High performance phthalonitrile/phenolic epoxy (PNP/PEP) copolymers and their GFRP composites

Xulin Yang, Kui Li, Mingzhen Xu, Xiaobo Liu*
Research Branch of Advanced Functional Materials, School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, P. R. China

*Corresponding author e-mail: liuxb@uestc.edu.cn

Abstract. In the design of advanced thermoset GFRP composites, balancing the processabilities of the resin and the comprehensive properties of final GFRP composites is the key. In this paper, phthalonitrile/phenolic epoxy (PNP/PEP) copolymers with well processabiity have been designed for the GFRP composites. The resulted PNP/PEP GFRP composites not only exhibit high mechanical properties at room temperature; but also show excellent high-temperature mechanical performance. After 300 oC/72h aging, the flexural strength retention ratios maintains over 93% while those of flexural modulus is near to 100%. Advanced PNP/PEP GFRP composites can be employed in some critical circumstances that need high mechanical properties and service temperatures.

1. Introduction
Phthalonitrile (PN) resin, as a high performance matrix resin, is an ideal polymer matrix for the advanced GFRP composites due to the high mechanical performance, excellent thermal and thermo-oxidative stability, superior flame-retardant property and well chemical resistance [1-8]. Nevertheless, the high melting point, poor solubility, high curing temperature and long curing time limited their applications to a large extent. On the other hand, epoxy (EP) resins are well-known for their outstanding mechanical properties, good chemical resistances and excellent processabilities and they have been widely applied in many fields. However, their main drawbacks are the poor thermal and thermal-oxidative stabilities [9-10].

Herein, PN/EP systems can intergroup well processabilities of EP with comprehensive properties of PN. PN/EP blends have attracted interest in composite field. Keller et al [5] first reported a BPA-based PN/EP blend with well thermal properties, but the process condition was very strict. Goo et al [6] prepared amine-based PN/EP blend and their GFRP composites. The preparation condition was mild but the mechanical properties, and especially thermal properties were not satisfying. In the view of polymer composite design, copolymerization system has advantages than blend system. Recently, our lab found that simultaneous introduction of amine and phenol into PN resin could improve processabilities and assure final properties [11]. Herein, blending amine-containing phthalonitrile prepolymer (PNP) with phenolic epoxy (PEP) may be a promising system to balance the process abilities and final properties. Thus in the current study, the backbone of both PNP and PEP were chosen as biphenyl A-based types to promote the compatibility and optimize the blend structure.
PNP/PEP blend and their GFRP composites were prepared and their curing behaviors, process abilities, and mechanical properties (at room temperature and at high temperature) were reported.

2. Experimental section

2.1. Materials
The green phthalonitrile prepolymer powder (PNP, density: 1.15g/cm³; melting point: 185°C), was obtained from Guangdong Shunned Great New Materials Co., Ltd. The translucent paste phenolic epoxy (PEP, hydroxyl equivalent: 210-230g/eq; softening point: 100°C) was supplied by Shengquan Industrial Park. High strength glass fiber fabric (GF, thickness: 0.18 mm; specific weight: 180g/m²), was purchased from Nanjing Fiberglass Institute.

2.2. Preparation of PNP/PEP blend and PNP/PEP GFRP composites
The PNP/PEP blend: a measured weight of PNP and PEP (0-20wt %) was added in MEK and refluxed for 60min. The solid/the solvent was 100/100. PNP/PEP GFRP composites: GF fabric (15×15cm²) was infiltrated with the various PNP/PEP solutions above and dried at 60°C for 30min. The prepare was designed to give a 40wt% PNP/PEP blend and 60wt% GF in theory. 12 layers of prepare were hot-pressed under 10 MP pressure with a procedure of 180°C/2h; 220°C/2h; 260°C/2h; 300°C/2h, respectively. PNP/PEP GFRP composite laminates were obtained after cooling to room temperature.

2.3. Characterizations
The solvent in PNP/PEP blends were removed in a vacuum oven before differential scanning calorimetric (DSC) and dynamic rheological (DR) analyses. DSC curves of PNP/PEP blend were carried out with TA Instruments Modulated DSC-Q100 at a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min. DR analysis of PNP/PEP blends was performed using TA Instruments Remoter AR-G2 at 1Hz in air. The samples were melted between 25mm diameter parallel plates with an environmental testing chamber of the remoter. Three-point bending flexural tests of PNP/PEP GFRP composites were performed with a SANS CMT6104 series desktop electromechanical universal testing machine with a support span/sample of 15:1, a capacity of 10kN, a displacement speed of 10mm/min and gained as average value for every five samples.

3. Results and Discussion

![Figure 1](image_url)  
**Figure 1.** (a) DSC curves of PNP/PEP systems; (b) η* of PNP/PEP systems

Figure 1(a) gives the DSC curves of PNP/PEP systems from 50°C to 350°C. It can be seen that PNP prepolymer exhibited a melting peak around 180°C. As PEP content increased from 5wt% to 20wt%, the melting peak dramatically decreases to lower temperatures. It can be due to the decline effect of low melting point PEP introduction. In addition, the melt point peak of PNP/PEP system becomes smaller with the increasing PEP content. It is because that the melting process is also accompanied...
with the copolymerization process as PEP content increases. Compared with the pure PNP, all PNP/PEP systems show a small co-curing peak, indicating that the addition of PEP could effectively catalyze the curing of PNP. This catalyzing effect became more and more obvious as the PEP content goes. Compared with other PN/EP systems, these results are quite different. Cu et al [8] reported that the addition of EP could obviously make the curing peak of examine-containing PN shift to higher temperature. Goo et al [6] found that the existence of EP increased the curing temperature of amino-containing PN. Similar results were also reported by PN/EP systems [4, 7]. In these studies, the employed EP or PN are hard to be cured without the help of curing agent. When a small amount of curing agent was introduced, the PN and EP competed with each other for the curing agent. Since the curing reactivity of EP is higher than that of PNP, most of curing agent is consumed by EP. As a result, these systems were dominated by blend structure rather than copolymer molecular; and thus their DSC curves showed double curing peaks. In our study, the PNP is the PN prepolymer while the PEP is the phenolic EP. Both PNP and PEP could be cured without other curing agent. The nitrile groups in PNP can react with phenolic groups of PEP; the epoxy groups in PEP can react with amine groups in PNP. Herein, the PNP/PEP system showed a single co-cure peak and the results are copolymers.

The melt complex viscosity (η*) curves of the PNP/PEP system are displayed in Figure 1 (b). The η* of PNP first decreases, and reaches to a plateau, then increases dramatically and finally stabilizes. These η* changes correspond to gradual softening, fully melting, curing and being cured, respectively. The η* plateau region from 190°C to 240°C is called “process window”. The η* change of PNP/PEP systems show similar trend with that of PNP, but there are still some differences in PNP/PEP systems. First, the initial η* values decrease with the increasing PEP content. Second, the temperature of the η* initial decrease is shifted to lower temperatures, so is the temperature for η* initial increase. Thus, “process window” becomes narrow as PEP composition goes. In addition, the final η* values increase with the increasing PEP loading. These differences can be attributed to addition of low η* of PEP and co-curing reaction of PNP/PEP systems. As EP content increases, both amino-containing PN/EP [6] and oxazine-containing PN/EP blends [8] showed similar narrowed “process window” as PNP/PEP systems, but in the plateau region, their η* values are higher than that of PN. The probable reason was that the independent curing of higher reactivity EP led to the η* increases. Herein, combined with the results of curing behavior and process properties, the appropriate curing procedure for PNP/PEP blends can be settled as 180°C/2h; 220°C/2h; 260°C/2h; 300°C/2h.

As a promising advanced material, mechanical properties PNP/PEP GFRP composites were essentially concerned, as displayed in Figure 2. In general, both flexural strength and flexural modulus improved obviously with the increasing PEP content. At room temperature, flexural strength and flexural modulus of PNP-only GFRP composite are 653 MPa and 1862 MPa, respectively. With a small content of 5wt% PEP, flexural strength and flexural modulus of PNP/PEP GFRP composite are 710 MP and 1838 MP, which are increased by 57 MP and 215 MP respectively, in comparisons of those of PNP GFRP composite. Flexural strength and flexural modulus reached to their maximums when PEP content is 15 and 20 wt. %, respectively. Flexural strength and flexural modulus here are 772 MPa and 2094 MPa, leading to 18.22% and 7.91% increase compared with those of PNP-only GFRP composite, respectively. Flexural strength of most PN-based GFRP composites reported by references [4, 6] is lower than 700 MPa and hard to be called advanced materials. Astir et al [12] prepared a PN GFRP composite with flexural strength as high as 819 MPa. However, a top curing temperature as high as 375°C and a total curing time as long as 21h had to be employed. The process conditions are too rigid to realize the industrial manufacture and application. After 300°C/72h thermal aging, flexural strength of PNP/PEP GFRP composite still increases under the 15wt% PEP content. When the PEP content is 20wt%, flexural strength of PNP/PEP GFRP composite decreases and its value is 709 MPa, but it is still higher than those of PNP GFRP composite. Flexural modulus of PNP/PEP GFRP composite steadily increase, and reach its maximum when PEP content is 10wt%, then slightly decreased with the increasing PEP content. Figure 2(c) displays the retention ratio of flexural properties after 300°C/72h thermal aging relative to those at room temperature. The retention ratio for flexural strength of PNP/PEP GFRP composite slightly decreases with PEP content,
but the overall retention ratio is higher than 93%. The retention ratio for flexural modulus of PNP/PEP GFRP composite steadily increase, and reach its maximum when PEP content is 10wt%, then slightly decreases with the increasing PEP content. The overall retention ratio is near to 100%. These results indicate that after thermal aging at 300°C for 72h, most of mechanical properties of PNP/PEP GFRP composites are maintained. PNP/PEP GFRP composites may have a promising long-term service temperature as high as 300°C.

**Figure 2.** Mechanical properties of PNP/PEP GFRP composite: (a) Flexural strength; (b) Flexural modulus; (c) Retention ratio

4. Conclusion
A phthalonitrile/phenolic epoxy (PNP/PEP) copolymer with excellent processability and low-temperature curing behavior have been designed for the GFRP composites. The resulted PNP/PEP GFRP composites not only exhibit excellent mechanical properties at room temperature (with flexural strength over 700MPa and flexural modulus more than 18GPa); they also exhibit excellent mechanical retention ratio after 300°C/72h thermal aging (with strength retention ratio over 93% and modulus retention ratio of near to 100%). Advanced PNP/PEP GFRP composites can be employed under some critical circumstances that need high mechanical properties and service temperatures.
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