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Effect of Processing Conditions on Physical Properties of 3-Aminophenoxyphthalonitrile/Epoxy Laminates

Heng Guo, Zhiran Chen, Xiaobo Liu
Research Branch of Functional Materials, Institute of Microelectronic & Solid State Electronic, High-Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China
Correspondence to: X. Liu (E-mail: liuxb@uestc.edu.cn).

ABSTRACT: To develop high performances of polymer composite laminates, differential scanning calorimetry and dynamic rheological analysis studies were conducted to show curing behaviors of 3-aminophenoxyphthalonitrile/epoxy resin (3-APN/EP) matrix and define cure parameters of manufacturing processes. Glass fiber reinforced 3-APN/EP (GF/3-APN/EP) composite laminates were successfully prepared through different processing conditions with three parameters such as pressures, temperatures, and time. Based on flexure tests, dynamic mechanical analysis, thermal gravimetric analysis, and scanning electron microscope, the complementary catalytic effect of the three processing parameters is investigated by studying mechanical behavior, thermomechanical behavior, thermal behavior, and fracture morphology of GF/3-APN/EP laminates. The 50/50 GF/3-APN/EP laminates showed a significant improvement in flexural strength, glass transition temperature (T_g), and thermal stability with favorable processing parameters. It was also found that the T_g and thermal stability were significantly improved by the postheated treatment method. The effect of manufacturing process provides a new and simple route for the polymer–matrix composites application, which indicates that the composites can be manufactured at low temperatures. But, they can be used in a high temperature environment. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39746.

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INTRODUCTION

Fiber-reinforced polymer composite laminate have attracted considerable attention in a wide range of applications because of their high mechanical performances such as strength, stiffness, and weight reduction.[1–3] However, there are several factors for determining mechanical and thermal properties of the fiber-reinforced composite laminates, including the types of fibers, the fiber–matrix interface, the matrix properties and the manufacturing process conditions.[4–7]

It is well known that glass fiber (GF) reinforced composite laminates exhibit superior performances such as high strength, high toughness, and large modulus.[8,9] However, the smooth and inert characteristics of GF surface lead to the weak interfacial interaction, which plays a key role in its shock resistance properties such as mechanical properties. Thus, the surface treatment of GFs with various surface treating agents is a simple and effective method to improve the fiber–matrix interfacial adhesion.[10] Many efforts have been made to grow and coat aligned carbon nanotubes and nanofibers onto the surface of the prepreg.[11–13] Further efforts have been directed at the incorporation of organic and inorganic particles in matrix between prepreg layers.[14–17] However, poor dispersibility, chemical inertness, and high cost of these nanostructures or particles are the main processing limitations. On the other hand, the mechanical and thermal properties of GF reinforced composite laminates not only depend on the properties of the matrix, but the manufacturing process conditions of the composite laminates also play a main role.

Nowadays, epoxy resin (EP) has been widely used commercially in the applications such as coatings, adhesives, electrical insulating materials, and aerospace composites because of its excellent mechanical properties, good chemical resistances, and great electrical properties. More importantly, EP has been widely used as matrix in advanced composites in the applications such as sporting goods, electrical insulating materials, and aerospace composites because of its excellent properties.[18–20] Meanwhile, the epoxy matrix in the composites provides bulk and has good impregnation and adhesion between fiber reinforcements.[21,22] However, an epoxy matrix is relatively brittle and has poor thermal stabilities. Generally speaking, the curing agents have a great advantage in providing the mechanical properties and heat resistance of the curing agent/EP systems. Hence, a significant amount of effect and many techniques have been applied to select the proper curing agents.

In this article, a phthalonitrile containing amine (3-APN) was used in the polymerization reaction of EP as comonomer and coreactive curing agents. Importantly, the functional groups, reactive nitrile groups, incorporated into the 3-APN, have a great tendency to improve the thermal stability of the epoxy matrix. Meanwhile, 3-APN exhibits self-promoted curing behavior in the absence of curing agents and the APN/EP system has the double curing reactions.

The final objective of the present work is focused on the fabrication of glass fiber reinforced 3-aminophenoxyphthalonitrile (3-APN)/EP (GF/3-APN/EP) laminates with different manufacturing process conditions with three parameters such as pressures, temperatures, and time. The mechanical, thermomechanical, and thermal properties of GF/3-APN/EP composite laminates were investigated in terms of the effectiveness of process conditions. Furthermore, both favorable processing parameters and post-heated treatment method were found to be important for improving compatibility between GF and 3-APN/EP matrix.

EXPERIMENTAL

Materials

All the reagents were analytical grade and were used without further purification. Glass fabrics, 0.082-mm thick designated Type 106 (222 g/m^2), were purchased from Sheng Yi Technology. 3-APN was synthesized from 4-nitrophthalonitrile and 3-aminophenol according to the reference reported previously with minor modification.[23,24] It has a melting point of 175°C and exhibits self-promoted curing behaviors with a peaking curing temperature at 239 °C. EP (diglycidyl ether of bisphenol A) with 213–244 g/epoxy equivalent was supplied by Blue Star New Chemical Material. Then, the 3-APN/EP system was used as the matrix for the composites.

Preparation of 3-APN/EP Matrix

The preparation of the 3-APN/EP matrices was as followed: the viscous liquid EP and 3-APN were mixed using a mechanical stirrer at a stirring speed of 300 rpm to obtain a homogeneous mixture. The weight ratio of 3-APN to EP were 25/75, 50/50, 75/25, and 100/0, respectively. Then, the 3-APN/EP matrix blends were obtained for differential scanning calorimetric (DSC) and viscosity studies. Additionally, the same 3-APN/EP matrix blends were treated at 120–140°C for 45 min, and the homogeneous melt was cooled rapidly to room temperature. Then, the 3-APN/EP matrix prepolymers were obtained for viscosity studies and pulverized to prepare the impregnation solution for GF/3-APN/EP composite laminates. Additionally, the same melt 3-APN/EP matrix prepolymers were poured into a preheat polytetrafluoroethylene mold with cavity dimensions 65 mm × 15 mm × 5 mm. The samples were thermally cured in an air-circulation oven at 200°C for 1 h, 240°C for 4 h, and 280°C for 2 h. Then, the obtained cured 3-APN/EP resins were pulverized for thermogravimetric analysis.

Fabrication of GF/3-APN/EP Laminate

The 3-APN/EP matrix prepolymers were dissolved in N, N-dimethylformamide (DMF) and the prepolymer concentration was 100% (w/v) with respect to DMF. The reactive mixture was stirred during heating to 160°C. After maintaining this temperature for 1 h, the resultant solution was cooled to room temperature and the impregnating solution was obtained. Whereas for the preparation of GF/3-APN/EP laminates, glass fabric pieces (length and width equal to 200 and 200 mm, respectively) were impregnated with the different solutions of the 3-ANP/EP prepolymers. The obtained prepregs were vacuum-dried after the solvent evaporated with a temperature of 180°C for 15 min. The 20 plies of prepregs were cured between two steel plates used to ensure a smooth surface of the final cured GF/3-APN/EP laminates. The laminates were fabricated by a hand lay-up method using different manufacturing process parameters, such as temperature, time, and pressure. The processing conditions, postheated treatments, specification and physical of the GF/3-APN/EP laminates were given in Table I. The schematic diagram of the fabrication procedure of GF/3-APN/EP laminates was shown in Figure 1. Then the laminates were cut into strips for mechanical and thermal tests.

Measurements

Differential Scanning Calorimetric. DSC analysis was performed by TA Instruments Modulated DSC-Q100 at a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min.

Dynamic Rheological Analysis. Dynamic rheological analysis (DRA) was performed using TA Instruments Rheometer AR-G2 with a frequency of 1 Hz at different temperatures in air.

Table I. Processing Parameters, Postheated Parameters, Specification and Physical of the GF/3-APN/EP Laminates

Samples	TTP (°C/h/MPa)	TT (°C/h)	RC (%)	*T* (mm)
25/75	200/1/20	-	38.2	2.336
50/50	200/1/20	-	39.7	2.338
75/25	200/1/20	-	38.8	2.377
100/0	200/1/20	-	39.2	2.352
50/50	200/1/15	-	39.2	2.433
	200/1/30	-	39.3	2.313
50/50	200/1/20→ 240/4/20	-	39.6	2.301
	200/1/20→ 240/4/20→ 280/2/20	-	38.4	2.110
50/50	200/1/20	240/4	39.1	2.381
	200/1/20	240/4→280/2	39.5	2.408

TTP, temperature, time, and press (TTP) of different manufacturing processes.
TT, heated temperature and time (TT) of GF/3-APN/EP laminates.
RC, resin content (RC) of GF/3-APN/EP laminates.
T, thickness (*T*) of GF/3-APN/EP laminates.

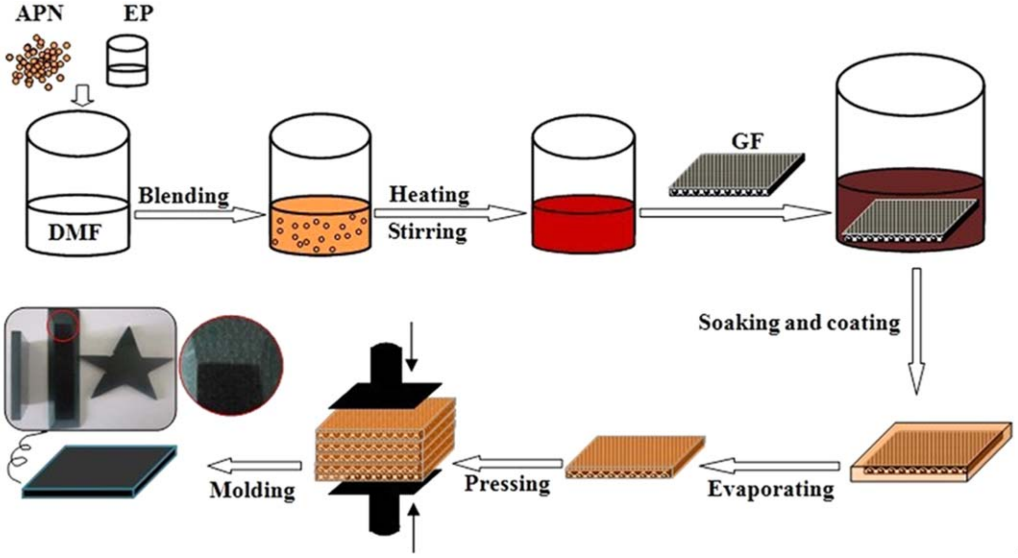

Figure 1. Schematic diagram of fabrication procedure of GF/3-APN/EP laminates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The samples (0.5–1 g) were melted between 25 mm diameter parallel plates with an environmental testing chamber of the rheometer.

Flexure Tests. Flexure tests were performed on an Electronic universal testing machine CM T6104 at room temperature. The mechanical tests were carried out according to the standard ISO178–1993(E).[4] At least, five specimens were tested for each set of samples and values were reported.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) in a three-point-blend mode was used to determine with a TA Instruments QDMA-800 operating with a frequency of 1.0 Hz and the dimensions of the samples were 30 mm × 10 mm × 2 mm. Data were collected from 50°C to 300°C at a temperature ramp of 3°C/min.

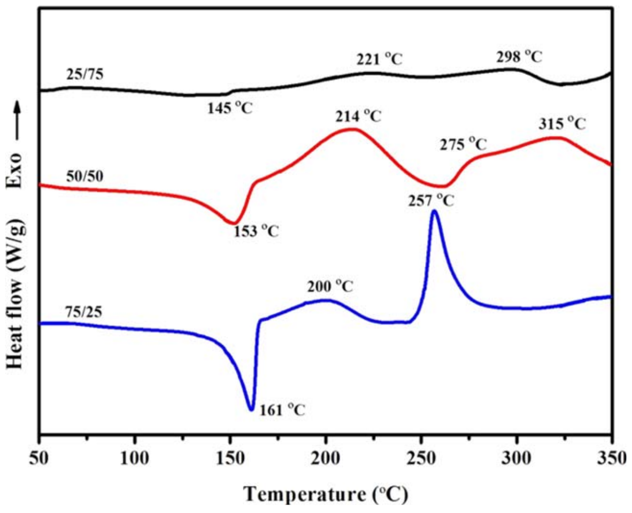

Figure 2. DSC curves of 3-APN/EP matrix blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA Q50. The samples (10–15 mg) were heated from ambient to 800°C at a heating rate of 20°C/min under air flow with a purge of 40 mL/min.

Scanning Electron Microscope. Scanning electron microscope (SEM) was utilized to observe fracture surfaces of the GF/3-APN/EP laminates and identify failure interface and adhesion of GF/3-APN/EP matrices.

RESULTS AND DISCUSSION

Processing Behavior of 3-APN/EP Matrices

To define cure parameters of manufacturing processes being considered, the curing behaviors of 3-APN/EP matrix blends of were studied by DSC in Figure 2. The melting temperature (T_m), first peaking curing temperature (T_{fp}), second peaking curing temperature (T_{sp}), third peaking curing temperature (T_{tp}), first curing temperature enthalpy (ΔH_{fc}), second curing temperature (ΔH_{sc}), and third curing temperature (ΔH_{tc}) were listed in Table II. The T_m increases with the increase in the 3-APN content, which was dependent on the composition of the blends. For 100/0 3-APN/EP matrix, the sample exhibited a single endothermic peak (175°C) with the exothermic transition temperature (239°C).[24] EP is a mixture of linear oligomers in

Table II. Curing Properties of 3-APN/EP MATRIX BLENDS

Samples	T_m (°C)	T_{fp} (°C)	T_{sp} (°C)	T_{tp} (°C)	ΔH_{fc} (J/g)	ΔH_{sc} (J/g)	ΔH_{tc} (J/g)
25/75	145	221	298	–	43.9	56.13	–
50/50	153	214	275	315	143.1	8.8	27.7
75/25	161	200	257	–	100.4	192.7	–
100/0	175	239	–	–	179.3	–	–

the amorphous phase without a single melting peak. The 3-APN exhibits a single characteristic endothermic peak, which is attributed to the melting transition. Then, it was evident that the 3-APN/EP matrix blends exhibited one melting peak because of the existence of one predominant component, and the peak shifted to higher temperature with the increasing 3-APN content. All the 3-APN/EP matrix blends exhibited two exothermic peaks, representing two curing reactions. The first exothermic peak was because of the ring-open polymerization reaction of EPs via amino groups of the 3-APN and the peak temperature shifted with gradual decrease as the 3-APN content increased. Presumably, this is because the increase of amino group concentration enhanced the supply ability of the active hydrogen. However, the heat of reaction, ΔH_{fc}, for 50/50 3-APN/EP matrix blend was also marginally higher than that for both 25/75 and 75/25 3-APN/EP matrix blends, suggesting an increase in the degree of cure. This is related to the curing reaction mechanisms, the concentration of epoxy functional group in curing system and any possible catalytic effect of amino groups. The second peak corresponded to the polymerization reaction of nitrile groups of the 3-APN, indicating the cyclotrimerization of phthalonitrile via its amino groups and nitrile groups. Similar behavior was observed in the DSC curves of other self-catalytic phthalonitriles.[24] In addition, for 50/50 APN/EP matrix blend, the presence of an additional exothermic peak (T_{tp}) may be related to the decomposition reaction of unreacted EPs. These results showed that a large processing window (> 100°C) for 3-APN/EP matrix blends was obtained, implying that the matrix had good flowability at relatively low temperature and can react at high temperature. Therefore, the processing temperature is very desirable for producing prepregs and then can be set far blow T_{tp} with gradual elevation.

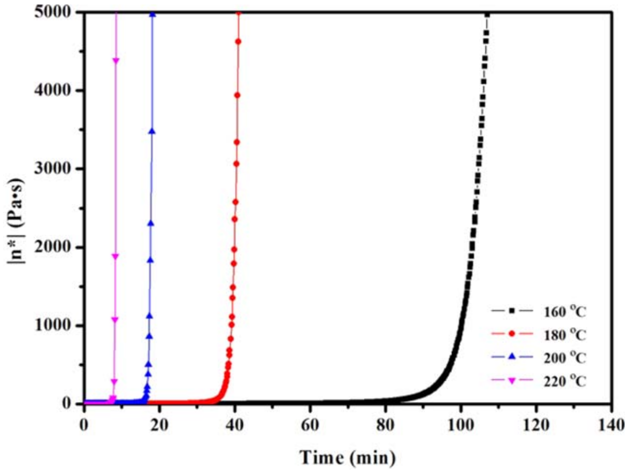

Figure 4. Complex viscosity (η^*) as a function of time at various temperatures for 50 : 50 3-APN/EP matrix prepolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Rheological measurements were conducted on the matrix material to identify optimal prepregging parameters and predict processability because viscosity is the most critical parameter for the processing of prepregs. The complex viscosity of the 3-APN/EP matrix blends was determined as a function of temperature from 150°C to 300°C. In Figure 3, the initial melt viscosities are low ranging between 0.01 and 1 Pa·s and the initial responses of the matrix blends were similar to that of neat epoxy in terms of the Newtonian behavior. As the temperature increases, the 3-APN/EP (25/75, 50/50, and 75/25) matrix blends displayed a rapid increase in viscosity on melting at 225°C, 232°C, and 238°C, respectively. This behavior, indicative of the gelation of the matrix from a Newtonian fluid to a rubbery state, revealed that polymerization of the matrix blends was progressing. The viscosities vs. temperature measured for the matrix blends are useful to determine rheological parameters of the 3-APN/EP matrix prepolymers. It is well-known that a desirable prepolymer for thermosetting resins was important to fabrication of the prepreg tape. Figure 4 shows complex viscosity change vs. time for the 50/50 3-APN/EP matrix prepolymer at several different temperatures. At higher the temperature, the viscosity increased at a faster rate. Based on these data, high temperature has a great tendency to accelerate polymerization reaction of the matrix prepolymer. For

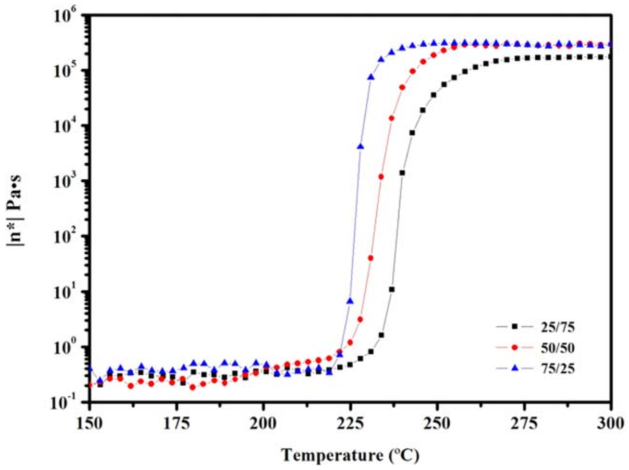

Figure 3. Complex viscosity (η^*) as a function of temperature for 3-APN/EP matrix blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

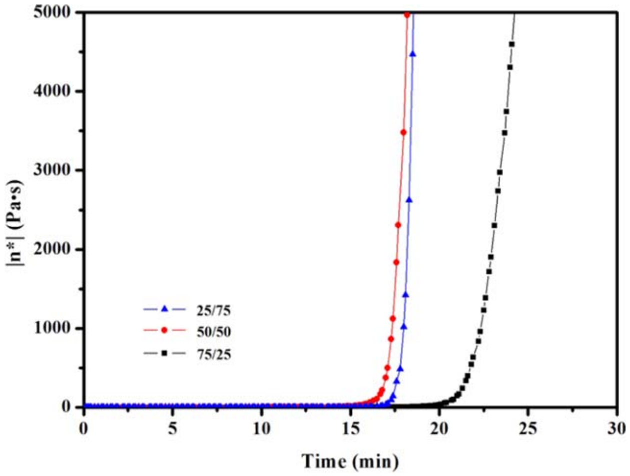

Figure 5. Complex viscosity (η^*) as a function of time at 200°C for 3-APN/EP matrix prepolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

comparison, isothermal viscosity measurements were recorded on the 3-APN/EP prepolymers at 200°C as a function of time. As depicted in Figure 5, a complex melt viscosity of around 0.01–0.1 Pa·s was observed for all the matrix prepolymers at 200°C, initially. These low-melt viscosities may prove useful for processability and good wetting of fibers. Then, all the matrix prepolymers exhibited a dramatic increase viscosity when held at 200°C. Obviously, complex viscosity of 3-APN/EP (25/75, 50/50 and 75/25) matrix prepolymers increased to 500 Pa·s in about 18, 16, and 22 min, respectively. It is understood that the complex viscosity changes accompanying the gel time is consistent with the start of cross-linking network formation. Therefore, these data revealed that the matrix blend has the desirable processing temperature for producing prepregs. Several important processing parameters, such as value of viscosity, gel time, processing temperature, and the effects of 3-APN content were evaluated to manufacture GF/3-APN/EP laminates.

Mechanical Behavior of GF/3-APN/EP Laminates

Flexural properties for these GF/3-APN/EP laminates were analyzed to determine room temperature mechanical behavior by 3-point bend test. Flexural strength can be calculated using the standard ISO178–1993. Figure 6(a) shows flexural strength for different laminates obtained by averaging five flexural tests for each sample. The 25/75 GF/3-APN/EP laminate has the highest ultimate flexural strengths (737 MPa). Compared to the 25/75 GF/3-APN/EP laminate, the decrease in the flexural strength is significant (15% for 50/50, 23% for 75/25, and 29% for 100/0) as the 3-APN content increases. This is because epoxy only accounts for less than 25 wt % of the laminates. It should be noted that EP can contribute in an effective way to improve mechanical properties of the composite laminate because of good impregnation and adhesion between fiber reinforcements. Therefore, it is important to select the favorable epoxy content for the laminates.

Then, it is interesting to note mechanical behavior for 50/50 GF/3-APN/EP laminate by processing conditions with different processing pressures. In Figure 6(b), we were surprised to see the significant improvements in flexural strength for the samples (20 MPa pressure) which compare with that of the samples (15 MPa pressure). There was, however, a small growth in flexural strength with increasing the processing pressure (30 MPa pressure), indicative of the pressure in saturation. The increase in laminate strength is believed to be mainly attributable to the improvement in interfacial interaction between the matrix and the fiber by physical effect of processing pressures. Then, to further study the effect of processing pressures and any possible catalytic effect of processing temperatures and time, the flexural strength of 50/50 GF/3-APN/EP laminate was plotted against

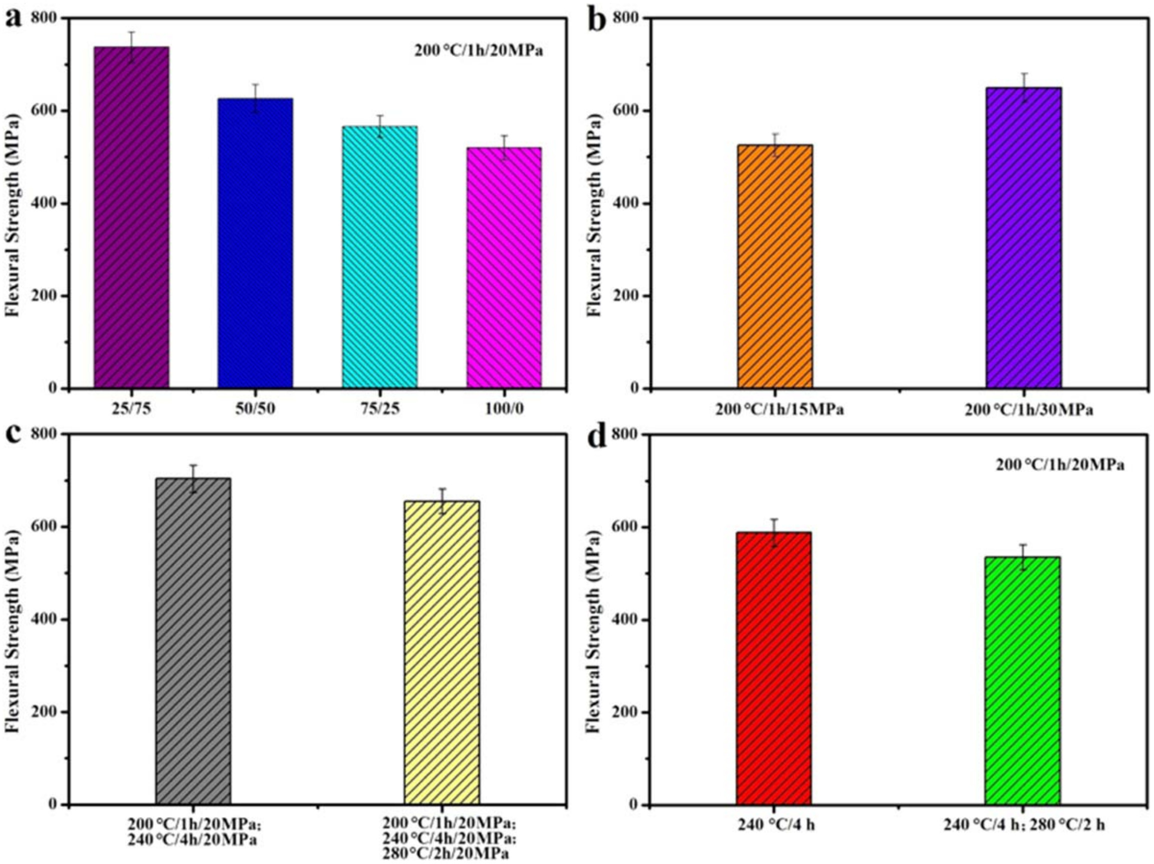

Figure 6. Flexural strength of GF/3-APN/EP laminates vs. processing conditions: (a) different proportions, (b) different processing pressures, (c) different processing temperatures and time, and (d) different postheated temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

processing temperatures and time [Figure 6(c)]. The flexural strength of 50/50 GF/3-APN/EP laminate manufactured at 200°C for 1 h and 240°C for 4 h with 20 MPa pressure, about 704 MPa was marginally higher than that for the other two processing conditions. The improved strength is believed to be a consequence of high degree of cure between 3-APN and EP on the fabric–matrix surface interfaces. The observed changes are evidence that the matrix are coreacting to form higher crosslinking density.[25,26] However, when the processing temperature is further elevated, the flexural strength will be decreased. This behavior can be interpreted as that the additional intercrosslinking networks was formed through nitrile groups of the 3-APN when the processing pressure is relatively increased. However, in the presence of rigid heterocyclic structure such as isoindoline, diimino, triazine, and phthalocyanine,[27–29] the interfacial surface area between the matrix and GF cannot be increased. Another factor might be because of the decomposition of untreated EP, which was harmful to load transfer. To explore this possibility, 50/50 GF/3-APN/EP laminate manufactured at 200°C for 1 h with 20 MPa pressure, was postheated at elevated temperatures without processing pressures [Figure 6(d)]. With increasing postheated temperatures, the flexural strength decreases gradually. This phenomenon might be resulted from more possibility of the existence of voids in composite laminates, which is because of the decomposition of untreated EP. To obtain a good balance of maintaining the mechanical behaviors, the copolymerization of 3-APN and EP must be eliminated by control of manufacturing processes. Hence, the manufacture processing adopted in this work guarantees that the flexural strength of GF/3-APN/EP laminates are dependent upon the complementary catalytic effect of the processing pressures, temperatures and time.

Thermomechanical Behavior of GF/3-APN/EP Laminates

The variation of storage modulus (G') and glass transition behavior (T_g) of GF/3-APN/EP laminates were investigated by means of DMA. Figures 7 and 8 show the thermomechanical behavior of GF/3-APN/EP laminates manufactured by different processing conditions. All composite laminates show similar storage modulus at 16–26 GPa up to 50°C; whereas each sample increases in modulus (18–32 GPa) suggesting continued curing as the sample is heated. However, as shown in Figure 7(d), 50/50 GF/3-APN/EP laminate manufactured at 200°C for 1 h with 20 MPa pressure and postheated at 240°C for 4 h and 280°C for 2 h, displays a small drop in modulus 50–150°C and ∼ 0.7 GPa. These data provide evidence that high temperature is

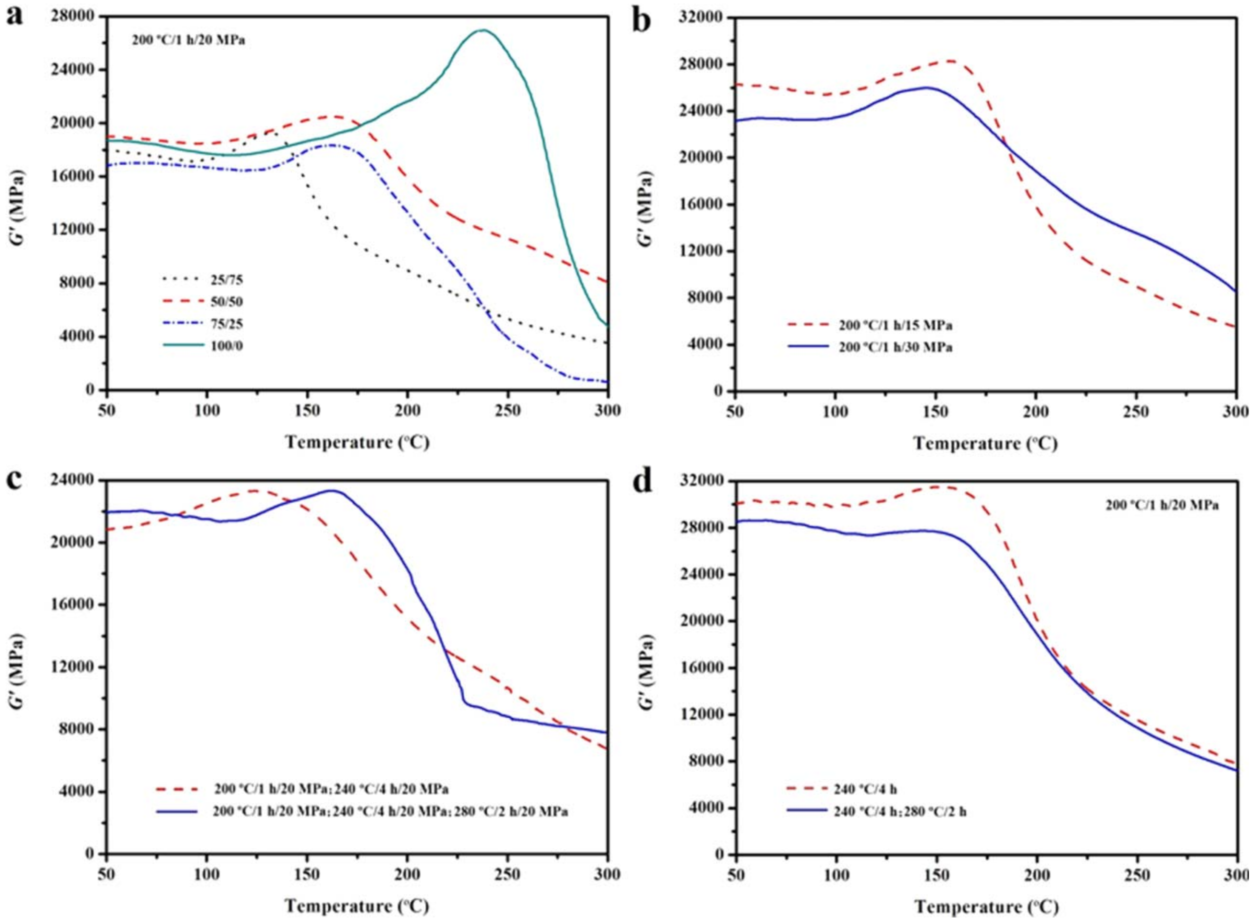

Figure 7. Storage modulus (G') behavior of GF/3-APN/EP laminates vs. processing conditions: (a) different proportions, (b) different processing pressures, (c) different processing temperatures and time, and (d) different post- heated temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

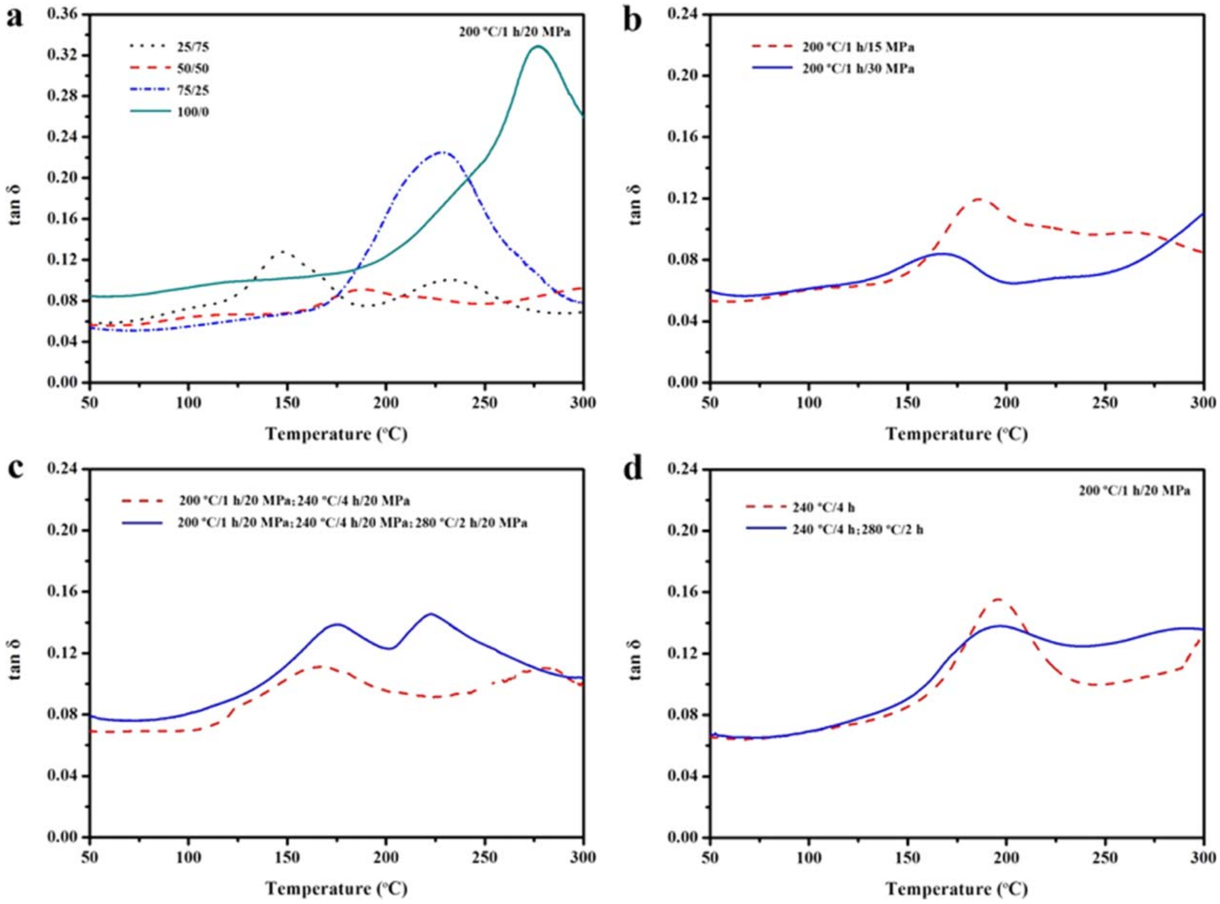

Figure 8. Tan δ behavior of GF/3-APN/EP laminates vs. processing conditions: (a) different proportions, (b) different processing pressures, (c) different processing temperatures and time, (d) different postheated temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

important to the copolymerization of phthalonitriles and EP because the curing process of these phthalonitriles carried out very slowly even at the fairly high temperatures.[30] This result is significant that GF/3-APN/EP laminates display superior thermomechanical performance at elevated temperatures.

Shown in Figure 8 are Tan δ curves providing valuable insights on the relationships between T_g, mechanical response, and morphology. The appearance of two separate glass transitions indicates that the 3-APN/EP matrix of the laminates have a two-

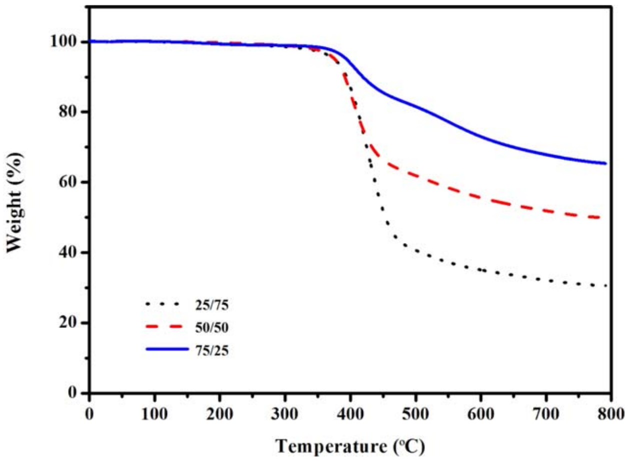

Figure 9. TGA curves of 3-APN/EP copolymers in nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

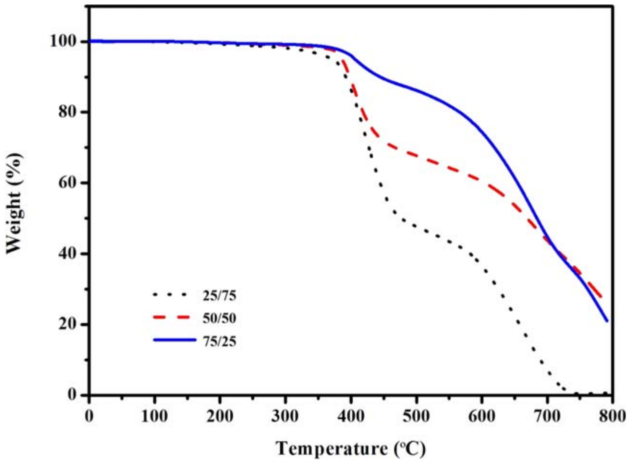

Figure 10. TGA curves of 3-APN/EP copolymers in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal and Thermo-Oxidative Stabilities of 3-APN/EP Matrix Copolymers

	Nitrogen				Air			
Samples	T_{on} (°C)	T_{m1} (°C)	T_{m2} (°C)	Char yield (%) at 800°C	T_{on} (°C)	T_{m1} (°C)	T_{m2} (°C)	Char yield (%) at 800°C
25 : 75	375	429	534	31	376	419	668	0.5
50 : 50	378	402	562	50	386	400	673	21
75 : 25	395	412	559	66	406	404	681	25

T_{on} is the onset decomposition temperature at which the weight loss is 5%.
T_{m1} is the maximum-rate decomposition temperature of first stage.
T_{m2} is the maximum-rate decomposition temperature of second stage.

phase structure, showing that the GF/3-APN/EP laminates display two high T_gs. The fact could lead to the conclusion that a partial phase separation of the 3-APN from the EP phase can occur. As the 3-APN content increases, the T_g of the EP phase on the matrix increases, indicating an increase in crosslink density. In the ring-open polymerization of EP, the increase of amino group concentration causes the higher supply ability of the active hydrogen resulting in a higher degree of cure and therefore higher crosslink density and a higher T_g. In addition, the second glass transition increased with an increase content of 3-APN. This observation is attributed to the polymerization reaction of nitrile groups of 3-APN. It is seen that the 3-APN/EP matrix were indeed phase-separated and exhibited the double curing reactions. However, the 75/25 and 100/0 GF/3-APN/EP laminates showed only one transition in Figure 8(a), which is in a good agreement with the existence of one predominant component. We also performed the DMA analysis for only 50/50 GF/3-APN/EP laminates in order to observe if a transition associated to the processing pressures. As shown in Figure 8(b), a small reduction in T_g, indicative of the uncompleted cure of EP phase, is because of the present of increasing processing pressure physically hindered the molecular mobility and the cross-linking reaction in inherent space. Nevertheless, the improvement in the glass transition of 3-APN phase is associated with better fluidity of 3-APN monomer. Meanwhile, the effect of processing temperatures and time loading on the T_g is investigated and shown in Figure 8(c). It is obvious that the increasing temperature and time showed a decrease relationship to the T_g of both EP and 3-APN phases, suggesting the decomposition of untreated EP. There appear to be one main explanation for nonstoichiometric balance between epoxy and curing agent with the inhibition of cross-linking reaction.[31] Figure 8(d) also indicates that the effect of postheated treatment method without processing pressures is determined. As the postheated temperature increases, the T_g of the 50/50 GF/3-APN/EP laminate increases. It is worthy to stand out that temperature ramping DMA data only provide a guide on processing the cure reaction of GF/3-APN/EP laminates in the presence of different manufacturing parameters. It is related to that the variation in processing pressures and temperatures changes the rate and degree of cure for the double curing reaction steps. Finally, it was demonstrated that the fabrication of the GF/3-APN/EP laminates can be appreciated separately. Then, the composite laminates can be prepared at low temperature and used at high temperature.

Thermal Behavior of GF/3-APN/EP Laminates

As the basic properties of the matrix, the thermal and thermo-oxidative stabilities of the 3-APN/EP matrix copolymers that had been cured without addition of any other curing additives were determined by TGA analysis. Results of these studies were shown in Figures 9 and 10. A weight loss of 5% (T_{on}), the maximum-rate decomposition temperature of first stage (T_{m1}), maximum-rate decomposition temperature of second stage (T_{m2}), and the percentage of residue remaining (char yield %) after heating the samples to 800°C in nitrogen and air atmosphere are listed in Table III. Obviously, the decomposition temperatures for the 3-APN/EP copolymers were greatly improved compared with that of the neat EP. According to these results, T_{on} is somewhat higher with EPs, which may be ascribed to heterogeneity of the crosslink density of the 3-APN/EP copolymers. Moreover, these improvements in the thermal and thermo-

Table IV. Thermal Properties of GF/3-APN/EP Laminates

			Air		
Samples	TTP (°C/h/MPa)	TT (°C/h)	T_{on} (°C)	T_{m1} (°C)	T_{m2} (°C)
25/75	200/1/20	-	354	347	561
50/50	200/1/20	-	394	335	576
75/25	200/1/20	-	427	332	586
100/0	200/1/20	-	540	-	586
50/50	200/1/15	-	379	332	574
	200/1/30	-	425	334	581
50/50	200/1/20→ 240/4/20	-	412	330	576
	200/1/20→ 240/4/20→ 280/2/20	-	427	324	574
50/50	200/1/20	240/4	496	348	576
	200/1/20	240/4→ 280/2	490	-	582

TTP, temperature, time and press (TTP) of different processing conditions.
TT, postcuring temperature and time (TT) of GF/3-APN/EP laminates.
T_{on} is the onset decomposition temperature at which the weight loss is 5%.
T_{m1} is the maximum-rate decomposition temperature of first stage.
T_{m2} is the maximum-rate decomposition temperature of second stage.

oxidative stabilities were attributed to the increase cyano group concentration from the 3-APN monomer. Meanwhile, the 3-APN/EP matrix copolymers show a two-stage decomposition process: the T_{m1} was centered at 400–429°C; the T_{m2} occurred at 534–681°C. Additionally, the T_{on} was centered at 375–406°C. The results indicated the 3-APN/EP matrix have a two-phase structure, which is consistent with the DSC, DRA, and DMA studies. The 31–66% and 0.5–21% char yields remained at 800°C under nitrogen and air, respectively. Then, the 3-APN/EP copolymers exhibited good thermal and thermal-oxidative stabilities, owing to the high aromatic nature of the system and the cross-linking density after cured. Therefore, these data revealed that high thermal and thermal-oxidative stabilities of the 3-APN/EP copolymers appeared to be very used to the application.

Additionally, the 3-APN/EP system was used as matrix in GF composite laminates in the applications. Therefore, thermal properties of different GF/3-APN/EP laminates were investigated in air atmosphere and the main results were listed in Table IV. It also showed that the occurrence of reaction-induced phase separation has an influence on thermal behavior of GF/3-APN/EP laminates by different processing conditions. The laminates show a two-stage decomposition process: the maximum-rate decomposition temperature of first stage (T_{m1}) was centered at 324–427°C; the maximum-rate decomposition temperature of second stage (T_{m2}) occurred at 534–628°C. Additionally, a weight loss of 5% (T_{on}) were centered at 354–496°C. For the 50/50 3-APN/EP matrix, the T_{on} of the GF/3-APN/EP laminates increased relative to the 3-APN/EP copolymers. But, T_{m1} and T_{m2} decreased obviously. The reduction of thermal stability is related to the fact that the influence of the manufacture processes. Overall, the thermal result revealed that the 3-APN/EP matrix and GF/3-APN/EP laminates have high thermal and thermo-oxide stabilities for a particular application tailored by different processing conditions.

Fractures Surface Morphology of GF/3-APN/EP Laminates

Fracture surface of different GF/3-APN/EP laminates were observed by SEM at low magnification and shown in Figure 11.

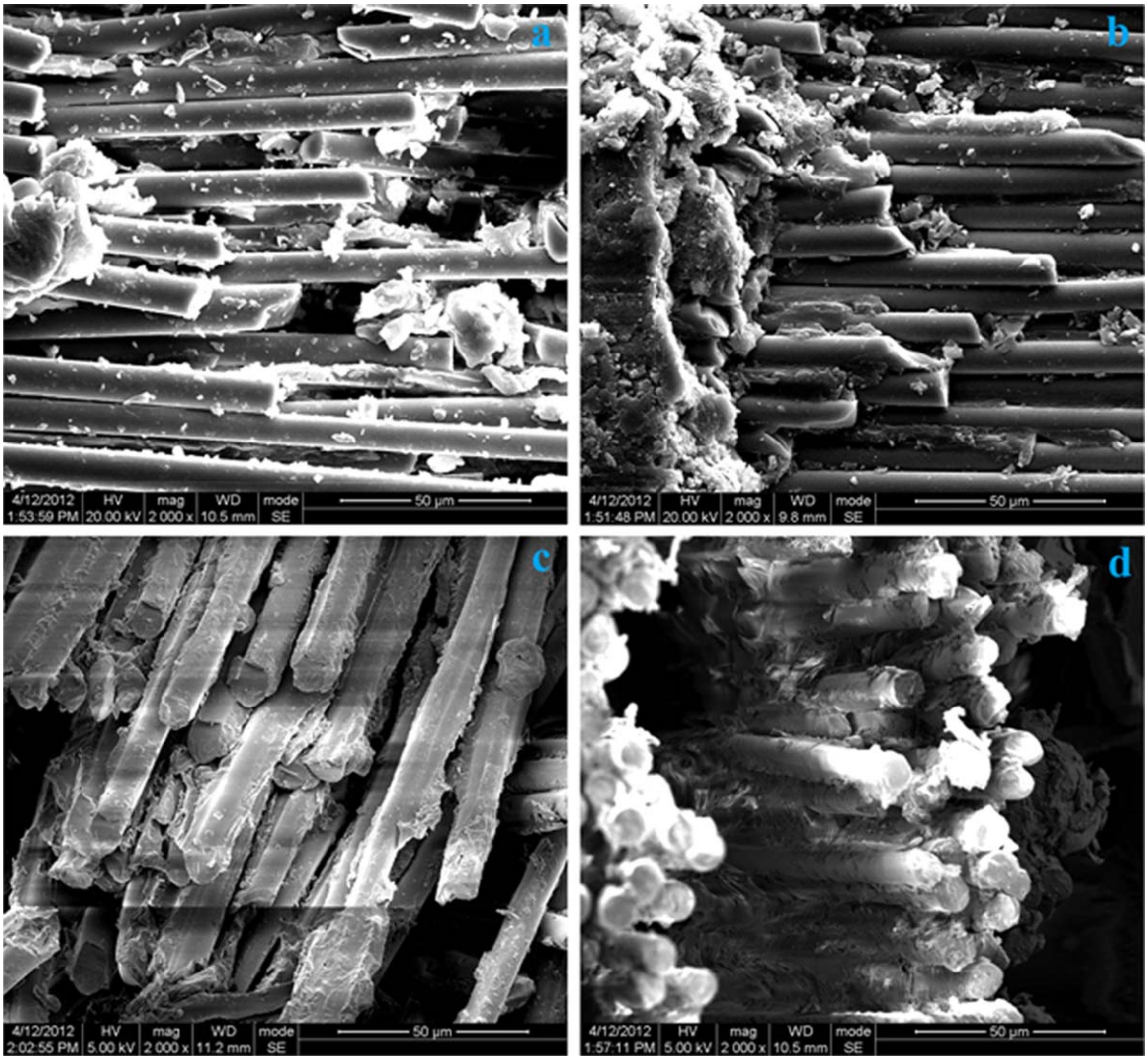

Figure 11. SEM micrographs (at low magnification) of 50/50 GF/3-APN/EP laminates vs. processing conditions: (a) 200°C/1 h/15 MPa, (b) 200°C/1 h/20 MPa, (c) 200°C/1 h/20 MPa; 240°C/4 h/20 MPa, and (d) 200°C/1 h/20 MPa; 240°C/4 h and 280°C/8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

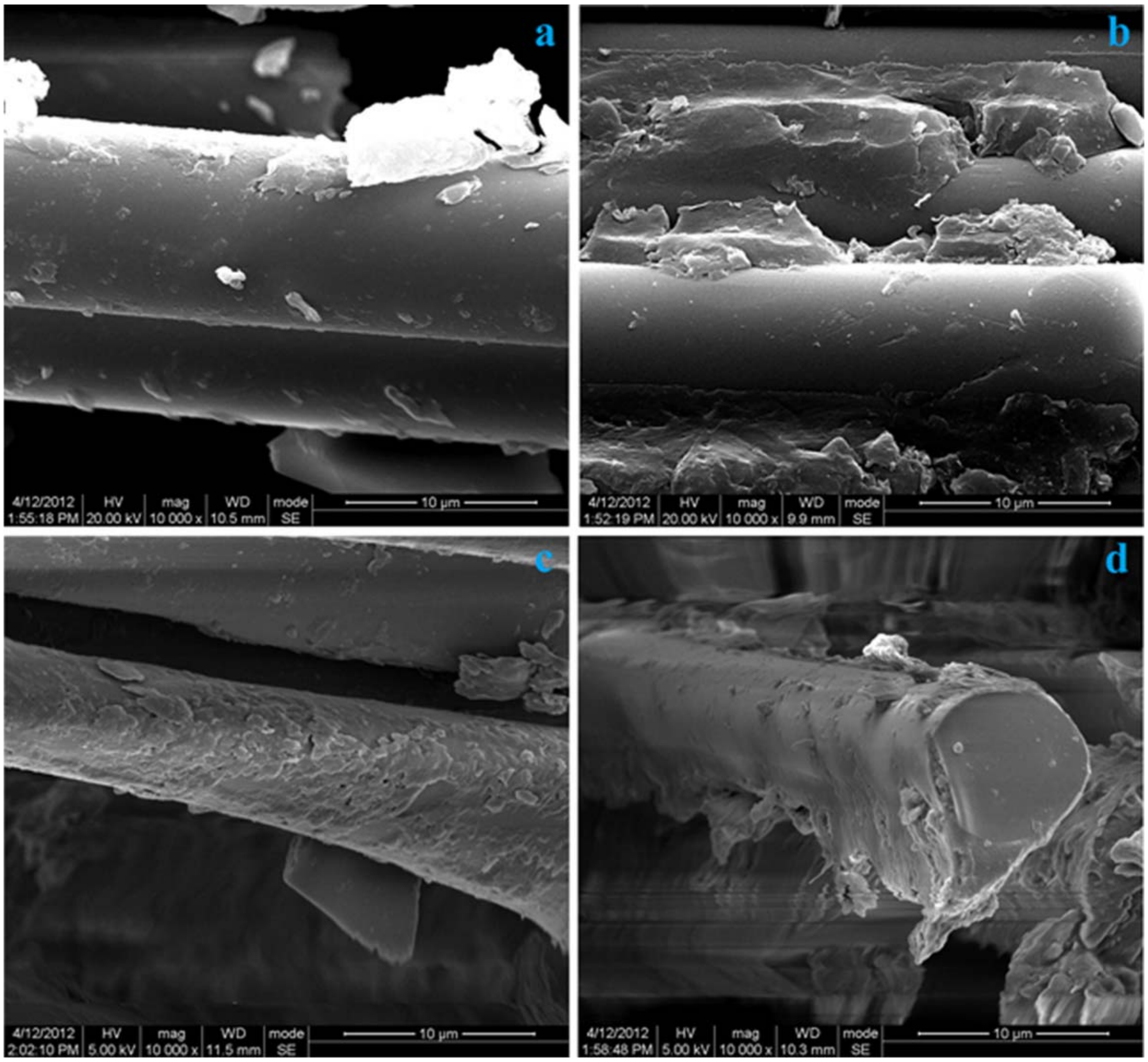

Figure 12. SEM micrographs (at high magnification) of 50/50 GF/3-APN/EP laminates vs. processing conditions: (a) 200°C/1 h/15 MPa, (b) 200°C/1 h/20 MPa, (c) 200°C/1 h/20 MPa; 240°C/4 h/20 MPa, and (d) 200°C/1 h/20 MPa; 240°C/4 h and 280°C/8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To better illustrate the degree of compatibility and fracture morphology, the SEM micrographs with the higher magnification are depicted in Figure 12. At high magnification, a good adhesion has been achieved by high pressures and temperatures. This demonstrates that the processing pressure of manufacturing process enables the effective interfacial interaction between GFs and the 3-APN/EP matrix. Also, the post-heated treatment method can improve the degree of copolymer coverage on the surface of GFs. The fracture surface analysis confirms that the dependency of fracture morphology on processing conditions will affect the laminate mechanical performance, which also is in a good agreement with the observation by means of flexure tests of GF/3-APN/EP laminates.

CONCLUSION

Different manufacture processing conditions were used to fabricate the GF/3-APN/EP laminates with different parameters such as pressures, temperatures, and time. Meanwhile, post-heated treatment as another parameter was also carried out to study the properties of the 50/50 GF/3-APN/EP laminate, revealing a comparable behavior. Consequently, The 50/50 GF/3-APN/EP laminates, manufactured at 200°C for 1 h and 240°C for 4 h with 20 MPa pressure, demonstrated an enhanced flexural strength (> 700 MPa) and T_g (> 280°C), showing excellent thermal and thermal-oxide stabilities. The reported experiments show that the modification of the mechanical properties, thermal stability, and fracture morphology of GF/3-APN/EP laminates depends on the complementary catalytic effect of the processing pressures, temperatures, and time. The study of manufacturing process offers a very effective advantage in application of the composite laminates. The composite laminates can be manufactured at low temperatures and simultaneously be used as advanced composites at high temperatures.

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