

Preparation and Properties of Bisphenol A-Based Bis-phthalonitrile Composite Laminates

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ABSTRACT: A series of bisphenol A (BPA)-based 2,2-bis-[4-(3,4-dicyanophenoxy)phenyl]propane (BAPh) prepolymers and polymers were prepared using BPA as a novel curing agent. Ultraviolet-visible and Fourier transform infrared spectroscopy spectrum were used to study the polymerization reaction mechanism of the BAPh/BPA polymers. The curing behaviors were studied by differential scanning calorimetry and dynamic rheological analysis, the results indicated that the BAPh/BPA prepolymers exhibit large processing windows (109.5–148.5°C) and low complex viscosity (0.1–1 Pa·s) at moderate temperature, respectively. Additionally, the BAPh/BPA/glass fiber (GF) composite laminates were manufactured and investigated. The flexural strength and modulus of the composite laminates are 548.7–632.8 MPa and 25.7–33.2 GPa, respectively. The thermal stabilities of BAPh/BPA/GF composite laminates were studied by thermogravimetry analysis. The temperatures at 5% weight loss ($T_{5\%}$) of the composite laminates are 508.5–528.7°C in nitrogen and 508.1–543.2°C in air. In conclusion, the BAPh/BPA systems can be used as superior matrix materials for numerous advanced composite applications. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2621–2628, 2013

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INTRODUCTION

High-performance polymers are important materials, which have been widely utilized in aerospace, microelectronic, and marine. Phthalonitrile polymers are a kind of high temperature resistant polymers, which have been developed at the Naval Research Laboratory.^{1–3} The high temperature resistant properties of phthalonitrile polymers are mainly resulted from the high level of aromatic character and heterocyclic ring structure. The phthalonitrile-based polymers exhibit amount of superior properties such as excellent mechanical properties, outstanding thermal and thermal-oxidative stabilities, high glass transition temperatures, good moisture resistance, and fire resistance,^{4–8} which lead to their dominant position as structural components in aerospace, marine, and electronic fields.⁹ However, the high processing temperature, low curing rate, and narrow processing window (temperature between the melting point and the exothermic curing temperature) have prevented phthalonitrile polymers from further applications.^{10,11} Therefore, considerable research efforts have been made to solve these shortcomings during the past 30 years.

It was discovered that a small amount of phenols,¹² organic amines,¹³ and metallic salts^{14,15} can significantly promote the

curing reaction of phthalonitrile monomers. Therefore, the phthalonitrile monomers can be easily processed into void-free polymers that showed excellent thermal and thermal-oxidative stabilities with the assistance of the foresaid curing agents. Recently, more interests are focused on the phthalonitriles and phenolic resins,^{12,16} due to the economical availability and good flame resistance. The polymerization reaction between the phenolic resins and phthalonitriles occurred because the protons stem from the hydroxyl group of nucleophilic phenolic resins can catalyze the polymerization of the nitrile groups in phthalonitriles.^{16,17} Nonetheless, nucleophilic phenolic resins with hydroxyl groups which were used as curing additives to catalyze the phthalonitrile monomers have not been fully investigated. In addition, 2,2-bis-[4-(3,4-dicyanophenoxy)phenyl]propane (BAPh) monomer has been effectively and widely used as the matrix resin, which was proved to be cost effective for the easy availability of the building unit bisphenol A (BPA).¹⁸

Herein, we report the preparation of BAPh/BPA polymers using BPA as a novel curing agent, also, the possible polymerization mechanism of the polymers has been discussed. The BAPh/BPA prepolymers with various proportions and polymerization reaction times were performed and characterized by ultraviolet-

visible (UV–Vis) and Fourier transform infrared spectroscopy (FTIR) spectra, aiming at investigating the detail polymerization mechanism of the BAPh/BPA polymers. Meanwhile, the effects of various proportions and various polymerization reaction hours of BAPh/BPA systems on thermal properties have been studied in this article. The differential scanning calorimetry (DSC) and dynamic rheological analysis (DRA) were used to study the curing behaviors of the BAPh/BPA prepolymers. Additionally, the BAPh/BPA/glass fiber (GF)-reinforced composite laminates have been manufactured in this article. The mechanical properties and the thermal stabilities of the composite laminates were discussed in this article, which may be conducive to expanding the industrial applications of BAPh/BPA systems.

EXPERIMENTAL

Materials

BPA ($T_m = 157^\circ\text{C}$) and *N*-methyl-2-pyrrolidone (NMP, purity > 99%) were obtained from BODI Chemicals (Tianjin, China). BAPh ($T_m = 194\text{--}200^\circ\text{C}$)¹⁹ was synthesized in our laboratory, the materials were used without further purification.

Preparation of BAPh/BPA Prepolymers and Polymers

BAPh and NMP were charged to a 100-mL three-neck round bottom flask equipped with a mechanical stirrer and refluxing condenser, followed by heating for 30 min. Then, the molar measured BPA was added to obtain a homogeneous solution. The mixtures of BAPh/BPA (molar ratios of BAPh/BPA = 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2) were refluxed at 200°C for 8 h to obtain BAPh/BPA prepolymer solutions. Afterward, four kinds of prepolymer solutions were dried in air circulation oven at 150°C for 12 h to remove the NMP. The BAPh/BPA prepolymers with different polymerization reaction times were prepared in a procedure analogous to the foresaid methods. The systems of BAPh and BPA with a molar ratio of 2 : 2 were taken. The solution reaction mixtures were refluxed at 200°C for 4 h, 8 h, and 12 h, respectively. The longer hours of refluxing, the color of the prepolymer solution became darker green. The prepolymers were obtained by drying the prepolymer solutions at 150°C for 12 h under vacuum.

The BAPh/BPA polymers were prepared as following: the prepolymers without NMP were cured in the oven at 200°C , 2 h; 220°C , 2 h; 250°C , 4 h; and 300°C , 4 h. The BAPh/BPA polymers were pulverized for FTIR and thermogravimetry analysis (TGA) studies. The typical infrared (IR) characteristic data: 2231 cm^{-1} (—CN), 3290 cm^{-1} , 1010 cm^{-1} (phthalocyanine ring), 1360 cm^{-1} , 1520 cm^{-1} (triazine ring), and $1630\text{--}1670\text{ cm}^{-1}$ (C=N band in isoindole ring).

Preparation of BAPh/BPA/GF Composite Laminates

The BAPh/BPA/GF composite laminates were prepared as following. The BAPh/BPA prepolymer solutions with various molar ratios were obtained as the method mentioned in “Preparation of BAPh/BPA prepolymers and polymers” section. Fifteen layers of GF cloth (the size of the cloth was $20\text{ cm} \times 20\text{ cm}$) were impregnated with the BAPh/BPA prepolymer solutions, and the preimpregnated clothes were vacuum-dried at 200°C until no solvent left. Finally, the BAPh/BPA/GF composite laminates were manufactured by putting the vacuum-dried impreg-

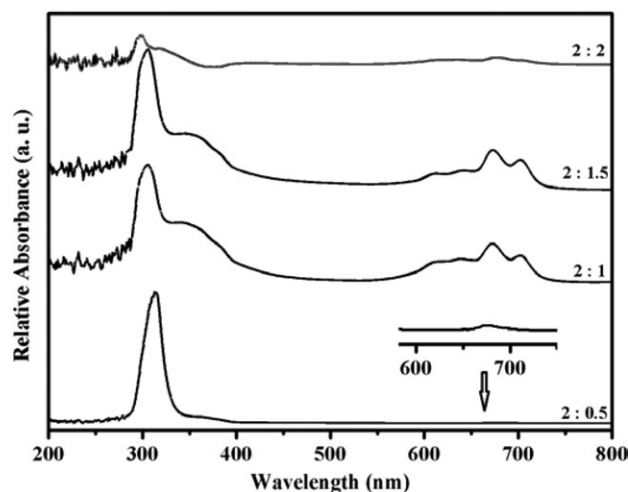


Figure 1. UV–Vis spectra of BAPh/BPA prepolymers with various proportions.

nated clothes between two stainless steel mold and hot pressed with a pressure of 15 MPa at 200°C , 2 h; 220°C , 2 h; 250°C , 4 h; and 300°C , 4 h. The BAPh/BPA/GF composite laminates were cut into various strips (three strips were needed to gain an average value) according to the GB/T 9341-2000 for mechanic performance testing.

Characterizations

The UV–Vis spectra of BAPh/BPA mixtures in the solution of NMP were investigated by TU 1800 ultraviolet–visible spectroscopy of Beijing Purkinje GeneralInstrument Co. Ltd. The FTIR spectra of BAPh/BPA mixtures and polymers were recorded on NICOLET MX-1E Fourier Transform Infrared spectrometer in KBr pellets between 4000 cm^{-1} and 400 cm^{-1} in air. DSC was carried out by TA Instrument Modulated DSC Q100 with a heating rate of 5°C min^{-1} and a nitrogen flow rate of 50 mL min^{-1} . Rheological behaviors of the prepolymers were investigated using TA Instruments Rheometer AR-G2 with a frequency of 1 Hz and a heating rate of 3°C min^{-1} . TGA was investigated by the TA Instrument Q50 thermogravimetric with a heating rate of $20^\circ\text{C min}^{-1}$ under nitrogen or air atmosphere. Mechanical properties of the composite laminates were investigated on a SANS CMT 6104 Series Desktop Electromechanical Universal Testing Machine.

RESULTS AND DISCUSSIONS

UV–Vis and FTIR Spectra

The UV–Vis spectra of the BAPh/BPA prepolymers with various proportions were shown in Figure 1, which were measured in the NMP solution. Two strong absorption bands can be seen in Figure 1: around the 290–340 nm is a Soret B band and around the 620–750 nm is a Q band.²⁰ The existence of phthalocyanine ring can be confirmed by the Q band. Characteristic absorption band at around 370–380 nm is observed in the UV spectrum in Figure 1, which is assigned to the isoindole ring.¹⁷ Obviously, the 2 : 1 and 2 : 1.5 BAPh/BPA prepolymers both possessed similar spectra of Q band, and the 2 : 0.5 and 2 : 2 BAPh/BPA prepolymers both had the weaker Q band, which demonstrates the formation of phthalocyanine ring. The 2 : 0.5, 2 : 1, 2 : 1.5,

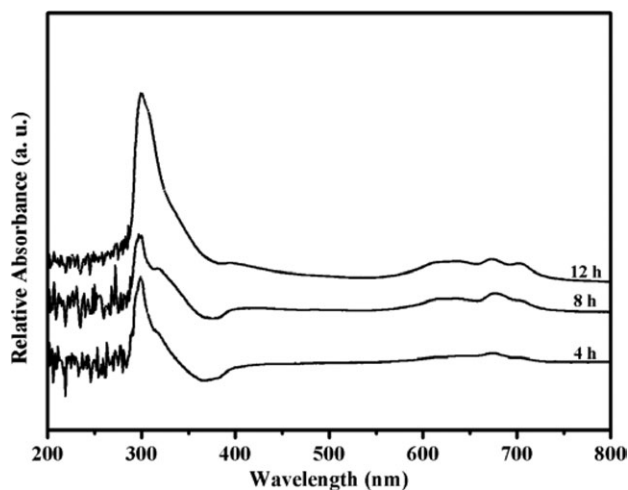


Figure 2. UV-Vis spectra of 2 : 2 BAPh/BPA prepolymers with various polymerization reaction hours.

and 2 : 2 BAPh/BPA prepolymers all show weak characteristic bands of isoindole ring. Figure 2 shows the BAPh/BPA prepolymer with various polymerization reaction hours. Compared with the UV spectrum shown in Figure 1, absorption with a band at around 370–380 nm and around 620–750 nm in Figure 2 exhibit the same tendency. In conclusion, phthalocyanine ring and isoindole ring were formed during the polymerization reaction between BAPh and BPA. To further investigate the formation molecular structures of BAPh/BPA systems, the BAPh/BPA prepolymers and polymers were investigated by FTIR spectrum.

The FTIR spectra of BAPh/BPA prepolymers with various proportions were shown in Figure 3. The peaks at around 1010 cm^{-1} , 1520 cm^{-1} , and 1660 cm^{-1} are belonged to the characteristic absorptions of the NH stretching and bending vibration in phthalocyanine ring,²¹ stretching vibration in triazine ring²², and C=N bond in isoindole ring,¹⁷ respectively, suggesting the beginning of polymerization reaction between BAPh and BPA.

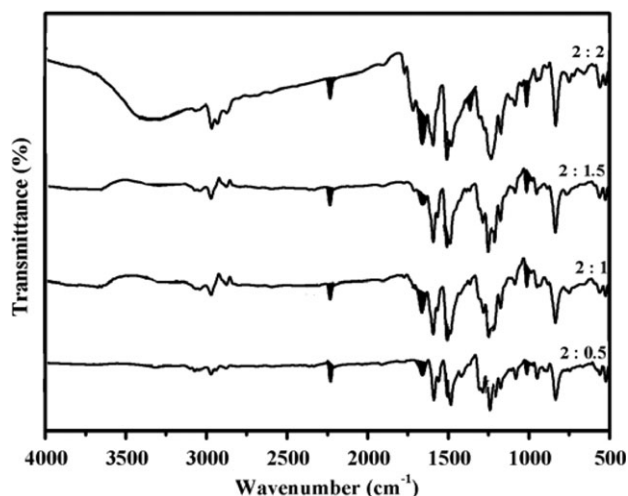


Figure 3. FTIR spectra of BAPh/BPA prepolymers with various proportions.

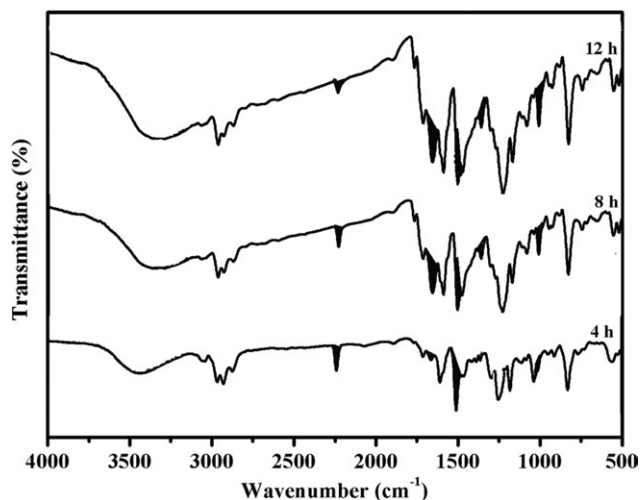


Figure 4. FTIR spectra of 2 : 2 BAPh/BPA prepolymers with various polymerization reaction hours.

The FTIR spectra of BAPh/BPA prepolymers with various polymerization reaction hours were shown in Figure 4. The peaks at around 1660 cm^{-1} , 1360 cm^{-1} , and 1010 cm^{-1} demonstrate changed intensity with the increase in polymerization reaction hours. In Figure 4, the noticeable characteristic absorption peak at 2234 cm^{-1} decreased with increasing polymerization reaction hours of BAPh/BPA, which is attributed to the increased degree of polymerization. In Figure 3 and 4, it is obvious that the IR spectra of BAPh/BPA prepolymers were depended on the various proportions and prepolymerization time.

Figures 5 and 6 are the FTIR spectra of the BAPh/BPA polymers with various proportions and polymerization reaction hours, respectively. Compared with the characteristic peaks in Figure 3, the 2 : 0.5 and 2 : 1 BAPh/BPA polymers exhibit no peaks at around 1630–1670 cm^{-1} on postcuring at temperature above 300°C in Figure 5. Only in the FTIR curves of 2 : 1.5 and 2 : 2, the peaks of isoindole ring can be discovered, the findings

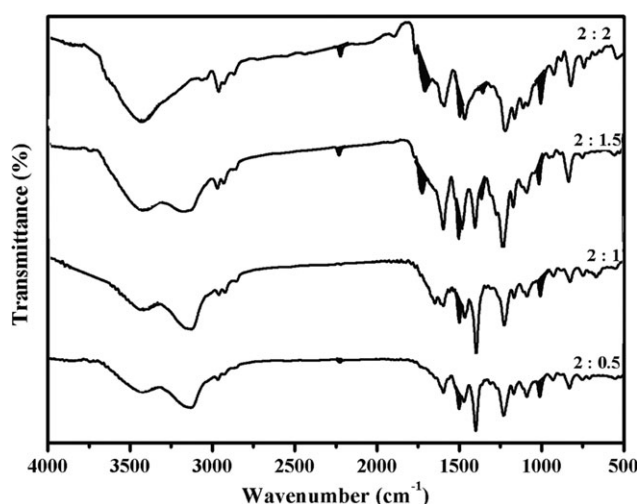


Figure 5. FTIR spectra of BAPh/BPA polymers with various proportions.

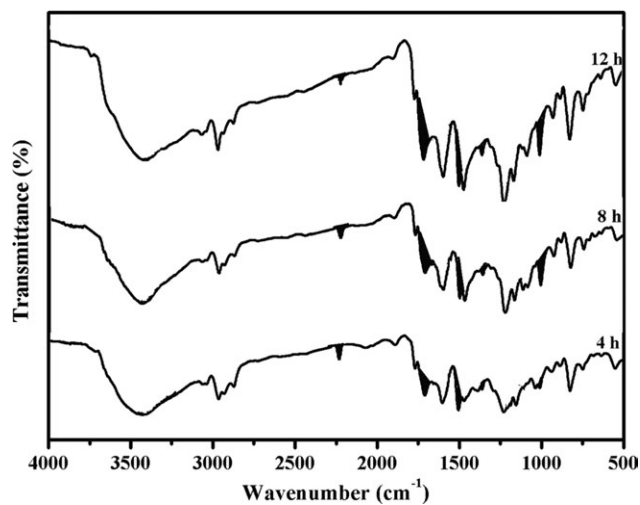


Figure 6. FTIR spectra of 2 : 2 BAPh/BPA polymers with various polymerization reaction hours.

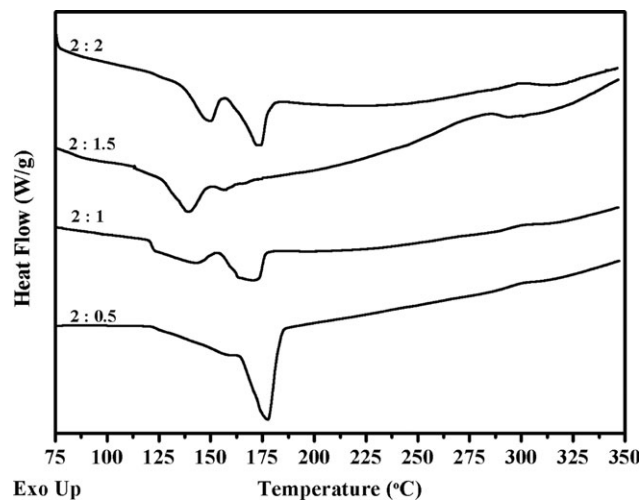
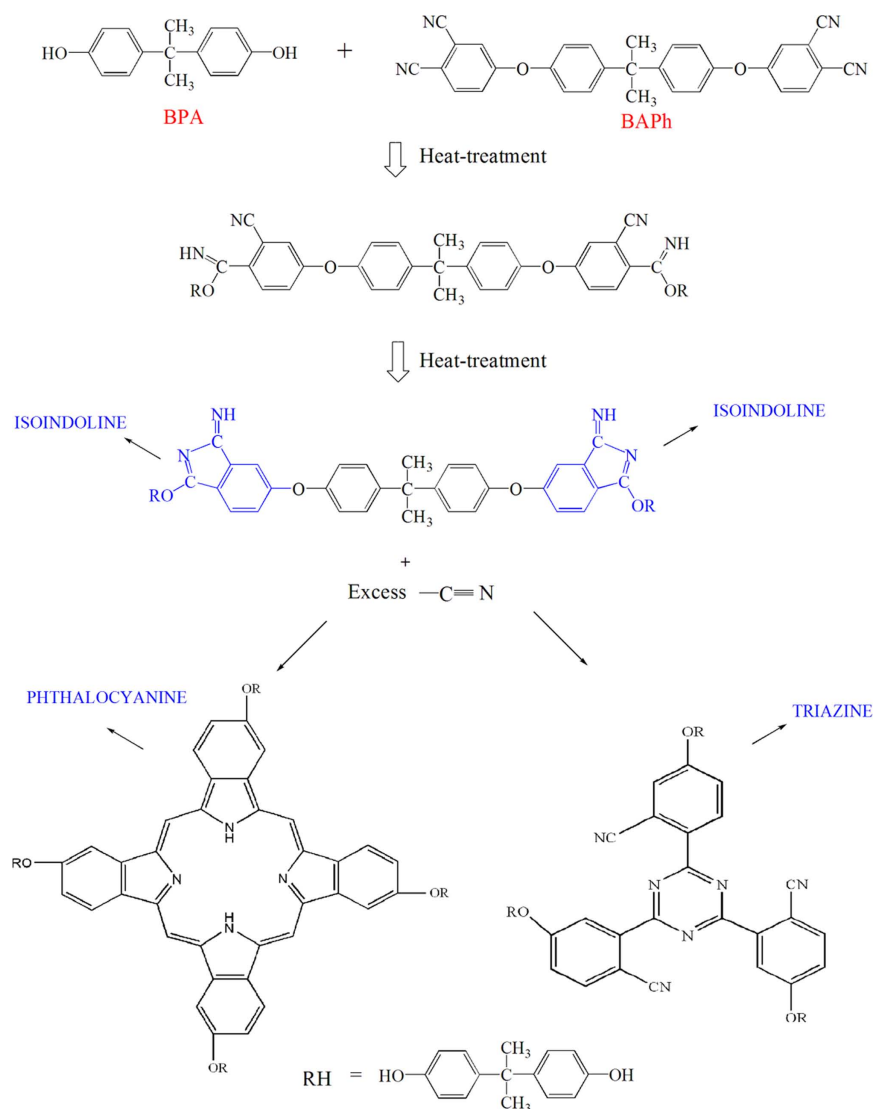


Figure 7. DSC curves of the BAPh/BPA prepolymers with various proportions.



Scheme 1. Possible reaction mechanism of BAPh/BPA systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

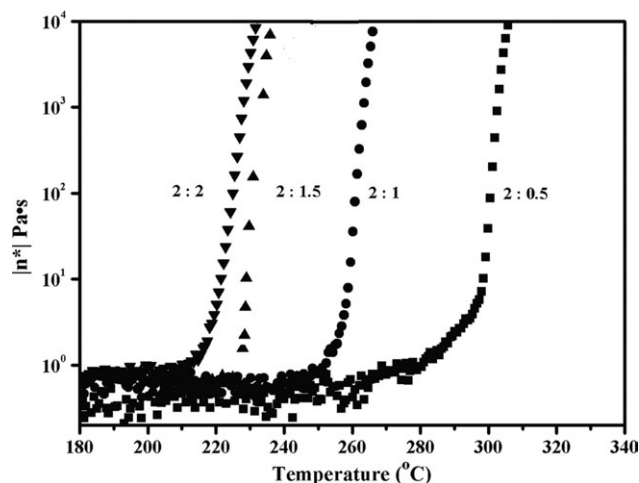


Figure 8. Complex viscosity (η^*) as a function of temperature for the BAPh/BPA prepolymers with various proportions.

means that BPA can completely react with BAPh when the ratios are 2 : 0.5 and 2 : 1. Therefore, the excess $-\text{CN}$ group in BAPh can make the isoindole ring intermediates completely reacted. However, the 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2 BAPh/BPA polymers all exhibited two peaks at around 1010 cm^{-1} and 1520 cm^{-1} which demonstrates the formation of phthalocyanine ring and triazine ring, respectively. In Figure 6, the characteristic peaks of phthalocyanine ring, isoindole ring and triazine ring still exist, which show the same tendency as shown in Figure 4. Along with the temperature increasing, the polymerization extent of BAPh/BPA polymers increases. Based on these results, the polymerization mechanism of BAPh/BPA is shown in Scheme 1.

Curing Behaviors of BAPh/BPA Prepolymers

The curing behaviors of BAPh/BPA prepolymers were studied by DSC and DRA, Figure 7 is the DSC curves of various proportions of BAPh/BPA prepolymers. From the DSC thermograms, the 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2 BAPh/BPA prepolymers each exhibits two endothermic peaks and one small exothermic peak. The two endothermic peaks at around 138.6--

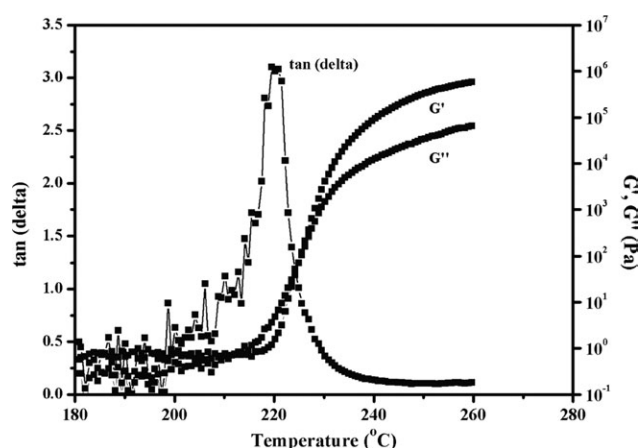


Figure 9. Temperature sweep curves of the 2 : 2 BAPh/BPA prepolymers with polymerization reaction for 8 h.

Table I. The Thermal Properties of BAPh/BPA Prepolymers with Various Proportions

Samples	$T_{\text{melt}1}$ (°C)	$T_{\text{melt}2}$ (°C)	T_{top} (°C)	T_{window} (°C)	ΔH_{curing} (J g^{-1})
2 : 0.5	157.7	177.3	300.9	123.6–143.2	1.0
2 : 1	142.6	169.2	278.7	109.5–136.1	1.1
2 : 1.5	138.6	157.7	276.6	118.9–138.0	7.7
2 : 2	149.5	174.3	298.0	123.7–148.5	5.1

157.7°C and $157.7\text{--}177.1\text{°C}$ are attributed to the melting peaks of BPA and BAPh, respectively. The small exothermic peak is assigned to the polymerization reaction between the nitrile groups of the BAPh and the hydroxyl groups of BPA. With increasing concentration of BPA, the exothermic heat flows for the BAPh/BPA prepolymers are 1.0 J g^{-1} , 1.1 J g^{-1} , 7.6 J g^{-1} , and 5.1 J g^{-1} , respectively. The results indicated that the curing enthalpy (ΔH_{curing}) increases when more BPA are introduced. However, the ΔH_{curing} for 2 : 2 decreased, which is believed to be caused by the volatilized of residual BPA in the prepolymers, and the existing small exothermic peak suggested that BPA has improved the curing reaction of BAPh. Compared with the other three kinds of molar ratios, the temperatures of the two melting peaks and one curing peak of BAPh/BPA 2 : 1.5 all exhibited at relatively lower temperature, which indicates the rapid curing reaction exist in the BAPh/BPA systems and the easy formation of heterocyclic rings between the nitrile groups of phthalonitrile and the hydroxyl groups of BPA.²³ Meanwhile, it is observed that 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2 BAPh/BPA prepolymers all exhibit large processing windows ranged from 109.5°C to 148.5°C , which is wider than the neat BAPh ($\sim 55\text{°C}$), the wider processing windows make the BAPh/BPA prepolymers competitive with other high-performance polymers.^{8,24}

The rheological behaviors play an important part in determining the processability of materials.²⁵ Therefore, Figure 8 shows the complex viscosity of the BAPh/BPA prepolymers with various proportions as a function of temperature range from 180°C to 340°C . In the DSC analyses, BPA readily reacts with BAPh between 276.6°C and 300.9°C , and it is difficult to discover the detail differences in the reactivities of BAPh/BPA. However, the detail differences in the reactivities of BAPh/BPA accompanying

Table II. Thermal and Thermal-Oxidative Properties of BAPh/BPA/GF with Various Proportions in Nitrogen and Air

Samples	Nitrogen		Air	
	$T_{5\%}$ (°C)	The retention of weight (%) at 800°C	$T_{5\%}$ (°C)	The retention of weight (%) at 800°C
2 : 0.5	508.5	84.5	508.1	79.3
2 : 1	513.8	86.6	517.6	86.2
2 : 1.5	528.7	89.4	543.2	89.9
2 : 2	525.6	90.1	523.0	84.6

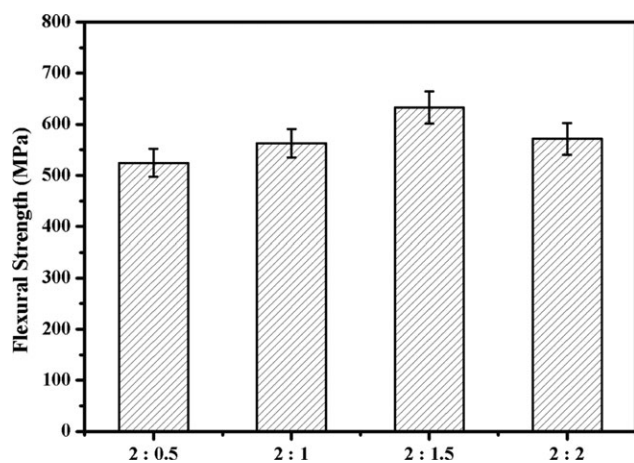


Figure 10. Flexural strength of the BAPh/BPA/GF composite laminates.

the viscosity changes can be monitored by rheometric studies. With various concentration of BPA, the polymerization reaction between BAPh and BPA progresses at different rates. For each prepolymer, the initial viscosity was 0.1–1 Pa·s. The 2 : 2, 2 : 1.5, 2 : 1, and 2 : 0.5 BAPh/BPA prepolymers exhibit an abrupt complex viscosity increase at 215, 225, 250, and 290°C, respectively. The data reveals that among the four kinds of proportions, the complex viscosity of 2 : 2 BAPh/BPA prepolymer increases at a relatively lower temperature compared with the 2 : 1.5, 2 : 1, and 2 : 0.5. The BAPh/BPA prepolymers display good processability for low complex viscosity at moderate temperature.

Temperature sweep curves of the BAPh/BPA prepolymers with polymerization reaction for 8 h from 180°C to 340°C are showed in Figure 9. The storage modulus (G') increases gradually from 210°C to 230°C, it can be discovered that the 2 : 2 BAPh/BPA prepolymer has been transferred from viscosity flow state to solid state. Meanwhile, the loss modulus (G'') increases, too. The complex viscosity of the BAPh/BPA prepolymer increases slowly until cross-point of G' and G'' occurred, the cross-point is 230°C, which means the BAPh/BPA resin has

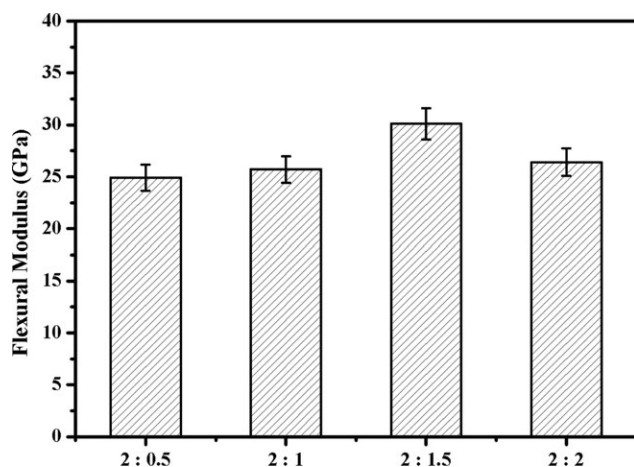


Figure 11. Flexural modulus of the BAPh/BPA/GF composite laminates.

underwent gelation transition. The delta curve shows a peak at 220°C, which indicates that the BAPh/BPA could be cross-linked at a certain temperature. The results demonstrate that the BAPh/BPA systems possess good processability, which is useful to the applications in engineering.

Thermal Stabilities of BAPh/BPA/GF Composite Laminates

The thermal and thermal-oxidative stabilities of the BAPh/BPA/GF composite laminates were investigated by TGA in nitrogen and air, respectively. The main results of the investigations were shown in Table II, in which the temperature of 5% weight loss ($T_{5\%}$), the retention of weight at 800°C in nitrogen and air atmosphere were displayed.

Heated in nitrogen atmosphere, the temperatures at weight loss of 5% are 508.5°C, 513.8°C, 528.7°C, and 526.6°C when the proportions of the BAPh/BPA are 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2, respectively. The retention of weight at 800°C is above 84.5%. In contrast, when heated in air atmosphere, the 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2 BAPh/BPA/GF composite laminates exhibited $T_{5\%}$ of 508.1, 517.6, 543.2, and 523.0°C, respectively. The retention of weight at 800°C is above 79.3%. With more BPA in the BAPh/BPA systems, the highly cross-linked network could be achieved, the temperature at weight loss 5% of the laminates increases simultaneously. However, the 2 : 2 BAPh/BPA/GF composite laminates exhibited relatively lower $T_{5\%}$ than 2 : 1.5 BAPh/BPA/GF, which is largely due to the volatility of the excess BPA when heated above 250°C. The TGA results are consistent with the results of DSC shown in “Curing behaviors of BAPh/BPA prepolymers” section. Meanwhile, the heterocyclic cross-linked structures can also result to higher $T_{5\%}$ in air atmosphere than in nitrogen.^{26,27} Owing to the fact that the heat transferring from the surface to the inside of the systems have been effectively prevented by the surface, the retention of weight at 800°C in nitrogen was higher than in air. As the degradation process starts, the temperature of catastrophic breakdown (means the maximum decomposition rate) of the BAPh/BPA/GF composite laminates occurs at around 525°C. The formation of phthalocyanine ring, triazine ring in the various proportions of BAPh/BPA polymers could lead to the good thermal and thermal-oxidative stabilities, which can be supported by the FTIR spectra results in Figures 5 and 6. Compared with other phthalonitrile-based/GF composite laminates which have to be cured above 300°C for a longer time, the excellent thermal and thermal-oxidative stabilities of the BAPh/BPA/GF composites can be widely explored in the practical processing.^{28,29}

Mechanical Properties of BAPh/BPA/GF Composite Laminates

According to the curing behavior results of BAPh/BPA prepolymers, the BAPh/BPA/GF composite laminates were manufactured with a pressure of 15 MPa at 200°C, 2 h; 220°C, 2 h; 250°C, 4 h, and 300°C, 4 h, respectively. The mechanical properties of BAPh/BPA/GF composite laminates were investigated by 3-point bend test at room temperature. As shown in Figures 10 and 11, with the increase in BPA content, the flexural strength and modulus increased from 524.6 MPa and 24.9 GPa to 632.8 MPa and 30.1 GPa, respectively. However, the flexural strength and modulus of BAPh/BPA (2 : 2) decreased to 571.1 MPa and 26.4 GPa, respectively. Tensile strength of the BAPh/

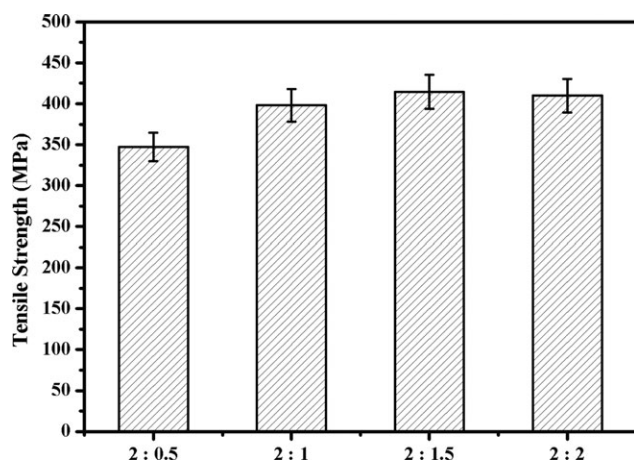


Figure 12. Tensile strength of the BAPH/BPA/GF composite laminates.

BPA/GF composite laminates was shown in Figure 12. The tensile strength of 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2 BAPH/BPA/GF is 347.5, 398.2, 414.5, and 410.1 MPa, respectively, which exhibits the same tendency as the flexural strength and flexural modulus. When the molar ratio of BAPH/BPA reaches to 2 : 2, the adhesion interaction between the BAPH/BPA polymer and GF decreases and the volatilization of the residual BPA, eventually result to the reduction of the mechanical properties of the BAPH/BPA/GF composite laminates.³⁰ The above mechanical results are consistent with those of curing behaviors and thermal stabilities.

To have a better understanding of the influence of heat treatment on the mechanical properties of BAPH/BPA/GF composite laminates, the laminates of 2 : 2 BAPH/BPA were treated in the oven at 300°C for 6 h, and the results of the mechanical properties were summarized in Table III. The flexural strength and modulus of the heated laminates are 570.7 MPa and 24.8 GPa, respectively, and the tensile strength is 354.8 MPa, which all decreases compared with the unheated laminates. Despite that the cure temperature of the laminates is below the decomposition temperature, the mechanical properties decrease, either. After the laminates are heated in the oven, the curing degree increased, but the interfacial interaction between the matrix and cloth surface decreases, which plays an important part in the mechanical properties of the composite laminates.

Table III. Mechanical Properties of 2 : 2 BAPH/BPA/GF Composite Laminates

Samples BAPH/ BPA, 2 : 2	Composite laminates	Composite laminates heated at 300°C, 6 h
Flexural modulus (GPa)	26.4	24.8
Flexural strength (MPa)	571.1	570.7
Tensile strength (MPa)	410.1	354.8

CONCLUSIONS

A series of bisphthalonitrile prepolymers and polymers were prepared from BAPH monomer and BPA, in which BPA was used as a curing agent. The prepolymers and polymers with various BPA contents and various polymerization reaction hours were investigated. The UV-Vis and FTIR spectra indicated that 2 : 0.5, 2 : 1, 2 : 1.5, and 2 : 2 BAPH/BPA prepolymers have formed the phthalocyanine ring, isoindole ring, and triazine ring in the process of polymerization. With the higher concentration of BPA, the mainly structure of 2 : 1.5 and 2 : 2 BAPH/BPA polymers were made up of isoindole rings, phthalocyanine rings, and triazine rings. Based on the DSC investigations and the rheometric studies, differences in the reactivity of BAPH monomer and the BPA were observed. The DSC results showed that the BAPH/BA prepolymers exhibited large processing windows ranged from 109.5°C to 148.5°C, and the polymerization rate of BAPH/BPA systems can be easily controlled by varying the concentration of BPA and curing temperature. The BAPH/BPA/GF composite laminates exhibited excellent mechanical properties, thermal and thermal-oxidation stabilities in nitrogen and air atmosphere, respectively. The BAPH/BPA polymers have enormous potential to be used as a matrix in advanced composites field.

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