Effect of surface modification of Poly-p-phenylenebenzobisoxazole fiber with lanthanum salt on flexural properties of composite with thermoset polyimide

Wang Minghui(王名辉)^a、YU liang^b、QIU zixue(邱孜学)^a a Shanghai Research Institute of Synthetic Resins(上海市合成树脂研究所) Shanghai 200233, P.R. China

b School of Mechanical & Power Engineering, Shanghai Jiao Tong University, Shanghai 200030, P.R. China

The effect of lanthanum (La) salt on surface treatment of Poly-p-phenylenebenzobisoxazole (PBO) fiber on flexural properties of PBO fibers reinforced thermoset polyimide composites was investigated. Experimental results mechanism of improvement in interfacial adhesion between PBO fiber and PMR matrix after La salt treatment was discussed. The increase in the amount of polar groups strengthened the interfacial adhesion between PBO fibers and thermoset polyimide matrix, and accordingly enhanced the flexural properties.

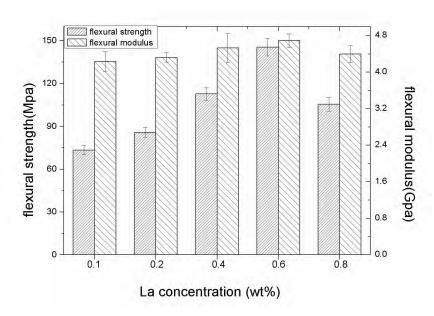


Figure 1 PBO/PI composites at room temperature (20 $^{\circ}$ C) flexural performance and the relationship of La salt concentration

From the figure 1 can be seen, after La salt modification of PBO/PI composite flexural strength and flexural modulus increases with the rare earth content of rare earth solution first increases gradually, until the rare earth content is 0.6 wt %, the flexural strength and flexural modulus of the composite reached maximum, and then with the increase of content of La salt, flexural strength and flexural modulus of the composite material is on the decline. This shows that La salt content in rare earth solution on flexural properties of PBO/PI composite material, and when La salt content about 0.6 wt %, the composites showed best flexural performance.

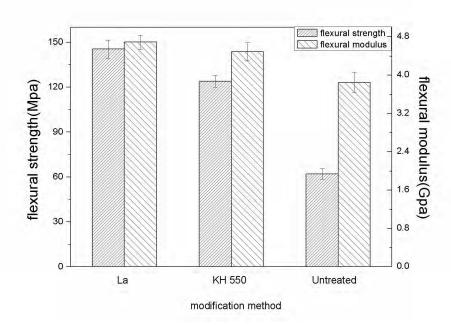


Figure 2 surface treatment of PBO/PI composite materials at room temperature (20 $^{\circ}$ C), the influence of the flexural performance

As can be seen from the figure 2, PBO treated by KH 550 treatment and La/PI composite cold flexural properties are better than without the surface treatment of composite materials. Compared with surface treatments not composites, PBO treated by KH 550/PI composite flexural strength and flexural modulus increased by about 99.72% and 16.7% respectively, while the La salt treatment increased by about 134.16% and 22.56% respectively. Test results show that the two modification methods can improve the interface bonding state of composite material, and La salt modification are more effective.

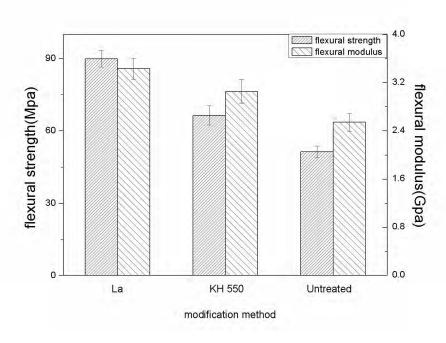


Figure 3 surface treatment of PBO/PI composite high temperature (210 ℃), the influence of the

flexural performance

From the figure 3 can be seen, under the condition of 210 $^{\circ}$ C, flexural properties of PBO/PI composites compared with normal temperature have varying degrees of decline phenomenon happens, but the surface treatment of PBO/PI composite flexural performance is still better than that of without surface treatment of composite materials, and composite materials treated by La salt flexural performance is best.Compared with figure 2, PBO treated by KH 550/PI composite flexural strength and flexural modulus is under the condition of normal temperature was reduced by 46.37% and 46.37% respectively, while the La salt processing was reduced by 38.11% and 38.11% respectively.Experimental results show that under the condition of 210 $^{\circ}$ C, the two modification methods still can improve the interface bonding state of composite material, and the stability of the La salt modification treatment at high temperature than KH 550 treatment is more superior.

The La atom carries large effective nuclear charge, thus making itself able to attract surrounding electrons of other atoms. The mechanism of La salt modification includes the following two aspects:

1) Some La atoms can be adsorbed to PBO fiber surface by reacting with the polar groups on PBO fiber surface, while other La atoms can form active centers in the fiber surface defects. Due to the large coordination number of La element, the La atom continues to react with reactive functional groups (such as carboxyl (—COOH) and amino (—NH $_2$) groups) in the La salt surface modifier. As a result, the concentration of reactive functional groups on fiber surface is increased through a method similar to chemical grafting. So, the compatibility between PBO fibers and PI matrix is improved. The schematic diagram of concentration increase of reactive functional groups on fiber surface is presented in Fig. 4.

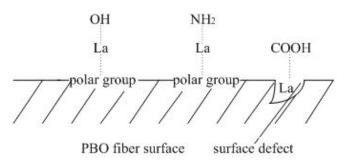


Fig. 4 The schematic diagram of concentration increase of reactive functional groups on PBO fiber surface

2) La atoms are capable of coordination reaction with the end group of PBO molecule. As the multiple coordination of La element, La atoms, which do not completely make coordination chemical reactions, can continue to react with functional groups of polymers (such as carbonyl groups (C=O) on PMR). The schematic diagram of the improvement of interfacial adhesion is presented in Fig. 5.

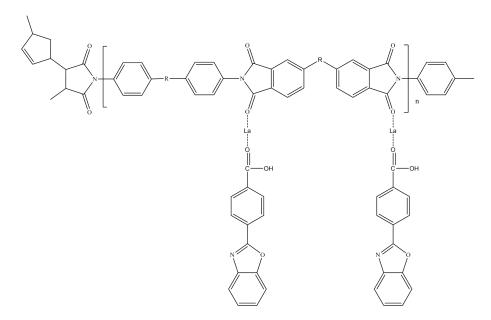


Fig. 5 The schematic diagram of the improvement of interfacial adhesion

(References continued from P218)

- [15] Zeng, K.; Hong, H. B.; Zhou, S. H.; Wu, D. M.; Miao, P. K.; Huang, Z. F.; Yang, G. *Polymer*. 2009, 50, 5002-5006.
- [16] Zeng, K.; Li L.; Xiang, S. R.; Zhou, Y.; Yang, G. Polym. Bull. 2012, 68, 1879-1888.
- [17] Wu, D. M.; Zhao, Y. C.; Zeng, K.; Yang, G. J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 4977-4982.
- [18] Zeng, K.; Zou, Y.; Yang, G. Des. Monomers Polym. 2014, 17, 186-193.
- [19] Thompson, C. M.; Hergenrother, P. M. Macromolecules. 2002, 35, 5835-5839.
- [20] Hergenrother, P. M.; Connell, J. W.; Smith Jr, J. G. Polymer. 2000, 41, 5073-5081.
- [21] Wood, K. H. The Thermal Cure of Phenylethynyl Terminated Polyimides and Selected Model Compounds. [D]. College of William & Mary, 1997.
- [22] Fang, X. M.; Xie, X. Q.; Simone, C. D.; Stevens, M. P.; Scola, D. A. *Macromolecules*. 2000, 33, 1671-1681.
- [23] Knijnenberg, A.; Weiser, E. S.; StClair T. L.; Mendes, E.; Dingemans, T. J. *Macromolecules*. 2006, 39, 6936-6943.
- [24] Li, Y. T.; Morgan, R. J. J. Appl. Polym. Sci. 2006, 101, 4446-4453.
- [25] Lee, J. Y.; Choi, H. K.; Shim, M. J.; Kim, S. W. Thermochim. Acta. 2000, 343, 111-117.