance and thermal stability of the corresponding resins. The obtained blends show lower onset and peak exothermic temperatures than that of a phenol/phenylamine-based benzoxazine. Additionally, the cured blends possess much better heat resistance, higher char yields, and better thermal stability than monofunctional benzoxazine resins.

1. Introduction
Polybenzoxazines, which formed by the thermal ring-opening of oxazine rings without any catalysts, continuously receive considerable interests of researchers since they possess many impressive properties including excellent thermal, dielectric and mechanical properties [1-4]. These advantages result in a broader applications than traditional phenolic resins. Recently, in order to further improve the performance of benzoxazine thermosets, many strategies have been proposed. For example, the thermal properties of polybenzoxazines can be deeply modified by introducing some specific functional groups or increasing the cross-linking density of polymers [5-9]. In addition, blending benzoxazines with high performance polymers is another effective way to modify certain commercial benzoxazine thermosets with poor thermal properties [10]. The resulted mixture are quite homogeneous when high performance benzoxazines are utilized as modifier. Also, the complex crosslinked networks of cured blending resins can be formed, resulting in better thermal properties.

Presently, a high performance tetra-functional benzoxazine (BQTPF), as shown in Fig. 1, containing both functional quinoxaline and furan groups has been reported [11]. After curing, the obtained thermoset have excellent heat resistance with a high glass transition temperature (Tg) of 418 °C, good thermal stability with a 5 % weight loss decomposition temperature (Td) of 430 °C, and high char yield (Yc) of 72 %. In order to improve the thermal properties of commercial benzoxazine resin, a series of polybenzoxazine blends were prepared in this study. A monofunctional benzoxazine, P-a, is performed as matrix resin and the above mentioned tetra-functional benzoxazine, BQTPF, is synthesized to be used as filler. The effects of the high performance benzoxazine on monofunctional resin are studied by DSC, DMA and TGA tests.
2. Materials & Methods

2.1. Materials
Both BQTPF and P-a monomers were synthesized according to the literature [10-11].

2.2. Preparation of tetra-functional quinoxaline-based benzoxazine /P-a blends
The tetra-functional quinoxaline-based benzoxazine /P-a blending monomers were prepared by mixing the blends thoroughly at 120 °C until a clear homogeneous mixture was obtained. The weight percent of tetra-functional benzoxazine ranged from 10% to 30%.

2.3 Preparation of benzoxazine resins and blending thermosets
The resulted monomers and blends were heated in an air-circulating furnace. None initiator or catalyst were added into them. The curing process was performed following the schedule: 180 °C /2 h, 200 °C /2 h, 220 °C /3 h, and 240 °C /1 h.

2.4 Characterizations
A Q200 differential scanning calorimeter made by TA was used to do DSC tests. At the room temperature, samples were put into a hermetic aluminum sample pan and heated from 30 to 300 °C with a rate of 20 °C/min under a nitrogen atmosphere. TA Q800 dynamic mechanical analyzer was utilized to perform DMA analysis under air atmosphere. The rectangular solid resins were loaded in single cantilever mode with a frequency of 1 Hz, an amplitude of 20 mm, and a heating rate at of 3 °C /min ranging from 30 to 480 °C. What’s more, TGA analysis was done by TA Instruments Q50. Samples were heated in a furnace, which is full of nitrogen. And the temperature ranged from 40 to 820 °C at a temperature ramp of 20 °C/min

3. Results & Discussion

3.1. Polymerization Behavior of BQTPF/P-a
The curing behavior of BQTPF /P-a blends are shown in Fig. 2. From Fig. 2, all of the monomers exhibits only one exothermic peak, and the initial and peak temperatures are decreased as the tetra-functional benzoxazine content increases. The reduction may be attributed to the catalytic effect of the lone pair of nitrogen of quinoxaline [11]. In addition, the existence of oligomers in the blends can also reduce the curing temperature through promoting the ring opening of oxazines at the lower temperature. Furthermore, the heat amounts of blending monomers decrease with the addition of BQTPF contents.
3.2. The Thermomechnical Properties of Poly (BQTPF/P-a)
The storage modulus ($E'$) and the heat resistance of cured resins were studied by DMA instrument and displayed in Fig. 3. The related parameters such as values of $E'$ and $T_g$ of the corresponding resins are summarized in Table 1. From Table 1, we can observe that the storage modulus of all blending resins at 50 °C are slightly increased with the addition of BQTPF content. The backbone rigidity contributed by quinoxaline groups, which possess abundant rigid aromatic rings, plays an important role on the improvement of mechanical properties. In the meantime, it can be clearly seen from the graphics that all of the poly (BQTPF/P-a) blending monomers possess much higher $T_g$ values than poly(P-a). The values increase accompany with the increasing additions of tetrafunctional quinoxaline-based benzoxazine compound. When loading to 30 wt. % of BQTPF, the $T_g$ value of cured blending attains 251°C, and the difference between poly (BQTPF/P-a) 30% and monofunctional benzoxazine resin are nearly 94 °C. This can be explained by the existence of functional groups, mainly furan and quinoxaline groups, in the backbone of blending polymers. The former can improve the cross-linking density of blends, and the latter can increases the backbone rigidity by restrain the thermal motion and internal rotation of polymer chains [12]. Additionally, possessing more oxazine rings can also form a higher cross-linking density [13].

3.3. The Thermal Stability of Poly (BQTPF)/P-a
TGA tests were performed to examine the thermal stability of poly (BQTPF/P-a). The parameter concerned with the thermal stability of resins are $T_5$, $T_{10}$ and $Y_c$ within or above 800 °C. The derivative weight loss curves of poly (BQTPF /P-a) blends are depicted in Fig. 4, and the related values are shown in Table 1. The obtained blending resins exhibit excellent thermal stability with $T_5$ over 350°C. There is a significance difference of 59–93 °C between the prepared blends and poly(P-a). The char yield of poly (BQTPF /P-a) are also higher than poly(P-a) of 6–16%. The significantly improvement of thermal properties could be explained by the existence of rigid quinoxaline groups in polymer segment and highly cross-linking structure of cured blends [14-16]. Both multifunctional oxazine rings and furan groups can promote the cross-linking density of blending resins.
4. Conclusions
In this paper, we have successfully prepared a set of tetra-functional quinoxaline-based benzoxazine/P-a blends. Their curing behavior are studied by DSC tests, and the results shows that the blends own lower curing temperatures than P-a when cured. The thermal properties of the resulted cured thermosets are also considered using DMA and TGA tests. The results prove that the addition of BQTPF has a
positive effect on P-a since poly(BQTPF /P-a) blends possess much better heat resistance and thermal stability than neat poly(P-a).

Acknowledgments
We deeply appreciate the vigorous supports from the foundation of Young Innovative Talents in General Colleges of Guangdong Province (Project No. 2018WQNCX298) and the Scientific Research Foundation of Guangdong Baiyun University.

References
[1] Ishida, H., Agag, T. (2011) Handbook of benzoxazine resins, Elsevier, Oxford.
[2] Feng, T. T., Wang, J., Pan, L., Derradji, M., Ramdani, N. Liu, W. B., Zhou H. R. (2016) Tunable properties of novel tetra-functional fluorene-based benzoxazines from mixed amines: Synthesis, characterization and curing kinetics. Thermo. Acta., 633:1-11.
[3] Kiskan, B., Gacal, B., Tasdelen, M. A., Colak, D., Yagci, Y. (2006) Macromol. Symp., 245: 27-33.
[4] Yang, P., Gu, Y. (2011) J. Polym. Res., 18:1725-1733.
[5] Ning X., Ishida, H. (1994) J. Polym. Sci. B: Polym. Phys., 32:1121-1129.
[6] Herrera, P. V., Doyama, K., Abe, H., Ishida H. (2008) Macromolecules., 41:9704-9714.
[7] Espinosa, M. A., Galià, M., Cádiz, V. (2004) Polymer., 45:6103-6109.
[8] Rimdusit, S., Tiptipakorn, S., Jubsilp, C., Takeichi, T. (2013) React. Funct. Polym., 73:369-380.
[9] Liu, W. B., Feng, T. T., Wang, J. (2017) Fluorene-based high molecular weight benzoxazine/mono-functional benzoxazine blends. In: Ishida H., Froimowicz, P. (Eds.), Advanced and Emerging polybenzoxazine Science and Technology. Elsevier., Amsterdam, pp.1-52.
[10] Wang, J., Liu, W. B., Feng, T. T. (2017) Furan-based benzoxazines. In: Ishida H., Froimowicz, P. (Eds.), Advanced and Emerging polybenzoxazine Science and Technology. Elsevier., Amsterdam, pp.1-35.
[11] Chien, H. C., Tsung, Y. Y., Wu, J.H., Mathivathanan, A., Juang, T. Y., Mahdi, M. A., Lin, C. H. (2019) Synthesis and properties of quinoxaline-containing benzoxazines and polybenzoxazines. ACS. Omega., 4:9092-9101.
[12] Zhang, T., Wang, J., Feng, T. T., Wang, H., Ramdani, N., Derradji, M., Xu, X. D., Liu, W. B., Tang, T. (2015) RSC. Adv., 5:33623-33631.
[13] Wang, H., Wang, J., He, X. Y., Feng, T. T., Ramdani, N., Luan, M. J., Liu, W. B., Xu, X. D. (2014) RSC. Adv., 4:64798-64801.
[14] Liu, Y. L., Chou, C. I. (2005) J. Polym. Sci. Part. A: Polym. Chem., 43:5267-5282.
[15] Wang, J., He, X. Y., Liu, J. T., Liu, W. B., Yang, L. (2013) Macromol. Chem. Phys., 214: 617-628.
[16] Wang, J., Wu, M. Q., Liu W. B., Yang, S. W, Bai, J. W., Ding, Q. Q., Li, Y. (2010) Eur. Polym. J. 46:1024-1031.