

Effect of Polyarylene Ether Nitriles on Processing and Mechanical Behaviors of Phthalonitrile-Epoxy Copolymers and Glass Fiber Laminated Composites

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ABSTRACT: A series of copolymers and glass fiber composites were successfully prepared from 2,2-bis [4-(3,4-dicyanophenoxy) phenyl] propane (BAPh), epoxy resins E-44 (EP), and polyarylene ether nitriles (PEN) with 4,4'-diaminodiphenyl sulfone as curing additive. The gelation time was shortened from 25 min to 4 min when PEN content was 0 wt % and 15 wt %, respectively. PEN could accelerate the crosslinking reaction between the phthalonitrile and epoxy. The initial decomposition temperatures (T_i) of BAPh/EP copolymers and glass fiber composites were all more than 350°C in nitrogen. The T_g of 15 wt % PEN glass fiber composites increased by 21.2°C compared with that of in comparison with BAPh/EP glass fiber composite. The flexural strength of the copolymers and glass fiber composites reached 119.8 MPa and 698.5 MPa which increased by 16.6 MPa and 127.3 MPa in comparison with BAPh/EP composite, respectively. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: phthalonitrile-epoxy; polyarylene ether nitriles; mechanical properties; thermal properties; glass fiber laminated composites

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INTRODUCTION

Thermosets are well known for their stiffness and dimensional stability. There are various thermosetting resins like epoxy resin, phthalonitrile resins, and so forth are available in the market.^{1–4} Epoxy resins are widely used for their excellent properties and cost effectiveness. However, the main drawback of epoxy resins is their limitation where high thermal stability and flame retardancy are needed. Phthalonitrile resins have attracted tremendous attention due to their outstanding rigidities, thermal and thermo-oxidative stabilities, excellent mechanical properties, superior moisture, and fire resistances.^{5–7} Besides, fiber-reinforced polymeric composite material is composed of a polymeric matrix and continuous reinforced fibers. Recently, much work has been focused on the modified epoxy and their glass fiber composites with thermosetting resins, such as phthalonitrile resins.^{8–15}

Polyarylene ether nitriles (PEN) are a kind of engineering thermoplastic, which exhibits excellent mechanical strength, solvent and flame resistance.¹⁶ PEN is used in this high technology because of their very excellent mechanical properties and high glass transition temperatures.^{17–21} The thermoset-thermoplastic interpenetrating polymer networks (IPN) materials can exhibit

synergistic properties of both the component polymers, which exhibit more excellent than single component.

In our laboratory, the previous investigations demonstrated that phthalonitrile could enhance processability of epoxy resins, without sacrificing high temperature resistance, thermal stability, and mechanical properties.²² However, the performances of this 2,2-bis [4-(3,4-dicyanophenoxy) phenyl] propane/epoxy resins E-44 (BAPh/EP)-based system are limited in intrinsic brittleness of the network structure and low glass transition temperatures. To overcome these problems, IPN tend to be an effective method. Herein, to investigate the effect of PEN on properties of BAPh/EP copolymers and glass fiber composites, a series of BAPh/EP-PEN copolymers and glass fiber composites were prepared. The effects of PEN on the mechanical and thermal properties were assessed systematically. The thermal properties and processing behavior of the phthalonitrile-epoxy system were also investigated by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and rheological measurement.

EXPERIMENTAL

Materials

BAPh monomer and the phenolphthalein-based PEN were synthesized in our laboratory in China. The synthetic procedure and raw

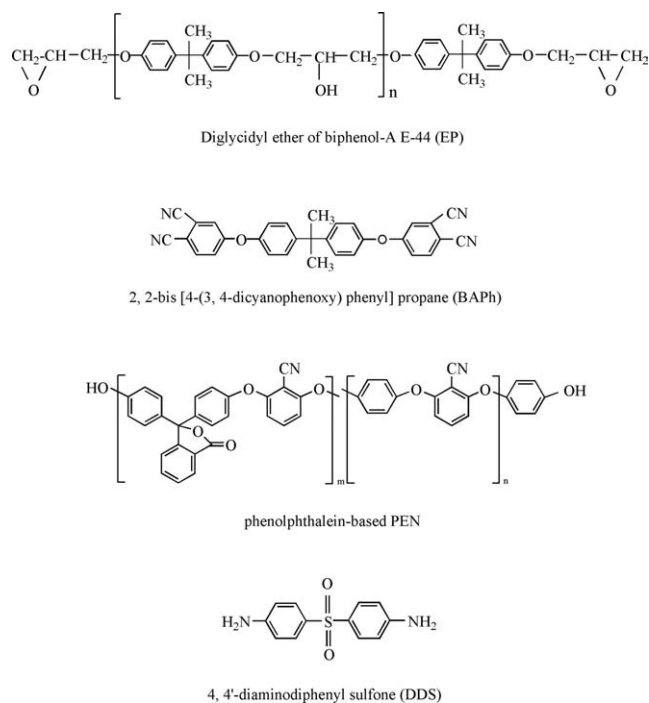


Figure 1. Chemical structures of BAPh/EP-PEN prepolymers.

materials were reported previously.^{23,24} Diglycidyl ether of biphenol-A E-44 (EP), *N,N*-dimethylformamide (DMF), and 4,4'-diaminodiphenyl sulfone (DDS) were obtained from Tianjin BODI chemicals. The E-type electronic glass fiber clothes were purchased from SICHUAN EM Technology. The structures of BAPh/EP-PEN copolymers and curing agent are shown in Figure 1.

Preparation of the BAPh/EP-PEN Prepolymers and Copolymers

In a three-neck round bottom flask equipped with a mechanical stirrer, phthalonitrile monomer were melted at 200°C, then epoxy resins, aromatic diamine curing additive (DDS), and PEN were added to the melted phthalonitrile monomer to form a homogeneous mixture. The weight ratio of BAPh/EP kept 50 : 50. The mixture was cooled rapidly to room temperature for use in DSC and viscosity studies. All the BAPh/EP-PEN prepolymers were poured into pre-heated molds. With the weight ratio of PEN contents increasing from 5 wt % to 15 wt %, the prepolymers were cured in the air by the procedure as follows: 200°C/4 h; 220°C/2 h; 250°C/2 h; 270°C/2 h, respectively.^{22,25} The copolymers were cooled gradually to room temperature, and then removed from the molds.

Preparation of Glass Fiber Reinforced BAPh/EP-PEN Composites

Compression molding technique was used to fabricate the BAPh/EP-PEN glass fiber composites. And glass fiber mat was cut into 20 mm × 20 mm. To get 1.5 mm thickness for the BAPh/EP-PEN glass fiber composites, 15 layers of fiber mats were added successively. PEN was dissolved in DMF, and then BAPh and DDS was added. After prepolymerization, EP was mixed to the solution. The weight ratio of the BAPh/EP was 50 : 50, and the PEN contents increased from 5 wt % to 15 wt

%. The DDS content was 27 wt % of EPs. The glass fibers were implanted by glue and prepreg was prepared. The laminates of BAPh/EP-PEN glass fiber composites were compressed in a mold for 1 h at 200°C under 15 MPa.

Measurements

The FTIR spectra were recorded on Shimadzu FTIR-8400 S (Beijing, China) Fourier Transform Infrared spectrometer in KBr pellets between 4000 and 400 cm⁻¹ in air. The thermal curing behaviors of the oligomers were measured by TA Instruments Modulated DSC-Q100 with a heating rate of 10 °C/min and a nitrogen flow rate of 50 mL/min between 100 and 350°C. The thermal decompositions of the polymers were determined by TA Instruments Q50 thermogravimetric analyzer with a heating rate of 20 °C/min in nitrogen between 50 and 600°C. Rheological behavior of curing process was performed using TA Instruments Rheometer AR-G2 at low strain value (0.5%) and with a frequency of 1 Hz in air (20% oxygen) environments in 1 h. TA Instruments Q-800 dynamic mechanical analysis was performed in the torsional mode at a heating rate of 3°C/min, 0.5% torque range, and 1 Hz frequency between 50 and 300°C. Mechanical properties of the blends were measured using SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine from Shenzhen SUNS Technology Stock Co, Ltd. and gained as average value for every sample. The specimens were tested at room temperature with a crosshead displacement speed of 10 mm/min and the test fixture was mounted in a 10 kN capacity. The BAPh/EP-PEN glass fiber composites were prepared by DXR-500KN of Weidi Electromechanical Technology. The morphology of flexural fractured surface of BAPh/EP-PEN glass fiber composites were observed on SEM (JSM-5900 LV, Tokyo, Japan) operating at 20 kV after the gold sputtering.

RESULTS AND DISCUSSION

FTIR Spectra

The structure of BAPh/EP-PEN copolymers was verified by FTIR spectra, as shown in Figure 2. The absorption intensity of epoxy groups at 1180 decreases with increasing PEN contents which indicates that PEN accelerates the crosslinking reaction of

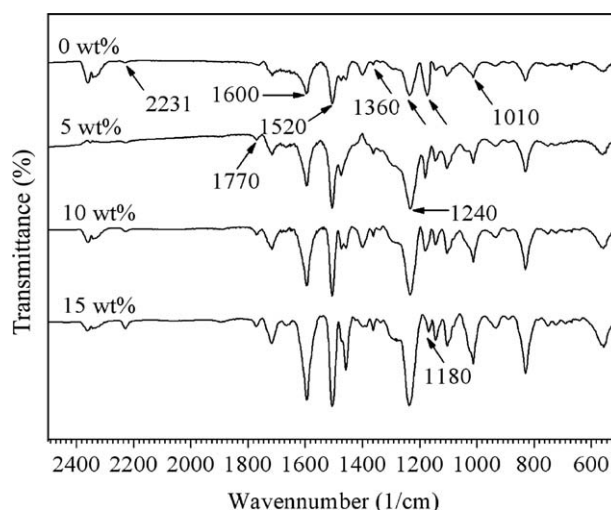


Figure 2. FTIR spectra of BAPh/EP-PEN copolymers.

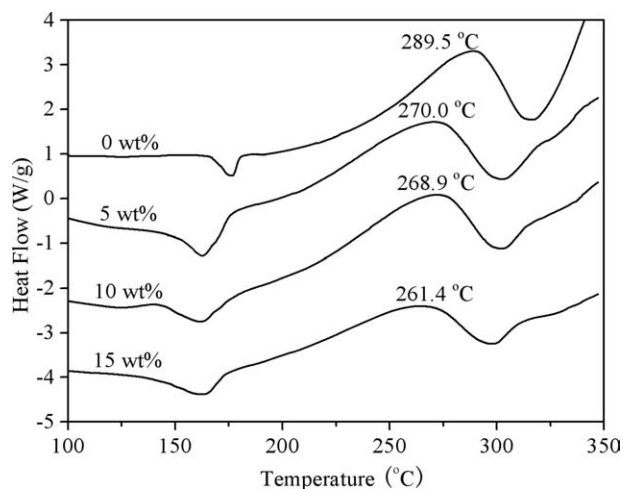


Figure 3. DSC curves of BAPh/EP-PEN blends.

epoxy groups. On the other hand, a characteristic peak at 1770 cm^{-1} is observed, which corresponds to the stretching vibration of $\text{C}=\text{O}$ of phenolphthalein lactone ring. And this absorption intensity increases with increasing PEN contents. The absorption peaks at 1010 cm^{-1} and 1600 cm^{-1} are attributed to the formation of phthalocyanine ring⁸ and isoindoline²⁶ during the polymerization of cyano groups, respectively. The peak at 1360 and 1520 cm^{-1} are assigned to triazine ring.⁸ The absorption intensity of this four peaks increases with increasing PEN contents, which are due to the reaction between the epoxy and phthalocyanine. The absorption band at 2231 cm^{-1} and 1240 cm^{-1} are assigned to the cyano group and ether band, respectively. They also increase with increasing PEN contents.

DSC and Rheological Behaviors

The curing and rheological behaviors of the BAPh/EP-PEN blends were investigated by differential scanning calorimeter and rheological measurement, as shown in Figures 3–5. The DSC thermograms of the BAPh/EP-PEN blends with different contents of PEN are shown in Figure 3. Every blend exhibits a characteristic melting transition (T_{melt}) and a polymerization exotherm.²⁷

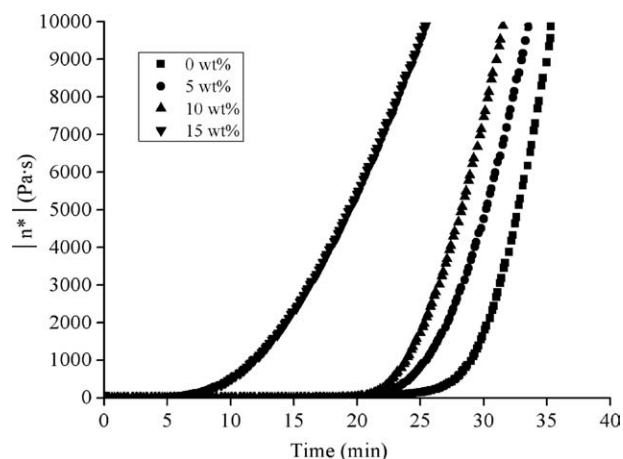


Figure 4. Time sweep viscosity curves of BAPh/EP-PEN blends with different PEN contents at 200°C .

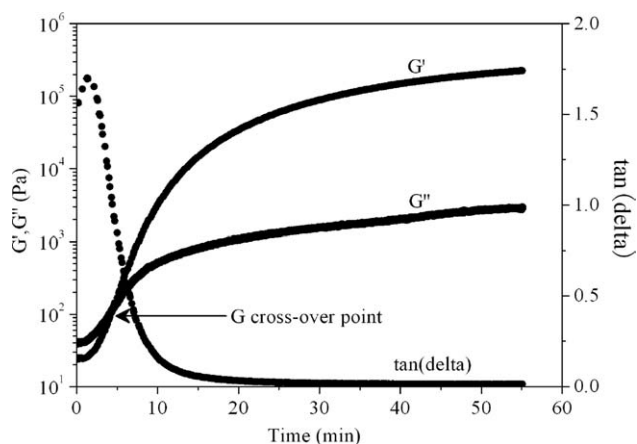


Figure 5. Time sweep curves with 15 wt % PEN content of BAPh/EP-PEN copolymer at 200°C .

All the peaks shift to lower temperature with increasing of PEN contents which indicate that PEN could efficiently improve cross-linking rate for BAPh/EP blends. These results revealed that PEN can decrease the processing temperature.

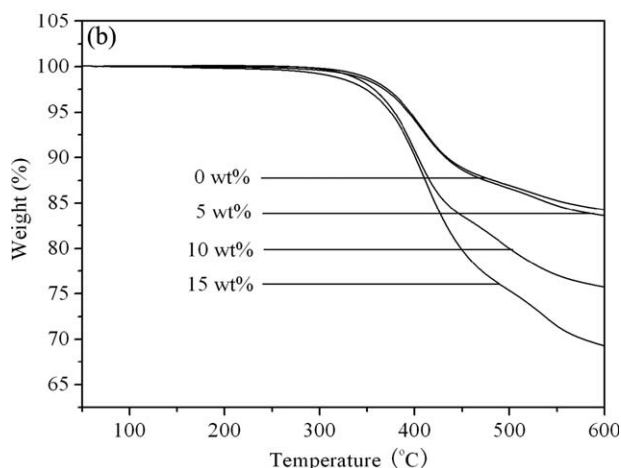
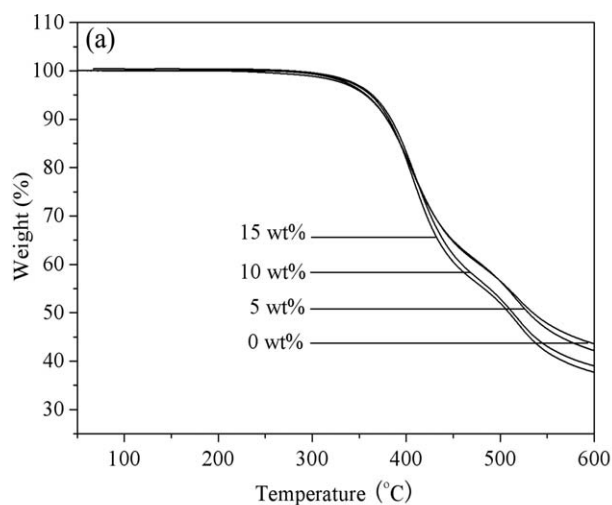


Figure 6. TGA curves of BAPh/EP-PEN in nitrogen (a: copolymers; b: glass fiber composites).

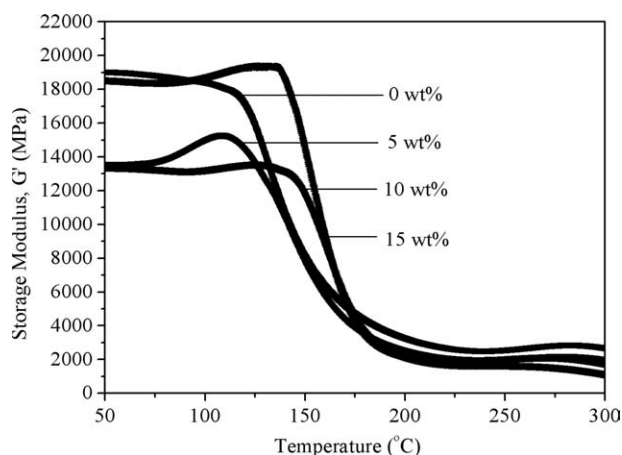


Figure 7. Storage modulus (G') as a function of temperature for BAPh/EP-PEN glass fiber composites heated in nitrogen.

The rheological behavior of a material is a key factor in determining its processability. From Figure 4, it could be observed that the viscosity of BAPh/EP-PEN blends was low before the curing reaction and increased sharply after the curing reaction started until gelation occurred. The viscosity of BAPh/EP-PEN blends increased sharply with increasing of PEN contents. This indicated PEN could accelerate the crosslinking reaction between the phthalonitrile and epoxy. Based on the principle of rheological theory, the gelation time (determined from the storage modulus (G') and the loss modulus (G'') crossover point)^{8,22} was 4 min when the PEN content was 15 wt %. The G' and G'' become stable for an extended period of time which indicates that the copolymers could be cured completely, as shown in Figure 5. These characters of BAPh/EP-PEN blends exhibit good processability and thermally activated polymerization.

TGA Analyses of BAPh/EP-PEN Copolymers and Composites

The thermal decomposition of BAPh/EP-PEN copolymers and glass fiber composites in the presence of the various concentration (0 wt %, 5 wt %, and 10 wt %) of PEN were examined by TGA. The results showed that BAPh/EP-PEN copolymers exhibit

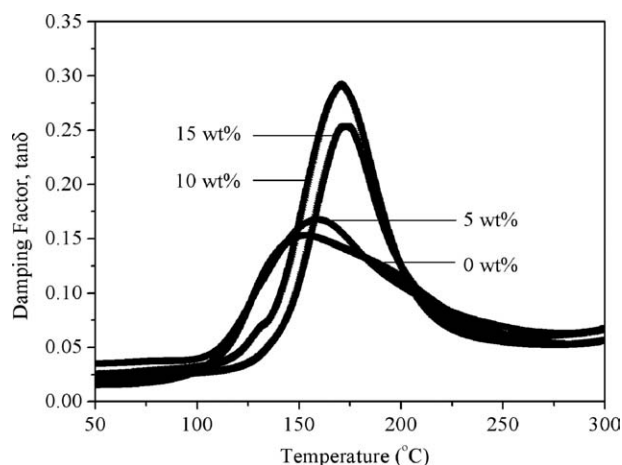


Figure 8. Damping factor ($\tan \delta$) as a function of temperature for BAPh/EP-PEN glass fiber composites heated.

Table I. Mechanical Properties of BAPh/EP-PEN Copolymers with Different PEN Contents

ω (PEN) (wt %)	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural strain (%)
0	103.2 ± 0.4	3.2 ± 0.1	2.83 ± 0.01
5	110.9 ± 1.0	3.8 ± 0.1	2.97 ± 0.02
10	119.8 ± 0.5	3.5 ± 0.1	3.19 ± 0.01
15	99.4 ± 0.3	3.1 ± 0.1	2.19 ± 0.03

good thermal stability in nitrogen, as shown in Figure 6. The initial decomposition temperatures (T_i) of BAPh/EP-PEN copolymers and glass fiber composites are all more than 350°C in nitrogen with increasing PEN contents. The results indicate that the thermal decomposition is influenced slightly by blending PEN and the BAPh/EP-PEN material still possess good thermal stabilities. It may be because the flexible PEN chains wind around the framework of BAPh, and have slight effect on the thermal properties. Besides, the char yield at 600°C decreases slightly with increasing PEN contents of BAPh/EP-PEN copolymers.

Dynamic Mechanical Properties of BAPh/EP-PEN Glass Fiber Composites

The dynamic mechanical properties of the BAPh/EP-PEN glass fiber composites were evaluated to ascertain changes in the sample modulus as a function of temperature and to determine the glass transition temperature (T_g) of the composite. Storage modulus (G') and damping factor ($\tan \delta$) generated on BAPh/EP-PEN glass fiber composites are presented in the Figures 7 and 8.

It can be seen from Figure 7 that there is a peak of the composites containing PEN at low temperature. And the peak shifts to higher temperature with increasing PEN contents. The results may be attributed to the reaction between hydroxyl and epoxy groups. The glass transition is from the frozen state to a state of relaxation for polymers. Polymer is in the glassy state when the temperature is below the T_g and molecular chains cannot move. When at the glass transition temperature, the chains begin to exercise, showing high-elastic properties. The whole molecular chain can move to show the nature of viscous flow with temperature rising again. G' would decrease sharply and take place the irreversible permanent deformation.

The T_g s values for the aforementioned are based on peak maxima in $\tan \delta$ vs. temperature plots as shown in Figure 8. T_g values are observed at 151.3°C, 160.3°C, 170.2°C, and 172.5°C

Table II. Mechanical Properties of BAPh/EP-PEN Glass Fiber Composites with Different PEN Contents

ω (PEN) (wt %)	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural strain (%)
0	571.2 ± 0.5	13.9 ± 0.4	2.84 ± 0.02
5	617.4 ± 0.4	17.7 ± 0.2	3.06 ± 0.03
10	698.5 ± 1.0	15.7 ± 0.1	3.16 ± 0.04
15	588.5 ± 0.8	15.4 ± 0.1	3.02 ± 0.01

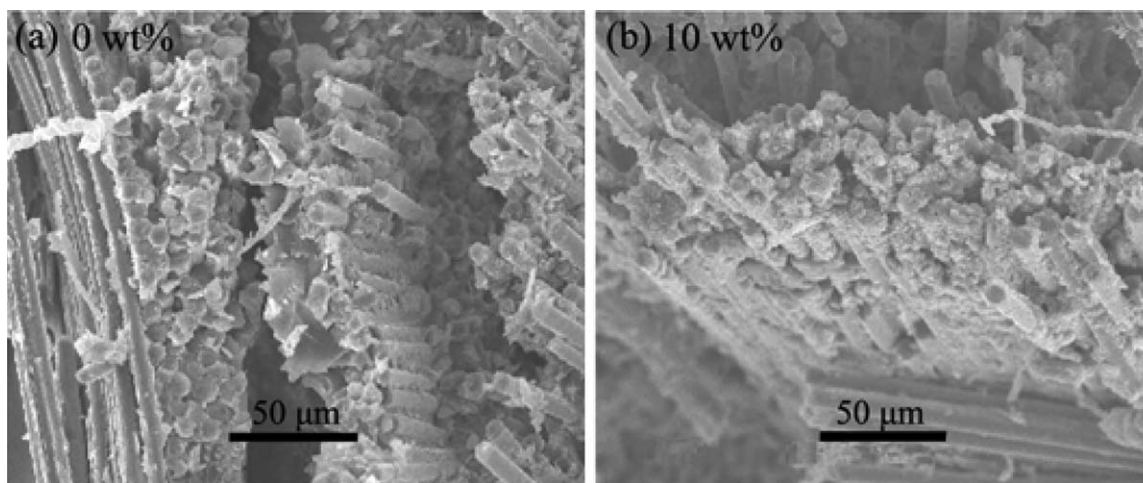


Figure 9. SEM micrographs of the flexural fractured surface of BAPh/EP-PEN glass fiber composites: (a) 0 wt % PEN; (b) 10 wt % PEN.

with different PEN contents, respectively. The T_g of 15 wt % PEN composite increases by 21.2°C compared with BAPh/EP composite. Therefore, it can be concluded that PEN enhances the T_g of BAPh/EP-PEN glass fiber composites. This verifies that the introduction of PEN into the BAPh/EP system could affect the motion of the polymeric segments. The peak width of $\tan \delta$ decreases with increasing PEN contents, which indicated the poorer compatibility the more PEN.

Mechanical Properties of BAPh/EP-PEN Copolymers and Glass Fiber Composites

The mechanical properties of BAPh/EP-PEN glass fiber composites are summarized in Table I. The results indicate that flexural strength and the flexural strain all increase until 10 wt % PEN and then decrease with further addition of PEN. The flexural strength reaches 119.8 MPa which is enhanced by 16.6 MPa in comparison with BAPh/EP copolymer. On the other hand, the flexural modulus increases with increasing PEN contents until 5 wt % PEN. The results are due to the synergistic effect of BAPh and PEN. BAPh network provides rigid frame while flexible PEN chains wind around the framework, serving as buffer zone for ambient pressure.^{22,28} With the further in 10 wt % introduction of flexible PEN chains, the modulus of BAPh/EP decreased slightly.

The mechanical properties of BAPh/EP-PEN glass fiber composites are summarized in Table II. The flexural strength of 10 wt % PEN composite achieves 698.5 MPa which is enhanced by 127.3 MPa in comparison with 0 wt % PEN composite. And the flexural modulus of 5 wt % PEN composite is 17.7 GPa which decreased 3.8 GPa than 0 wt % PEN composite. In addition, the flexural strain also increases to 3.19 % when the PEN content reached 10 wt %. Improvement of mechanical properties was attributed to the synergistic effect between flexible PEN chains and rigid frame of BAPh. Meanwhile, further in 10 wt % introduction of flexible PEN chains, the system tended to soften up to some extent and thus the modulus of BAPh decreased.

Morphological Analysis

It is well known that the resin can adhere on the glass fiber surface, which might be due to the interactions between different

resins and the glass fiber surface. The interfacial interaction can strengthen the glass fiber's interactions with matrix. Figure 9 shows the flexural fractured surface of 0 wt % and 10 wt % BAPh/EP-PEN glass fiber composites. It can be seen that composites exhibit eroded surfaces and several stages from the SEM. Fibers expose to the erosive environment which is due to a local removal of resin material from impacted surface.²⁹ In addition, the resin of 10 wt % BAPh/EP-PEN glass fiber composites in Figure 9(b) adheres on the glass fiber tighter than that of in Figure 9(a). The composite of Figure 9(b) possess good adhesive properties than Figure 9(a).

CONCLUSIONS

A series of BAPh/EP-PEN copolymers and glass fiber composites were prepared from BAPh, EP, and PEN with DDS as curing additive. The structure and thermal properties of copolymers were monitored by FTIR, DSC, rheology, and TGA. The T_i of BAPh/EP copolymers were more than 350°C in nitrogen. The T_g of 15 wt % PEN composite increased by 21.2°C compared with that of in comparison with BAPh/EP composite. The flexural strength of copolymers and glass fiber composites reached 119.8 MPa and 698.5 MPa when the PEN content is 10 wt %, respectively. These performances were the basement of the future processes and application for development of engineering materials.

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