

# RESEARCH ON PULTRUSION OF POLYBENZOXAZINE RESIN MATRIX Z-PINS

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## Introduction

As the appearance of novel phenolic family polymers, the polybenzoxazine resins attract significant attention to be developed as an alternative to traditional high-performance thermosetting resin for aerospace application.<sup>[1]</sup> Polymer benzoxazine resins, usually called ring-opening polyphenolic, not only inherit the outstanding inflaming retardance and ablating tolerance of phenolic resins, but also overcome many shortcomings, including releasing condensation by-products and needs of strong acids for catalysts.<sup>[2]</sup> Meanwhile, advantages of nearly zero cure condensation, low moist abortion and molecular design flexibility offer polybenzoxazines promising applications in engineering fields.

According to the investigation for now, mould pressing, laminates and RTM for polybenzoxazines have been developed, and no research of pultrusion has been reported, especially for micro diameters pultrusion. Z-pinning technology is considered as an important Z-direction reinforcement method for laminates, developed by Aztex Inc. (Waltham USA).<sup>[3]</sup> However, special demands for Z-pin's pultrusion require the low viscosity (below 800 mps) at room temperature or little higher, short gelation time (no more than 5 minutes), moderate cure temperature and well wetting property for reinforce fibers.

In this paper, Z-pins with different parameters of proceeding craft will be prepared, properties will be tested with various methods and appropriate parameters for polybenzoxazines pultrusion will be

determined.

## Experimental

### Materials

Polybenzoxazines resin was obtained from Sichuan University and used without any solvent. S4C9-252 glass fiber was obtained from Nanjing Research Institute of Glass Fiber.

### Apparatus and Procedures

Z-pins are prepared by with the self-developed automotive pultrusion machine at the diameter of 0.5mm (Fig. 1).

The short beam shear experiments were tested at room temperature at a rate of 2mm/s with the electronic universal testing machine produced by Shenzhen Sans Testing Machine CO. LTD.

The micro photo was taken by three-dimensional digital microscope.

The viscosity-time curve was tested by the Brookfield DV-II viscosimeter at 60°C at the rotate speed of 25r/min.

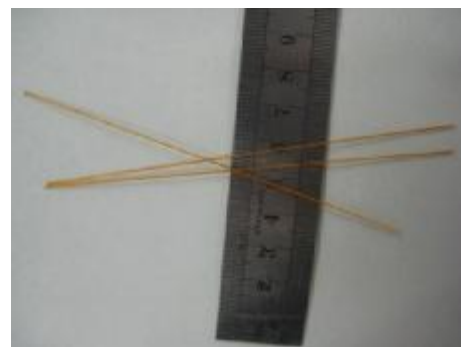


Fig. 1 Polybenzoxazine resin matrix Z-pins

## Results and Discussion

The Polybenzoxazine resin has a relatively high viscosity at room temperature, so the resin needs to be heated. The viscosity-time curve at 60°C is shown in Fig. 2. The curve showed that viscosity at 60°C is suitable for pultrusion and the preserve life is approximately 5 hours.

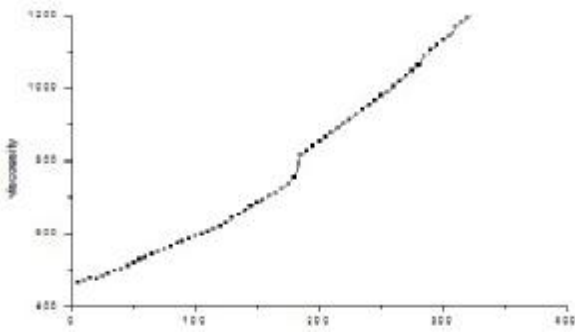


Fig. 2 Viscosity-time curve at 60°C

The short beam shear experiment is conducted to evaluate the shear retardant performance of Z-pins, which reflects the wetting properties with fiber. The maximum shear strengths of Z-pins with different die temperatures are listed in the Table 1, and higher shear strength means the better wetting properties. The results showed that the 140 °C is the most suitable die temperature.

Table 1 Results of short beam shear tests

Die temperature/ °C	110	120	130	140	150
Shear strength/Mpa	26.359	29.648	27.274	39.734	—

Ps: when the die temperature was 150°C, resin had cured and pultrusion was aborted.

The rules for choice of the oven temperature are making sure that resins partially cured and offer the toughness for pulling so that a round section of Z-pins can be obtained. According to the macro view, the oven temperature of 190°C can sacrifice

the rules well. Though when 200°C or higher temperatures can offer the same effect, cocuring of the Z-pins and laminates demand a low cure degree of Z-pins.

As we all know, resins matrix of composites is responsible for the transferring of loads to reinforce fiber, and pores in resins will effect more or less on the properties of Z-pins. Seen the micro photo in figure 3, the pores may come from residual solvent during the proceeding of polybenzoxazine synthetization. Therefore, more suitable resin need be explored.



Fig. 3 Pores in Z-pin

## Conclusion

The craft of polybenzoxazine pultrusion was researched. It is demonstrated that the polybenzoxazine resins are suitable for pultrusion, and the parameters, including resin, die and oven temperature were determined. More studies need be done to eliminate the pores in Z-pins.

## References

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