Copolymerization of phthalonitrile-based resin containing benzoxazine and cyanate ester: Curing behaviors, fiber-reinforced composite laminates and improved properties

L. Chen, D. X. Ren, S. J. Chen, H. Pan, M. Z. Xu, X. B. Liu*

Research Branch of Advanced Functional Materials, School of Materials and Energy, University of Electronic Science and Technology of China, 611731 Chengdu, P. R. China

Received 12 October 2018; accepted in revised form 31 December 2018

Abstract. Curing behaviors and copolymerization mechanisms between phthalonitrile-based resin containing benzoxazine (A-ph) and cyanate ester (CE) were characterized and discussed. Results indicated that copolymerization between A-ph and CE were comprised of ring-opening polymerization of oxazine rings and ring-forming polymerization of cyanate and nitrile groups. From them, ring-opening of oxazine occurred preferentially, followed by ring-forming of cyanate and nitrile groups, which were promoted by active hydrogen and amine structures generated from ring-opening of oxazine. Moreover, with increasing the content of CE (≥ 40 wt%), self-polymerization of cyanate would dominate the components of the resulting composites and reduces the thermal stability of fiber-reinforced composite laminates. Additionally, mechanical properties of composite laminates were also affected by the content of CE. Composite laminates with 10 wt% CE showed the highest flexural strength (622 MPa). The improved mechanical properties were also verified with investigation of dynamic thermo-mechanical analysis and morphology of fracture surfaces. These findings are helpful to improve the thermosetting resins in terms of their chemical structure, material properties, and processability.

Keywords: polymer composites, benzoxazine, phthalonitrile, composite laminates, mechanical properties

1. Introduction

Polymer composites have excellent properties, can be used in special environments, and are relatively easy to process, making them the main candidates for a variety of applications, from advanced microelectronic packaging to structural energy equipment in aerospace engineering. Due to the characteristics of high strength and modulus, light weight, good fatigue resistance, high heat distortion temperature, and good thermal stability [1–3] fiber reinforced composites of thermosetting resins such as epoxy, cyanate ester, benzoxazine, BMI and phenolic resin were widely and intensively investigated. These composites can significantly reduce weight, lower exhaust emissions and

can meet demands in particular fields. However, these thermosetting resins generally have some shortcomings, such as brittleness, high forming temperature, poor processability, poor interfacial adhesion with inorganic fibers and poor electrical properties. Thus, single thermosetting resin could not fit applications in many areas. To improve the defects and expand the applications of thermosetting resins, the method of incorporating a kind high performance thermosetting or thermoplastic resin has been widely used. This was a simple and effective way to prepare composites with improved properties. For example, composites were prepared by adding modified graphene into cyanate ester (CE), epoxy resin and benzoxazine

*Corresponding author, e-mail: liuxb@uestc.edu.cn
© BME-PT

thermosetting resin respectively. The mechanical and thermal properties of composites were improved effectively [4–6].

As a kind of high performance thermosetting resin, phthalonitrile resin had drawn much attention on researches and applications. Phthalonitrile resin possessed outstanding properties like high glass transition temperature, excellent thermal oxygen stability, good flame retardancy, low water absorption and high deformation temperature [7, 8]. But, there are some problems such as high melting temperature, narrow processing window, high curing temperature and lower curing rate, which have limited the applications of phthalonitrile resin to some extent. Benzoxazine resin is a novel kind of high performance thermosetting resin [9–11]. Due to high glass transition, nearly zero volume shrinkage and no volatile release during the curing processes, good flame resistance and good thermal stability, their fiber reinforced composite laminates were intensively studied and widely used [12–15]. As previous researches [16] indicated that the ring-formation reaction of the nitrile groups can be catalyzed by hydroxyl groups. Considering of the ring-opening reaction of benzoxazine ring could generate hydroxyl groups as well as combining the outstanding properties of benzoxazine, phthalonitrile-based resin containing benzoxazine was designed [17, 18]. With introducing benzoxazine ring into phthalonitrile resin, processing properties and curing temperatures were obviously improved. In addition, the unique reaction mode of benzoxazine can achieve flexible molecular design by changing the phenol source or ammonia source. Based on this, amine compounds containing aniline and phthalonitrile were used as the ammonia source. A new type of bisphthalonitrile monomer (A-ph) with both benzoxazine units and nitrile groups was obtained according to our previous work. Cyanate ester (CE) with excellent properties like good mechanical properties, high glass transition temperature, good heat-resistance and outstanding electric properties had drawn much attention. Their glass fiber (GF) reinforced composites were widely used as high performance materials in electronics, aerospace, optical instruments, medical equipment and so on [19–21]. In this work, the aniline and 3-aminophenoxyphthalonitrile (3-APN) (the mole ratio was designed as 3:1) were chosen as ammonia sources to synthesize phthalonitrile-based resin containing benzoxazine (A-ph). A-ph ds,ples with various mass ratios of CE

(A-ph/CE) were fabricated, and their GF reinforced composite laminates were prepared by hot compression. The A-ph/CE matrix exhibited low viscosity in low temperature and wide processing window (100–180 °C). The curing behavior of A-ph/CE matrix resin was studied by differential scanning calorimetric (DSC) and dynamic rheological analysis (DRA). Fourier transform infrared spectroscopy (FTIR) was applied to characterize the structures of A-ph/CE copolymers. Mechanical properties, dynamic mechanical analysis (DMA), as well as thermal stability of the laminates were studied. Improved mechanical properties were verified by fracture morphology and discussed in detail.

2. Experiment

2.1. Materials

N,N-dimethylformamide (DMF, purity 99%), formaldehyde (purity 99%), aniline (purity 99%) were obtained from Chengdu Kelong chemicals Co., Ltd. Chengdu, China. The 3-aminophenoxyphthalonitrile (3-APN) were prepared in our laboratory [22]. A kind of phthalonitrile-based resin containing benzoxazine was synthesized according to our previous work and structures were shown in Figure 1a [23–26]. Bisphenol A-based cyanate ester (CE) resin was obtained from Wuqiao Resins Co., Ltd. Yangzhou, China. The glass fiber (GF, EW170-100) fabric was obtained from Shenyang Gaote glass fiber Co., Shenyang, China. GF was treated at 200 °C for 1 h before the experiment. Other materials were used directly without any purification.

The heat treatment method was used to heat the glass fiber at a temperature of 200 °C for 1 h. The purpose of this was to remove the paraffin emulsion on the surface, improve the bonding ability of the glass fiber and the resin, and thereby improve the mechanical properties of the corresponding molded product. The GF before and after treatment was shown in the Figure 2. It can be observed from the figure that the

Figure 1. Structures of (a) phthalonitriles-containing benzoxazine (A-Ph) and (b) cyanate ester (CE).

Figure 2. TGA curve of glass fiber before and after treatment.

untreated GF curve had a lower content of decomposition, and the heat resistance of the treated GF was higher than that of the untreated GF, indicating that the heat treatment of GF was effective, it can remove the paraffin indicated by glass fibers and improve the heat resistance of glass fibers.

2.2. Preparation of A-ph/CE prepolymers

A-ph/CE prepolymers with various contents of CE (0, 10, 20, 30, and 40 wt%) were prepared as follows. First, A-ph monomer was poured into a three-necked flask equipped with a mechanical stirrer. This was heated into a dark brown liquid at 82 °C in a heating mantle. Various contents of CE and DMF by weight of A-ph were added into the solution. The mixed solvent was selected to control the reflux temperature at 135 °C and stirring for another 105 min to obtain A-ph/CE prepolymers.

2.3. Preparation of A-ph/CE/GF composite laminates

GF reinforced composite laminates were prepared as follows. First, ten layers of GF (10 cm×10 cm, 2.1 g/layer) were impregnated with the as-prepared A-ph/CE prepolymers as mentioned above. The prepreg was obtained according to 35 wt% matrix resin and 65 wt% GF. The calculated amount of components used in the processing of A-ph/CE/GF composites was shown in Table 1. Then, the impregnated GFs were maintained at 80 °C for 20 min and 170 °C for 25 min to remove the residual solvent. Ten layers of GF prepreg clothes were placed in a stainless steel mold and hot pressed under a pressure of 20 MPa at 180 °C for 2 h and 200 °C for 4 h, respectively.

Table 1. Calculated quantities of components used in the processing of A-ph/CE/GF composites.

Samples	0% [g]	10% [g]	20% [g]	30% [g]	40% [g]
GF	19				
A-ph	10.23	9.207	8.184	7.161	6.138
CE	0	1.023	2.046	3.069	4.092

2.4. Characterizations

DSC analysis was carried out through modulated DSC Q100 at a heating rate of 10 °C/min under nitrogen atmosphere (50 mL/min), TA Instruments, USA. Dynamic rheology analysis (DRA) was performed at different temperatures in air using Rheometer AR-G2 at a frequency of 1 Hz, TA Instruments, USA. The sample (0.5–1 g) melts between 25 mm diameter parallel plates and the rheometer's environmental test chamber. Fourier transform infrared (FTIR) spectra between 3500 and 500 cm⁻¹ in an air atmosphere were recorded in KBr particles using a Shimadzu 8400S FTIR Fourier infrared spectrometer, Shimadzu, Japan. The flexural experiments (three-point bending mode) were characterized with a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen SANS, Shenzhen, China) at room temperature. The morphology of the fractured surfaces of the composites was observed by scanning electron microscope (SEM, JSM25900LV, JEOL, Akishima, Japan) operating at 20 kV. DMA in a three-point bending mode with a frequency of 1 Hz was tested on a TA Instruments QDMA-800 (TA Instruments, Newcastle, DE, USA), the storage modulus and tan δ were investigated. The temperature was ranging from 50 to 350 °C (5 °C/min) in air atmosphere. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 (TA Instruments, Newcastle, DE, USA) at a heating rate of 20 °C/min from room temperature to 800 °C in a nitrogen atmosphere with a purge rate of 40 ml/min.

3. Results and discussion

3.1. Curing behaviors of A-ph/CE prepolymers

Curing behaviors of A-ph/CE prepolymers were investigated by DSC shown in Figure 3. The curves generated from DSC of A-ph/CE prepolymers with various CE contents were plotted in Figure 3. As can be seen, A-ph/CE prepolymers exhibited double distinct exothermic peaks, which can be assigned to

Figure 3. DSC curves of A-ph/CE prepolymers with various contents of CE.

ring-opening polymerization of oxazine rings and ring-forming polymerization of nitrile groups, including phthalonitrile and isocyanate, respectively [27, 28]. The initial cure temperatures of A-ph/CE prepolymers with 10, 20, 30, and 40 wt% CE appeared in the range at about 150–170 °C. In the prepolymer system with only A-ph, ring opening temperature of oxazine ring occurred at 150 °C and peaked at about 215 °C. From the DSC curve of pure cyanate ester in Figure 4, it can be observed that the curing temperature of pure cyanate ester was in the range of 270 to 320 °C without adding catalyst. But Figure 3 showed a lower curing temperature, which can be related to the promotion of active phenolic hydroxyl generated from ring-opening of oxazine ring [29–31]. Moreover, with the introduction of CE, the temperature of first exothermic peak in prepolymers decreased, indicating that copolymerization occurred between oxazine ring and cyanate ester. Besides, the synergistic promotion effects appeared

Figure 4. DSC curve of pure cyanate ester.

Table 2. Thermal Properties of the A-ph/CE prepolymers with various contents of CE.

Samples	0%	10%	20%	30%	40%
T_i [°C]	167.66	150.25	149.01	147.14	145.52
T_{top1} [°C]	213.71	208.40	199.11	197.10	195.52
T_{top2} [°C]		261.66	254.96	252.37	250.02
$\Delta H_{curing1}$ [J/g]	304.80	114.60	72.29	63.62	44.11
$\Delta H_{curing2}$ [J/g]		3.43	7.76	18.24	21.81

during copolymerization process, therefore improving the polymerization process of A-ph and decreasing heat of polymerization in the copolymer. In addition, polymerization of nitrile groups appeared at about 260 °C was obvious, which indicated that ring-forming polymerization of nitrile groups and cyanate was promoted.

As shown in Table 2, curing enthalpy assigned to the double exothermic peaks of A-ph/CE prepolymer was different from that of prepolymer containing only A-ph. The enthalpy for ring-opening polymerization of oxazine rings decreased with increasing the content of CE, attributed to the diluting effects of CE. Previous literature reported [28, 32] that oxazine ring preferentially reacts with ortho position of phenolic compound to form a dimer possesses a methylene-amine-methylene bridge structure, and no small molecule release. Then, the phenolic hydroxyl groups and imine structures catalyze nitrile groups and cyanate in A-ph/CE system to form a phthalocyanine ring and a triazine ring. It was obvious that with increasing the content of CE, the second exothermic peaks gradually decreased from 261.66 to 250.02 °C. Moreover, enthalpy for ring-forming polymerization of nitrile groups and cyanate increased from 3.43 to 21.81 J/g, correspondingly. This can be attributed to the promotion effects of active hydrogen and imine structures generated from ring-opening polymerization of oxazine rings. The possible polymerization processes and mechanisms were presented in Figure 5.

In Figure 5, it was obvious that ring-opening polymerization of oxazine rings occurred preferentially in the presence of trace hydrogen (Figure 5a). Then, more active hydrogen and amine structures generated, which would significantly promote the ring-forming polymerization of cyanate and nitrile groups (Figure 5b, 5c and 5d). In the end, the crosslinked network would be formed with various heteroaromatic rings (Figure 5e) including isoindole, triazine

Figure 5. (a) The Mannich bridge structure of ring-opened benzoxazine rings in A-ph; (b) and (c) cyanate esters form a triazine ring structure through phenolic hydroxyl groups and its thermal polymerization, respectively; (d) the nitrile group in A-ph forms an isoindole ring, a phthalocyanine ring and a triazine ring by the action of the stimulus; (e) the possible structures of the composites. A general formula for the representation of alkyl by 'R', R₃, R₄'.

Figure 6. DSC curves of the first scanning of A-ph/CE/GF composites with various contents of CE.

rings, and phthalocyanine, which would possess outstanding thermal stability.

Figure 6 showed the first DSC scan curve of the composite A-ph/CE/GF, from which the glass transition temperature can be observed, and as the CE content increased, the glass transition temperature decreased. In the DSC curve of Figure 7, after using the DSC instrument in the 50–350 °C temperature range, and then using the DSC instrument after the second test, the purpose was to eliminate the thermal history in the first test, and then from Figure 7 it was seen that for all blends, the two exothermic peaks almost disappeared after being treated at 180 °C/2 h and 200 °C/4 h. After the high temperature reaction at 350 °C, the DSC test did not significantly detect the glass transition temperature. It indicated that all the composite materials have an excellent glass transition temperature, and under this condition, ring-opening

Figure 7. DSC curves of secondary scanning of A-ph/CE prepolymers with various contents of CE.

polymerization of the oxazine ring and ring-forming polymerization of the nitrile group are completed.

3.2. Processability of A-ph/CE prepolymers

The processing properties of A-ph/CE prepolymers were tested by rheological tests to determine the viscosity changes as functions of temperatures, which reflected the curing processing of prepolymers. Figure 8 presented complex viscosity (η^*) of A-ph/CE prepolymers as a function of temperature from 50 to 300 °C. The complex viscosity of all A-ph/CE prepolymers varied significantly with temperature and CE content, indicating that curing reaction was dependent on temperature and CE content.

It can be clearly seen that the processing window of the system was in the temperature range of 100–180 °C, and the system exhibited a low melt viscosity in this interval, indicating that the A-ph/CE system had good processability. The increase of the complex viscosity was observed above 180 °C, mainly due to the influence of the cross-linking reaction, the movement of the molecular segment was affected, the inter-molecular friction increased, and the fluidity was weakened, which showed an increase in viscosity. And the viscosity growth in the system showed a trend of segmentation, corresponding to the unused reaction process, respectively, the polymerization of benzoxazine and nitrile groups, and the effects of these two reactions on the increase of molecular weight and crosslinking degree of the system were different. It can be seen from the figure that the polymerization of benzoxazine had a smaller effect on the viscosity of the system than the polymerization of the nitrile group, and the two reactions

Figure 8. Complex viscosity curves as a function of temperature for A-ph/CE prepolymers with various contents of CE.

had a clear sequence. Two-stage polymerization due to ring-opening polymerization of the oxazine ring and ring-forming polymerization of the hydroxyl group accelerated by the hydroxyl group provided by A-ph. This was in line with the DSC results. In summary, the effect of CE content on the copolymerization rate was obvious, and the copolymer had an ideal processing temperature.

3.3. Structures of A-ph/CE polymers

In order to confirm the structural transformation of the composites, structures of A-ph/CE polymer obtained after being cured at 180 and 200 °C were investigated by FTIR, and results were shown in Figure 9. In Figure 9, the intensity characteristic absorption band at 1478 cm⁻¹ was assigned to the in-plane C–H stretching of the tetrasubstituted benzene, indicating that the methylene bridges formed in the free ortho positions of the phenolic structures. Meanwhile, the characteristic band of oxazine near 967 cm⁻¹ did not appear in Figure 9 curve (a), confirming that oxazine ring was involved in the polymerization at 180 °C. And corresponding to the DSC diagram of Figure 3, the ring-opening polymerization of the oxazine ring was achieved in the temperature range of 180–220 °C, which was consistent with the infrared test. Meanwhile, the peaks observed at 1360 and 1520 cm⁻¹ corresponded to the characteristic peaks of the triazine rings. The peaks at 3290 and 1010 cm⁻¹ corresponded to the characteristic peaks of phthalocyanine rings. The triazine and phthalocyanine rings were produced by cyano groups from CE and A-ph [33, 34]. After the two curing stages, a new absorption peak at 1619 cm⁻¹ appears on infrared spectrum, which was the characteristic absorption peak of –C=N–, indicating that some isoindole were formed in cured product [35]. The absorption peak at 2969 cm⁻¹ was assigned to the stretching vibration of –CH₃ and no obvious changes were observed. DSC test results in Figure 2 showed that the temperature of nitrile ring formation was about 260 °C. Therefore, in Figure 9, the absorption peak of nitrile group (2227 cm⁻¹) decreased with the increase of curing temperature, but there was still a small amount of residual after 200 °C treatment, which was consistent with the reaction inertia of nitrile group reported in literature. In summary, Figure 9 showed the FTIR measurements of 20 wt% CE composites cured at 180 and 200 °C. Obviously, the absorption peaks of oxazine ring disappeared at 967 cm⁻¹ in A-ph/CE

Figure 9. FTIR spectra of the A-ph/CE system with 20 wt% CE cured at different temperatures: (a) 180 °C, (b) 200 °C.

polymer, and there were absorption peaks of triazine ring, phthalocyanine ring and isoindole structure in the range of 1010 to 3290 cm⁻¹. The results of FTIR spectra were consistent with those of DSC, which proved that there were various polymerization processes in the curing process of A-ph/CE.

3.4. Dynamic thermomechanical analysis of the A-ph/CE/GF composite laminates

The dynamic thermal mechanical properties were investigated to reveal the glass transition temperatures (T_g s) of composite laminates with various resin matrices. As is well known, the temperature corresponding to the peak of tan delta was defined as T_g [36]. Figure 10 showed the tan delta curves for various composite laminates. It can be seen that only one peak was found in A-ph/CE/GF composite system. Only one glass transition occurred, indicating that there was no phase separation in the composites. Table 3 collected glass transition temperatures of

Figure 10. tan δ of the A-ph/CE/GF composite laminates.

Table 3. Thermal stabilities of the A-ph/CE/GF composite laminates.

Samples	T_g [°C]	$T_{5\%}$ [°C]	$T_{10\%}$ [°C]	Char yield at 800 °C [%]
0%	308.47	401.41	469.26	72.75
10%	307.88	394.08	426.46	64.79
20%	292.87	361.61	413.23	57.94
30%	253.17	336.99	382.73	57.94
40%	219.14	325.75	361.03	53.14

A-ph/CE/GF composite laminates. With increasing CE in A-ph/CE/GF composites, glass transition temperatures of composite laminates gradually decreased. In fact, with CE content increasing in A-ph/CE/GF composite laminates, active hydrogen produced by ring-opening of A-ph decreased, which would result in a decrease in ring-forming rate of nitrile groups, leading to lower crosslinking degree. However, it was obvious that when the introduction of CE content was less than 30 wt%, the composite laminates showed outstanding T_g s. Among them, the glass transition temperature of composites with 10 wt% CE was very high, which was close to that of composites without CE. It showed that the crosslinking degree was high, which indirectly proved that the bending strength was high. When the content of CE was more than 30 wt%, T_g s of composite laminates decreased sharply. It can be attributed to copolymerization between A-ph and cyanate ester. As mentioned above, outstanding properties of composites would be derived from ring-opening polymerization of oxazine rings and ring-forming polymerization of cyanate and nitrile groups. When the content of CE was 40 wt%, self-polymerization of CE may be dominated by ring-forming polymerization of cyanate. As reported [37, 38], self-polymerization of CE would be

completed at about 270 °C. Thus, polymerization of cyanate should be incomplete at 200 °C in this work. Thus, when the content of CE was moderate, copolymerization between nitrile groups and cyanate can be completed at 200 °C, resulting to satisfactory thermal properties. Comparing the glass transition temperatures of Figure 6 and Figure 10, it can be seen that there were differences between the two different tests, because the sensitivity of the DSC instrument to the test T_g s was not as high as that of the DMA instrument, and the DSC test data was usually 20 to 40 °C lower than the DMA test data. Therefore, the glass transition temperature was based on the DMA test data, but it can be seen that two both showed a trend of decreasing T_g s as the content of CE increased.

3.5. Thermal stability of A-ph/CE/GF composite laminates

The thermal decomposition of composites was examined by TGA under nitrogen atmosphere from room temperature to 800 °C with a rate of 20 °C/min. Results of TGA curves were presented in Figure 11, and weight loss temperature at 95 wt% ($T_{5\%}$), 90 wt% ($T_{10\%}$) and char yield at 800 °C were listed in Table 3. Thermal stability of A-ph/CE/GF composites decreases with increasing CE content, which was due to low crosslink density and poor heat resistance of CE compared with that of A-ph and the content of A-ph decreases, resulting in a decrease in the number of free hydroxyl groups produced by the A-ph ring-opening reaction [39, 40]. These hydroxyl groups can catalyze the curing reaction of the nitrile group, leading to an enhancement in the degree of cross-linking and thermal stability. As the CE in the copolymer was added, the thermal stability of the A-ph/CE/GF composite

Figure 11. Thermal stability of the A-ph/CE/GF composite laminates. a) TGA curves, b) DTG curves.

Table 4. Comparison of thermal properties of different composite materials.

Samples	T _{5%} [°C]	T _{10%} [°C]	Char yield at 600 °C [%]
10 wt% CE/A-ph/GF	394	426	73.34
CE/EP-31 [43]	366	376	30.33
CNBZ/BMI(1/9) [44]	383	412	56.68
Boz/QFs/CE [45]	390	—	79.05
SH/BZ-CN/GF [46]	357	—	57.60
EP/BA-ph/GF [47]	409	471	87.15

deteriorates, resulting in a decrease in thermal stability. In addition, composite system with 10 wt% CE showed little change in $T_{5\%}$ and $T_{10\%}$ compared with that of A-ph/GF composite. At the same time, $T_{5\%}$ and $T_{10\%}$ were higher than those of the other CE-joined composites, which indicates that 10 wt% CE composite system possessed not only good mechanical properties but also showed excellent thermal stability performance. Moreover, it can be seen from DTG curve in Figure 11b that A-ph/CE/GF composite system possesses the highest decomposition rate in the range of 410–425 and 520–580 °C, respectively. Compared with that of reported thermosetting resin matrix, CE/A-ph/GF composites showed outstanding thermal stability (shown in Table 4). On the other hand, Boz/QFs/CE composite system and EP/BA-ph/GF composite system can be used for a long time at about 390 and 409 °C, respectively. But compared with that of CE/A-ph/GF composite laminates, they showed a lower mechanical property (Boz/QFs/CE flexural strength: 587.9 MPa; EP/BA-ph/GF flexural strength: 580 MPa). Overall, CE/A-ph/GF composite laminates with 10 wt% CE showed outstanding thermal properties, and it possessed a better comprehensive mechanical property that can be used in certain special circumstances.

3.6. Mechanical properties of A-ph/CE/GF composite laminates

In the above-mentioned part, curing behaviors and processability of A-ph/CE copolymers were investigated. Figure 12 and Figure 13 showed mechanical properties of A-ph/CE/GF composite laminates with various CE content. Flexural strength of A-ph/CE/GF composite laminates with 0, 10, 20, 30 and 40 wt% CE were 440.77, 622.29, 607.72, 566.98 and 558.97 MPa, respectively (shown in Figure 12). Flexural modulus was 21.35, 23.63, 24.59, 25.02, and 28.49 GPa, respectively (shown in Figure 13). It can be seen that prepolymer containing CE possessed

Figure 12. Flexural strength of A-ph/CE/GF composite laminates. **Figure 13.** Flexural modulus of A-ph/CE/GF composite laminates.

higher flexural strength and modulus than that of A-ph composite laminates. Among them, flexural strength of composite laminates with 10 wt% CE was the highest, while, flexural modulus of composite laminates increased with increasing the content of CE, correspondingly. In the discussion of DSC and DTA, the copolymerization of A-ph and CE was caused by the addition of cyanate ester, which affected the increase of crosslinking degree of the system, especially the mechanical properties of the composites. According to references, strength and modulus of composite laminates would be affected not only by the type of resin matrix but also the interfacial adhesion between the fibers and resin matrix [41, 42].

To further confirm the improved mechanical properties of composite laminates, fracture surface of composite laminates with various content of CE were investigated and presented in Figure 14. It was obvious that in Figure 14a, exposed fibers pulled out from resin matrix can be observed, indicating weak

Figure 14. The SEM images of the fracture surface of A-ph/CE/GF composite laminates with various CE content: (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 40% (the surface of fiber and the interfacial adhesion position were labeled with red cycles and arrows; both e) and f) are 40 wt% CE but different magnifications).

interfacial adhesion effects between fibers and A-ph. In Figures 14b, 14c, 14d and 14e, fibers were embedded into resin matrix and no exposed fibers were observed, indicating improved interfacial adhesion effects between fibers and A-ph/CE matrix.

In addition, the matrix resin was evenly distributed among glass fibers, and there were not lots of resin fragments at each ratio of the cross-section (Figure 14f). It indicated that A-ph/CE resin matrix possessed higher toughness, which can be due to amounts of heteroaromatic rings existed in composite laminates. In sum, results of SEM images confirmed that improved mechanical properties were assigned to the toughness of resin matrix itself and improved interfacial adhesion effects between fibers and resin matrices.

4. Conclusions

Copolymerization behaviors and processability of A-ph/CE systems were investigated. In A-ph/CE system, there was no clear boundary between ring-opening of oxazine ring and self-crosslinking polymerization of CE. Copolymerization occurred between A-ph and CE due to ring-opening polymerization of oxazine and ring-forming polymerization of nitrile groups and cyanate. When the content of CE was more than 40 wt%, the self-polymerization of cyanate would dominate ring-forming polymerization. Structural transition investigation indicates that ring-opening polymerization of oxazine occurs preferentially. Then ring-forming polymerization of cyanate and nitrile groups would be promoted by active hydrogen and amine structures generated from ring-opening of oxazine rings. The A-ph/CE/GF composite laminates with 10 wt% CE content shows the best flexural strength of 622 MPa and flexural modulus of 24 GPa, which was attributed to copolymerization between CE and A-ph, as well as interfacial adhesion effects between GFs and resin matrix. In addition, DMA test also indicates that A-ph/CE/GF composite laminates with 10 wt% CE showed satisfactory T_g . A notable finding was that A-ph/CE/GF composite laminates with 10 wt% CE content withstand high temperature up to 426 °C in atmosphere of N₂, showing excellent performance superior to other component composite laminates. Taking these performance considerations into account, composites with 10 wt% CE content can be determined as a suitable additive amount for enhancing the performance of A-ph/CE/GF composite laminates. This

study confirmed that A-ph/CE/GF composites can be used in certain critical environments with excellent mechanical properties and high-temperature resistance.

Acknowledgements

The authors wish to thank the financial support to this work provided by the Natural Science Foundation of China (No. 51803020)

References

- [1] Balázs Cs., Kónya Z., Wéber F., Biró L. P., Arató P.: Preparation and characterization of carbon nanotube reinforced silicon nitride composites. *Materials Science and Engineering: C*, **23**, 1133–1137 (2003).
<https://doi.org/10.1016/j.msec.2003.09.085>
- [2] Saha A. K., Das S., Bhatta D., Mitra B. C.: Study of jute fiber reinforced polyester composites by dynamic mechanical analysis. *Journal of Applied Polymer Science*, **71**, 1505–1513 (2015).
[https://doi.org/10.1002/\(SICI\)1097-4628\(19990228\)71:9<1505::AID-APP15>3.0.CO;2-1](https://doi.org/10.1002/(SICI)1097-4628(19990228)71:9<1505::AID-APP15>3.0.CO;2-1)
- [3] Abdelmouleh M., Boufi S., Belgacem M., Dufresne A.: Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading. *Composites Science and Technology*, **67**, 1627–1639 (2007).
<https://doi.org/10.1016/j.compscitech.2006.07.003>
- [4] Wang X., Jin J., Song M.: Cyanate ester resin/graphene nanocomposite: Curing dynamics and network formation. *European Polymer Journal*, **48**, 1034–1041 (2012).
<https://doi.org/10.1016/j.eurpolymj.2012.03.012>
- [5] Lin Q., Qu L., Lü Q., Fang C.: Preparation and properties of graphene oxide nanosheets/cyanate ester resin composites. *Polymer Testing*, **32**, 330–337 (2013).
<https://doi.org/10.1016/j.polymertesting.2012.11.014>
- [6] Zeng M., Wang J., Li R., Liu J., Chen W., Xu Q., Gu Y.: The curing behavior and thermal property of graphene oxide/benzoxazine nanocomposites. *Polymer*, **54**, 3107–3116 (2013).
<https://doi.org/10.1016/j.polymer.2013.03.069>
- [7] Jin L., Agag T., Ishida H.: Bis(benzoxazine-maleimide)s as a novel class of high performance resin: Synthesis and properties. *European Polymer Journal*, **46**, 354–363 (2010).
<https://doi.org/10.1016/j.eurpolymj.2009.09.013>
- [8] Keller T. M.: Phthalonitrile-based high temperature resin. *Journal of Polymer Science Part A: Polymer Chemistry*, **26**, 3199–3212 (1988).
<https://doi.org/10.1002/pola.1988.080261207>
- [9] Zhao Z., Lou Y., Dai Z., Fu F., Liu X.: Biobased composites prepared using an environmentally friendly water-slurry methodology. *Industrial and Engineering Chemistry Research*, **57**, 7881–7888 (2018).
<https://doi.org/10.1021/acs.iecr.8b00960>

- [10] Zhao Y., Xu Y., Xu Q., Fu F., Zhang Y., Endo T., Liu X.: Significant improvement on polybenzoxazine toughness achieved by amine/benzoxazine copolymerization-induced phase separation. *Macromolecular Chemistry and Physics*, **219**, 1700517/1–1700517/7 (2018).
<https://doi.org/10.1002/macp.201700517>
- [11] Fu F., Huang M., Zhang W., Zhao Y., Liu X.: Thermally assisted self-healing behavior of anhydride modified polybenzoxazines based on transesterification. *Scientific Reports*, **8**, 10325/1–10325/6 (2018).
<https://doi.org/10.1038/s41598-018-27942-9>
- [12] Xu Y. Z., Wang J., Fu F. Y., Liu X.: Copolymerization and phase separation behaviors of benzoxazine–amine thermosets. *RSC Advances*, **6**, 100590–100597 (2016).
<https://doi.org/10.1039/C6RA23509C>
- [13] Wang J., Xu Y. Z., Fu Y. F., Liu X. D.: Latent curing systems stabilized by reaction equilibrium in homogeneous mixtures of benzoxazine and amine. *Scientific Reports*, **6**, 38584/1–38584/7 (2016).
<https://doi.org/10.1038/srep38584>
- [14] Sun J. Q., Wei W., Xu Y. Z., Qu J. H., Liu X. D., Endo T.: A curing system of benzoxazine with amine: Reactivity, reaction mechanism and material properties. *RSC Advances*, **5**, 19048–19057 (2015).
<https://doi.org/10.1039/c4ra16582a>
- [15] Wang C. F., Sun J. Q., Liu X. D., Sudo A., Endo T.: Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine. *Green Chemistry*, **14**, 2799–2806 (2012).
<https://doi.org/10.1039/C2GC35796H>
- [16] Chen L., Ren D., Chen S., Li K., Xu M., Liu X.: Improved thermal stability and mechanical properties of benzoxazine-based composites with the enchantment of nitrile. *Polymer Testing*, **74**, 127–137 (2019).
<https://doi.org/10.1016/j.polymertesting.2018.11.032>
- [17] Brunovska Z., Ishida H.: Thermal study on the copolymers of phthalonitrile and phenylnitrile-functional benzoxazines. *Journal of Applied Polymer Science*, **73**, 2937–2949 (2015).
[https://doi.org/10.1002/\(SICI\)1097-4628\(19990929\)73:14<2937::AID-APP18>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1097-4628(19990929)73:14<2937::AID-APP18>3.0.CO;2-E)
- [18] Brunovska Z., Lyon R., Ishida H.: Thermal properties of phthalonitrile functional polybenzoxazines. *Thermochimica Acta*, **357**, 195–203 (2000).
[https://doi.org/10.1016/S0040-6031\(00\)00388-9](https://doi.org/10.1016/S0040-6031(00)00388-9)
- [19] Chen X., Liang G., Gu A., Yuan L.: Flame retarding cyanate ester resin with low curing temperature, high thermal resistance, outstanding dielectric property, and low water absorption for high frequency and high speed printed circuit boards. *Industrial and Engineering Chemistry Research*, **54**, 1806–1815 (2015).
<https://doi.org/10.1021/ie504333f>
- [20] Wang J., Liang G., Yan H., He S.: Mechanical and thermal properties of functionalized multiwalled carbon nanotubes/cyanate ester composite. *Polymer Engineering and Science*, **49**, 680–684 (2009).
<https://doi.org/10.1002/pen.21277>
- [21] Ye J., Liang G., Gu A., Zhang Z., Han J., Yuan L.: Novel phosphorus-containing hyperbranched polysiloxane and its high performance flame retardant cyanate ester resins. *Polymer Degradation and Stability*, **98**, 597–608 (2013).
<https://doi.org/10.1016/j.polymdegradstab.2012.11.015>
- [22] Guo H., Chen Z., Zhang J., Yang X., Zhao R., Liu X.: Self-promoted curing phthalonitrile with high glass transition temperature for advanced composites. *Journal of Polymer Research*, **19**, 9918/1–9918/8 (2012).
<https://doi.org/10.1007/s10965-012-9918-1>
- [23] Xu M. Z., Jia K., Liu X. B.: Effect of bisphenol-A on the structures and properties of phthalonitrile-based resin containing benzoxazine. *Express Polymer Letters*, **9**, 567–581 (2015).
<https://doi.org/10.3144/expresspolymlett.2015.53>
- [24] Yang X.-L., Li K., Xu M.-Z., Liu X.-B.: Designing a phthalonitrile/benzoxazine blend for the advanced GFRP composite materials. *Chinese Journal of Polymer Science*, **36**, 106–112 (2017).
<https://doi.org/10.1007/s10118-018-2033-y>
- [25] Xu M., Luo Y., Lei Y., Liu X.: Phthalonitrile-based resin for advanced composite materials: Curing behavior studies. *Polymer Testing*, **55**, 38–43 (2016).
<https://doi.org/10.1016/j.polymertesting.2016.08.008>
- [26] Xu M., Liu M., Dong S., Liu X.: Design of low temperature self-cured phthalonitrile-based polymers for advanced glass fiber composite laminates. *Journal of Materials Science*, **48**, 8108–8116 (2013).
<https://doi.org/10.1007/s10853-013-7623-z>
- [27] Xu M., Ren D., Chen L., Li K., Liu X.: Understanding of the polymerization mechanism of the phthalonitrile-based resins containing benzoxazine and their thermal stability. *Polymer*, **143**, 28–39 (2018).
<https://doi.org/10.1016/j.polymer.2018.04.004>
- [28] Ohashi S., Kilbane J., Heyl T., Ishida H.: Synthesis and characterization of cyanate ester functional benzoxazine and its polymer. *Macromolecules*, **48**, 8412–8417 (2015).
<https://doi.org/10.1021/acs.macromol.5b02285>
- [29] Li X., Luo X., Liu M., Ran Q., Gu Y.: The catalytic mechanism of benzoxazine to the polymerization of cyanate ester. *Materials Chemistry and Physics*, **148**, 328–334 (2014).
<https://doi.org/10.1016/j.matchemphys.2014.07.051>
- [30] Liu X., Yu Y., Li S.: Study on cure reaction of the blends of bismaleimide and dicyanate ester. *Polymer*, **47**, 3767–3773 (2006).
<https://doi.org/10.1016/j.polymer.2006.03.102>
- [31] Wang M. W., Jeng R. J., Lin C. H.: Origin of the rapid trimerization of cyanate ester in a benzoxazine/cyanate ester blend. *Macromolecules*, **48**, 2417–2421 (2015).
<https://doi.org/10.1021/acs.macromol.5b00334>

- [32] Xu M. Z., Liu M. D., Dong S. H., Qiu G. Y., Liu X. B.: Active diluents effects of 4-nonylphenoxy-1, 2-dinitrilebenzene on phthalonitrile containing benzoxazine and their copolymerization behaviors. *Express Polymer Letters*, **7**, 984–995 (2013).
<https://doi.org/10.3144/expresspolymlett.2013.97>
- [33] Badshah A., Kessler M. R., Heng Z., Hasan A.: Synthesis and characterization of phthalonitrile resins from ortho-linked aromatic and heterocyclic monomers. *Polymer International*, **63**, 465–469 (2014).
<https://doi.org/10.1002/pi.4527>
- [34] Snow A. W., Griffith J. R., Marullo N. P.: Syntheses and characterization of heteroatom-bridged metal-free phthalocyanine network polymers and model compounds. *Macromolecules*, **17**, 70–76 (1984).
<https://doi.org/10.1021/ma00138a033>
- [35] Sumner M. J., Sankarapandian M., Mcgrath J. E., Riffle J. S., Sorathia U.: Flame retardant novolac–bisphthalonitrile structural thermosets. *Polymer*, **43**, 5069–5076 (2002).
[https://doi.org/10.1016/S0032-3861\(02\)00354-3](https://doi.org/10.1016/S0032-3861(02)00354-3)
- [36] Gu J., Liang C., Zhao X., Gan B., Qiu H., Guo Y., Yang X., Zhang Q., Wang D-Y.: Highly thermally conductive flame-retardant epoxy nanocomposites with reduced ignitability and excellent electrical conductivities. *Composites Science and Technology*, **139**, 83–89 (2017).
<https://doi.org/10.1016/j.compscitech.2016.12.015>
- [37] Grenier-Loustalot M. F., Lartigau C., Metras F., Grenier P.: Mechanism of thermal polymerization of cyanate ester systems: Chromatographic and spectroscopic studies. *Journal of Polymer Science Part A: Polymer Chemistry*, **34**, 2955–2966 (2015).
[https://doi.org/10.1002/\(SICI\)1099-0518\(199610\)34:14<2955::AID-POLA13>3.0.CO;2-J](https://doi.org/10.1002/(SICI)1099-0518(199610)34:14<2955::AID-POLA13>3.0.CO;2-J)
- [38] Chen C-C., Don T-M., Lin T-H., Cheng L-P.: A kinetic study on the autocatalytic cure reaction of a cyanate ester resin. *Journal of Applied Polymer Science*, **92**, 3067–3079 (2010).
<https://doi.org/10.1002/app.20314>
- [39] Kim H-D., Ishida H.: A study on hydrogen-bonded network structure of polybenzoxazines. *Journal of Physical Chemistry A*, **106**, 3271–3280 (2002).
<https://doi.org/10.1021/jp010606p>
- [40] Kim H-D., Ishida H.: Model compounds study on the network structure of polybenzoxazines. *Macromolecules*, **36**, 8320–8329 (2003).
<https://doi.org/10.1021/ma030108+>
- [41] Sreekumar P. A., Thomas S. P., Saiter J. M., Joseph K., Unnikrishnan G., Thomas S.: Effect of fiber surface modification on the mechanical and water absorption characteristics of sisal/polyester composites fabricated by resin transfer molding. *Composites Part A: Applied Science and Manufacturing*, **40**, 1777–1784 (2009).
<https://doi.org/10.1016/j.compositesa.2009.08.013>
- [42] Hill C. A. S., Abdul Khalil H. P. S.: Effect of fiber treatments on mechanical properties of coir or oil palm fiber reinforced polyester composites. *Journal of Applied Polymer Science*, **78**, 1685–1697 (2015).
[https://doi.org/10.1002/1097-4628\(20001128\)78:9<1685::AID-APP150>3.0.CO;2-U](https://doi.org/10.1002/1097-4628(20001128)78:9<1685::AID-APP150>3.0.CO;2-U)
- [43] Wu F., Tuan C-C., Song B., Moon K-S., Wong C-P.: Controlled synthesis and evaluation of cyanate ester/epoxy copolymer system for high temperature molding compounds. *Journal of Polymer Science Part A: Polymer Chemistry*, **56**, 1337–1345 (2018).
<https://doi.org/10.1002/pola.29013>
- [44] Zhang J., Zhu C., Geng P., Wei Y., Lu Z.: Nitrile functionalized benzoxazine/bismaleimide blends and their glass cloth reinforced laminates. *Journal of Applied Polymer Science*, **131**, 41072/1–41072/7 (2014).
<https://doi.org/10.1002/app.41072>
- [45] Wang Y., Kou K., Zhuo L., Wu G.: Preparation of Boz/glass fibers/cyanate ester resins laminated composites. *Polymer Composites*, **38**, 523–527 (2017).
<https://doi.org/10.1002/pc.23611>
- [46] Yang X., Li K., Xu M., Jia K., Liu X.: Designing a low-temperature curable phenolic/benzoxazine-functionalized phthalonitrile copolymers for high performance composite laminates. *Journal of Polymer Research*, **24**, 195/1–195/8 (2017).
<https://doi.org/10.1007/s10965-017-1360-y>
- [47] Xu M., Yang X., Zhao R., Liu X.: Copolymerizing behavior and processability of benzoxazine/epoxy systems and their applications for glass fiber composite laminates. *Journal of Applied Polymer Science*, **128**, 1176–1184 (2013).
<https://doi.org/10.1002/app.38422>