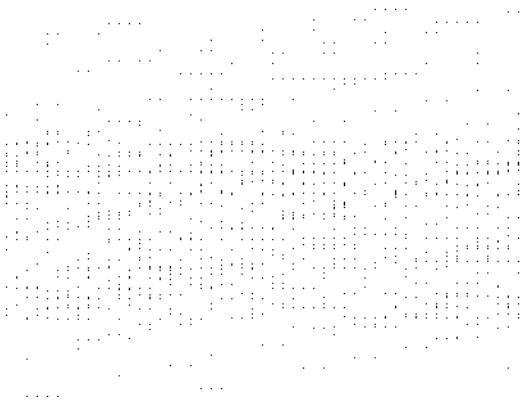
Polyimide Resins and Their Carbon Fiber-reinforced Composites With Excellent Processibility and High Toughness

Shiyong YANG(杨士勇), Biao LIU, Mian JI（冀绵）,

Laboratory of Advanced Polymer Materials, Institute of Chemistry, CA（中科院化学所）, Beijing 100190, P. R. China, E-mail: liubiao@iccas.ac.cn

Carbon fiber reinforced polyimide composites have been widely used in recent years due to their unique combination of thermal and mechanical properties.[1] The method to obtain polyimides composites with good processability and toughness has always been a scientific and technical challenge. PETI-5 composite has very high toughness with CAI value > 300MPa.[2] However, this material is difficult to process which restrict its applications. In order to fabricate composites with better quality, a resin with better melt flow is required. Moreover, a precursor solution with high solid content, low viscosity, and solvents which can be easily removed is also needed.[3] These requirements call for more challenges for the fabrication of high performance polyimide composites.

In present work, a series of biphenyl-type imide oligomers end-capped by 4-phenylethynyl phthalic anhydride (4-PEPA) were synthesized through a modified PMR route (as shown in **Scheme 1**). Stable resin solutions with solid content of 50% and viscosity of 40-60 mPa·s were obtained. The solvents and volatiles of the resins were easily removed at low temperatures. Different thermal treatments were discussed through TGA, DSC and FTIR to determine the best B-stage condition.



Scheme 1. A modified PMR route

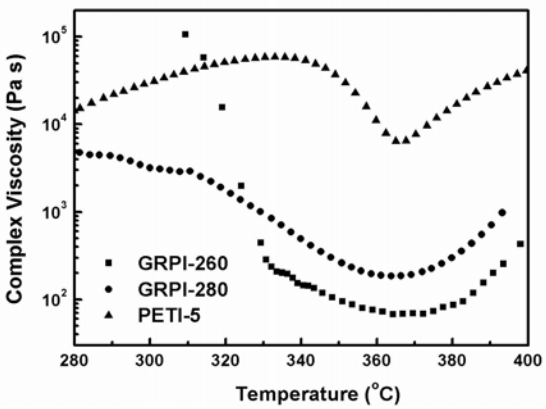


Fig.1 Rheology behaviors of oligomers

Polyimides with different oligomer molecular weights and copolymerization ratios were investigated. Two resins named GRPI-260 and GRPI-280, which exhibited cured T_gs of 260 °C and 280 °C respectively, had the best combined properties. As shown in **Fig. 1**, the melt flow of these oligomers was significantly improved compared to PETI-5. Wide processing windows and sufficiently low melt viscosities were obtained. At the same time, the cured resins had high mechanical strength and high toughness as shown in **Table 1**. They were selected to fabricate carbon fiber reinforced composites for further investigation.

Table 1 Characterizations and properties of cured polyimide resins

Samples	DMA		Tensile properties			Flexural properties	
	E' (℃)	tan δ (℃)	Strength (MPa)	Modulus (GPa)	Elongation (%)	Strength (MPa)	Modulus (GPa)
GRPI-260	260	280	118	2.3	12	154	3.8
GRPI-280	280	300	124	2.0	18	155	3.1

Through an optimized curing procedure, unidirectional and quasi-isotropic laminates were fabricated with good quality. After impacted at an energy of 6.7 kJ/m, only a small damage could be observed in the center of C_f/GRPI-260 laminate indicated by C-scan (**Fig.2**). The CAI of this composite was 313 MPa which means a very high toughness and damage tolerance. C_f/GRPI-280 composite had relatively low CAI (260 MPa) but better high temperature performance due to its higher T_g. The relationship between impact energy and CAI of C_f/GRPI-280 was also studied (**Fig.3**). As shown in **Table 2**, the two composites had high retention of mechanical properties at elevated temperatures and can be serviced at 230 °C and 250 °C, respectively. These properties indicated a promising potential for future aerospace applications.

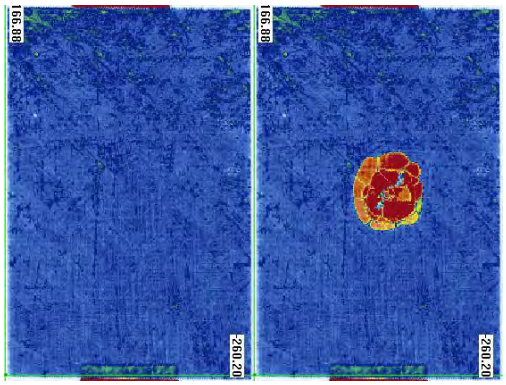


Fig.2 C-scan images before and after impact

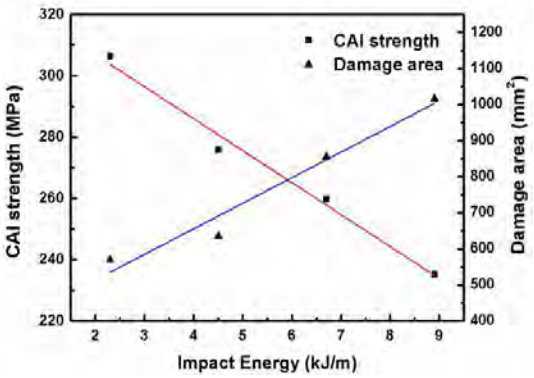


Fig.3 CAI of different impact energies

Table 2 Mechanical properties of the laminates

	Lay-up	GRPI-260	GRPI-280
0° Flexural strength, MPa	$[0°]_{12}$	1536 (R.T.) 682 (230 °C)	1537 (R.T.) 819 (250 °C)
0° Flexural modulus, GPa	$[0°]_{12}$	141 (R.T.) 141(230 °C)	144 (R.T.) 140(250 °C)
Interlaminar shear strength, MPa	$[0°]_{12}$	100 (R.T.) 53 (230 °C)	108 (R.T.) 53 (250 °C)
CAI strength, MPa	$[-45°,0°,45°,90°]_{3s}$	313	260
OHC strength, MPa	$[-45°,0°,45°,90°]_{2s}$	288	303
OHT strength, MPa	$[-45°,0°,45°,90°]_{2s}$	489	367

Acknowledgment

*Funding from the National Natural Science Foundation of China (NSFC) for distributed Young Scholars (No.******) is gratefully acknowledged.*

References

[1] Pater, R.H. and P.A. Curto, *Advanced materials for space applications.* Acta Astronautica, 2007. **61**(11-12): p. 1121-1129.

[2] Smith Jr, J., J. Connell, and P. Hergenrother, *The effect of phenylethynyl terminated imide oligomer molecular weight on the properties of composites.* Journal of Composite Materials, 2000. **34**(7): p. 614.

[3] Hou, T.H., B.J. Jensen, and P.M. Hergenrother, *Processing and properties of IM7/PETI composites.* Journal of Composite Materials, 1996. **30**(1): p. 109-122.