

Study on the heat resistance and mechanical properties of polytriazole resin matrix composite influenced by graphene oxide

Shen Zhen¹, Zeng Jin-fang, Dai Panyao, Wang Kaijie, Wang Xiu-yun

Xi'an Aerospace Composites Research Institute, Xi'an 710025, China

Keywords: Polytriazole resin, Graphene oxide, Heat resistance, Mechanical property, Composite

ABSTRACT

The dependence of heat resistance and mechanical properties of polytriazole (PTA) resin matrix composites on the post-treatment temperature and time and the introduction of graphene oxide (GO) and alkynyl-pendant GO was investigated in this study. The post-treatment temperature was conducive to the glass transition temperature (T_g) of T700/PTA resin composite, while the effect of post-treatment time on the T_g of composite was insignificant. As the post-treatment temperature increased from 180 °C to 220 °C, the improvement of T_g of composite reached 20.4 °C. T700/PTA resin composite showed the high bending strength and shear strength when the post-treatment temperature was 200 °C, however, the bending strength and shear strength decreased observably as the post-treatment temperature increased from 200 °C to 220 °C. The compatibility between PTA resin and GO might be enhanced by the hydrogen bond interaction, while both the hydrogen bond interaction and the Huisgen 1,3-dipolar cycloaddition of azide and alkyne groups might be conducive to the good compatibility between PTA resin and alkynyl-pendant GO. As the dosage of GO and alkynyl-pendant GO was 1.0%, the T_g of /PTA matrix resin composite increased by 15.7 °C and 27.9 °C, respectively. However, the bending strength and shear strength of composite with GO was closed to the composite with alkynyl-pendant GO. In conclusion, the introduction of alkynyl-pendant GO could make great contribution to the good heat resistance and high mechanical properties of PTA resin matrix composites at the appropriate post-treatment temperature and time, and it might have a good prospect in the application of solid rocket motor case.

1 INTRODUCTION

Recently, advanced composites have been widely used for structural materials in the field of aviation and aerospace due to their good heat resistance and the high specific strength and modulus. However, the high cost of advanced composites limits their applications. With the rapid development of polymer technology, the composite with low temperature molding (LTM) resin matrix, which can be manufactured at low temperature but exhibiting high performance, has been more and more popular. In the past 40 years, the ACG Corporation (U.K.) and the Air Tech Corporation (U.S.A.) have developed a series of LTM products [1].

¹Corresponding author. Tel.: +86 18392684776.
E-mail address: 1131294944@qq.com (Z. Shen).

The most studied matrix for LTM composite materials were epoxy resin, cyanate resin and polytriazole (PTA) resin. Epoxy resins have been widely used in the field of aviation and aerospace because of their outstanding mechanical and thermal properties and processability. However, the application of traditional epoxy resins could be limited by their low glass transition temperatures (T_g) [2]. The high post-treatment temperature imposes restrictions on its application of the cyanate resin. A series of PTA resins have been prepared from Huisgen 1,3-Dipolar cycloaddition reaction of an azide and an alkyne by East China University. These PTA resins are a novel kind of crosslinkable polymers presenting low temperature curing character (60~80 °C), good processability, good mechanical and thermal properties, which could be utilized for the matrix of high performance composites [3-8].

Graphene oxide (GO) is a single layer material prepared by the oxidation of graphite and ultrasonic dispersion, possessing the large specific surface area. There are a lot of hydroxyl and epoxy groups on the surface and some carboxylic groups at lateral side [9]. The functional groups on the surface of GO can enhance the dispersion of GO in a polymeric matrix and the interfacial interaction between GO and polymeric matrices [10]. Because of the active oxygen functional groups located at their surfaces, GO can be dispersed in polar polymers such as poly(vinyl alcohol) [11], polyurethane [12] and polyamide [13] at a molecular level with strong adhesions. Unfortunately, owing to the hydrophilic nature, GO is incompatible with most organic solvents and nonpolar polymers. GO tends to form agglomerates in nonpolar polymer matrices because of their incredible interlayer cohesive energy [14], thereby making the fabrication of GO-based nonpolar polymer composites unfeasible. In this regard, several strategies for the functionalization of GO have been proposed. Wherein, based on the reactive oxygen functionalities at GO surfaces, covalent modification of GO is suggested to be a promising method for achieving excellent compatibility between GO and polymers in that it can minimize the interfacial tensions between them [14,15]. Cao et al functionalize GO by covalent modification and found that SEBS-clicked GO showed excellent compatibility with a PS matrix, and remarkably improved mechanical properties and thermal stability [16].

The “click” reaction [17] of Huisgen 1,3-dipolar cycloaddition between azides and alkynes has been proved to be a versatile method to promote the development of polymer chemistry due to its high specificity, compatibility with a variety of functional groups, solvent insensitivity, and applicability under mild conditions. The introduction of azide or alkyne groups on the surface of GO might present a good compatibility with PTA resin.

To meet the stringent requirements for the heat resistance of matrix, the heat resistance of polytriazole resin matrix composite still need to be improved. In this paper, the optimization of post-treatment temperature and time and the introduction of nano-materials were used for the enhancement of heat resistance of polytriazole matrix composite. The effect of post-treatment temperature and time on the glass transition temperature (T_g), bending strength and shear strength of T700/PTA resin composite was investigated. Besides, the introduction of GO and alkynyl-pendant GO as nanofiller for the development of heat resistance and mechanical properties of polytriazole resin matrix composite was also studied. Both X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy were utilized for the characterization of the compatibility between GO or alkynyl-pendant GO and PTA resin. The thermal and mechanical properties of the PTA resin composite were also characterized. The investigation of thermal and mechanical properties of PTA resin composite could provide insight into a potential matrix for advanced composites.

2 EXPERIMENTAL SECTION

2.1 Materials

The PTA resin was provided by East China University of Science and Technology. The T700 carbon fibers were supplied by the Toray Corporation in Japan. GO was prepared pressurized oxidation method and ultrasonic dispersion, and the detailed pressurized oxidation method was adopted according to Bao et al. [18]. For the improvement of compatibility between GO and PTA resin, alkyne-pendant GO was prepared according to a procedure that was reported by Pan et al. [19]. Satin carbon cloth was purchased from Tianniao High Technology Co., Ltd.

2.2 Preparation of unidirectional T700/PTA resin composite

The prepreg for T700/PTA resin composite specimens with resin content about $30\pm 2\%$, can be prepared by impregnating the carbon fiber directly with the polytriazole resin solution (50wt%) at room temperature, and then going through the continuous drying stove with $150\text{ }^{\circ}\text{C}$. Unidirectional T700/PTA resin composite were manufactured using 10 prepreg tapes stacked onto the mold and pressed on a pressure machine for curing. The composite specimens were cured at $80\text{ }^{\circ}\text{C}$ for 3h under a pressure of 1.0-1.5 MPa, and the finished prepreg tape were transferred into an oven and postcured at different temperature and time.

2.3 Preparation of PTA resin modified by GO or alkynyl-pendant GO

PTA resin modified by GO or alkynyl-pendant GO was prepared by solution mixing method. Briefly, a mixture of GO or alkynyl-pendant GO aqueous solution and PTA solution was stirred to be homogeneous, and then transferred to ultrasonic-microwave combination system. After being ultrasonicated and strong mechanical stirred for 20 min, the PTA solution undergo final curing within an autoclave at $80\text{ }^{\circ}\text{C}$ for 3h. The cured PTA resin was transferred into another oven for being postcured at an appropriate post-treatment temperature and time.

2.4 Preparation of T300 carbon cloth/modified PTA resin composite

The acetone solutions containing varying concentrations of GO or alkynyl-pendant GO (0, 0.1%, 0.5 %, 1.0 %, 1.5% and 2.0% w/v) were introduced into the PTA solution, and then transferred to ultrasonic-microwave combination system ultrasonicated for 20 min. Furthermore, the test prepreg specimens were manufactured utilizing the hand lay-up process. Preforms undergo final curing within a pressure machine at $80\text{ }^{\circ}\text{C}$ for 4h under a pressure of 1.0-1.5 MPa, and then postcured at an appropriate post-treatment temperature and time. Thus, the composite laminate with resin content of $30\pm 2\%$ was obtained.

2.6 Characterization

To investigate the curing behavior of PTA resin, differential scanning calorimetry was carried out on the DSC204F1 (NETZSCH, Germany) analyzer under nitrogen with a heating rates of $5\text{ }^{\circ}\text{C}/\text{min}$. Moreover, FT-IR spectra (FTIR2000, US) were used to characterize PTA resin and modified PTA resin in the range of 500cm^{-1} to 4000cm^{-1} . XPS of modified PTA resin was obtained on a K-Alpha electron spectrometer (Thermo, US). For the characterization of T_g of composite, dynamic mechanical analysis (DMA) was conducted on a DMA 242C instrument (NETZSCH, Germany) with a fixed frequency of 1Hz from $30\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$. Besides, the dynamic storage modulus was also plotted. Thermal degradation of PTA resin, GO, alkynyl-pendant GO and modified PTA resin was studied by the TG209F3 (NETZSCH, Germany) analyzer at a linear heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from $30\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ under a nitrogen flow ($80\text{ mL}/\text{min}$). The bending strength and shear strength of composites

were determined by an electronic universal testing instrument (INSTRON-405, UK) in the light of the national standard of China GB/T1458-2008 and GB/T 1449-2005, respectively.

3. RESULTS AND DISCUSSION

3.1 Curing behavior of PTA resin

To work out an appropriate curing cycles and post-cured cycles for PTA resin, DSC test was conducted and the DSC curve of PTA resin was depicted in Figure 1. As shown in Figure 1, the DSC curve of PTA resin presented one endothermic peak and two exothermic peaks. The endothermic peak in the range of 30 °C to 50 °C was attributed to the evaporation peak of the acetone. The cycloaddition reactions of alkyne and azide groups contributed to the exothermic peak in the range of 80 °C to 200 °C, while the exothermic peak ranging from 200 °C to 230 °C might be ascribed to the reactions of the residual alkynyl groups. The exothermic reaction heat of PTA resin reaches 692 J/g that is much higher than that of modified bismaleimide resin (398 J/g) [19]. Owing to the high exothermic reaction heat, the curing rate needs to be controlled in case of the occurrence of violent polymerization during curing. Therefore, the initial curing of PTA resin should be conducted at the temperature of 80 °C for a long period of time to realize the reaction of most alkyne and azide groups, and then PTA resin could be post-cured at higher temperature making the curing continued.

Figure 2 shows the FT-IR spectra of PTA resin at different postcuring temperatures. The characteristic peak at 3133cm^{-1} can be attributed to the absorption of C-H on 1, 2, 3-triazole heterocycles resulted from the cycloaddition reactions between azide and alkyne groups. The peak at 2096cm^{-1} corresponds to the absorption of azides ($\text{N}=\text{N}=\text{N}$) and alkynes ($\text{C}\equiv\text{C}$), and its intensity decrease gradually for the PTA resin with the increase of postcuring temperature, clearly showing the gradual consumption of the reactive groups of the cycloaddition reaction.

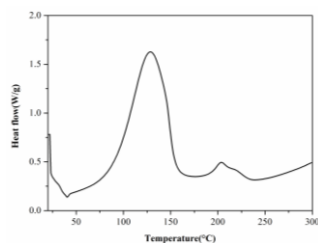


Figure 1: DSC curve of PTA resin

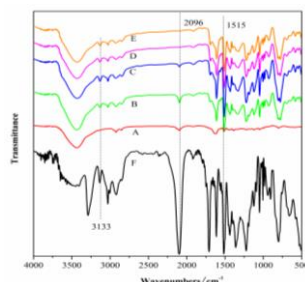


Figure 2: FT-IR spectra of PTA resin (F) and the resin (A-E) postcured at different temperatures

As shown in Table 1, the curing degrees of PTA resin increased with the postcuring temperature, which is consistent with the results from FT-IR measurement. The curing degrees of PTA resin based on the peak at 2096cm^{-1} , even though there existing slight difference. When the postcuring temperature of PTA resin reached 200 °C, the peak at 2096cm^{-1} almost disappeared. The curing degree

of PTA resin reached 99% after being postcured through 160 °C/2h+200 °C/3h. This phenomenon suggested that most of alkyne and azide groups had participated in the cycloaddition polymerization.

	Curing stage	Postcuring temperature	Curing degree (%)
A	80 °C/3h	80 °C/5h	78.5
B	80 °C/3h	160 °C/5h	95.7
C	80 °C/3h	160 °C/2h+180 °C/3h	99.5
D	80 °C/3h	160 °C/2h+200 °C/3h	99.9
E	80 °C/3h	160 °C/1h+200 °C/2h+220 °C/2h	100

Table 1: Curing degrees of the PTA resin at different postcuring temperature by DSC measurement.

3.2 Thermal properties of the PTA resin

The DMA curves of the PTA resin under different post-treatment temperature are shown in Figure 3 and the T_g of PTA matrix composite are listed in Table 2. As can be seen from Figure 3(a), the storage modulus of PTA matrix composite increased with the improvement of postcuring temperature, suggesting that the enhancement of curing degrees of PTA resin contributed to the rigidity of polymer chain. The peak at 210 °C for PTA matrix composite after being postcured through 160 °C/2h +200 °C/3h, which can be ascribed to the excessive un-reacted alkynyl groups. As shown in Table 1 and Figure 3(b), the T_g of the PTA matrix composite increased from 188.5 °C to 208.9 °C when the post-treatment temperature raised from 180 °C to 220 °C. Due to the fact that the alkyne groups could polymerize obviously with itself while the temperature was above 200 °C [7, 19], the T_g of the PTA matrix composite would increase as composite was postcured at 220 °C.

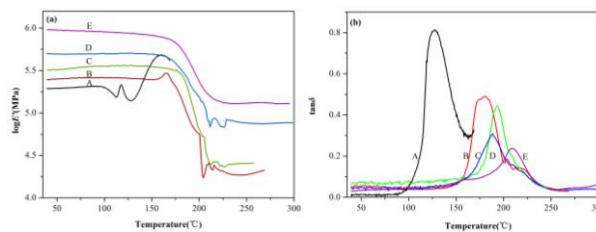


Figure 3: DMA curves of the T700/PTA resin composites (heating rate 3 °C/min, 1 Hz)

Post-treatment temperature (°C)	80	160	180	200	220
T_g (°C)	127.8	180.2	188.5	193.5	208.9
T_{d5} (°C)	351.3	349.9	350.2	349.8	351.5

Table 2: Thermal properties of the PTA resins with different post-treatment temperature

As shown in Table 2, the influence of post-treatment temperature on the decomposition temperature T_{d5} (the temperature of decomposition at 5% weight loss) of PTA resin under nitrogen was insignificantly, and the T_{d5} of PTA resin with different post-treatment temperature kept at 350 °C. The PTA resin exhibited higher thermal stability than that of universal epoxy resins [5]. The degradation of the cured PTA resin always initiated at the weakest points of cleavages in the crosslinked PTA network. As a matter of fact, the covalence energies for the bonds C-C (334 kJ/mol) is higher than that of C-N (276 kJ/mol). Therefore, the breakage of CH₂-N bond is easier than that of C-C bond, which is corresponds with the results investigated by Xue et al. [1].

After being cured through 80 °C/3h+160 °C/2h, the unidirectional T700/PTA matrix composite were postcured at 180 °C, 200 °C and 220 °C for 1h, 2h and 3h, respectively. The T_g of PTA matrix composite under different post-treatment time was list in Table 3. As shown in Table 3, the T_g of PTA matrix composite changed insignificantly with the extension of post-treatment time. Because the intermolecular steric hindrance of PTA resin inhibited the reaction of the residual groups, the extension of post-treatment time was uncondusive to the improvement of curing degree. Hence, the post-treatment time show insignificant effect on the of PTA matrix composite.

Post-treatment temperature (°C)	180			200			220		
Post-treatment time (h)	1	2	3	1	2	3	1	2	3
T_g (°C)	200.1	201.7	200.7	210.2	208.7	207.9	221.5	221.0	222.1

Table 3: T_g of the PTA resins with different post-treatment temperature (heating rate 20 °C/min, 1 Hz)

3.3 Mechanical properties of the unidirectional T700/PTA matrix composite

The experimental results for mechanical properties of PTA matrix composite with different post-treatment temperature (80 °C, 160 °C, 180 °C, 200 °C and 220 °C) are depicted in Figure 4. Figure 4 shows that the flexural and shear properties of PTA matrix composite increased insignificantly as the post-treatment temperature raised from 80 °C to 200 °C, because the adhesions between T700 carbon fiber and PTA matrix is strong enough, meanwhile the mechanical properties of PTA matrix arrived at an equilibrium, which suggested that the increased curing degree of PTA resin has little impact on the mechanical properties of PTA matrix composite. However, the flexural and shear strength of T700/PTA matrix composite after being postcured at 220 °C decreased by 26.16% and 21.18% in comparison to that of 200 °C. This result might be attributed to the fact that the self-crosslinking reaction of excessive alkyne groups weakened the adhesions between T700 carbon fiber and PTA matrix, and then the stress concentration and interface debonding is easier to take place when stress is applied to the composite material. Besides, the N₂ generated by thermal degradation of residual azide groups contributed to the appearance of stress concentration. Both interface debonding and stress concentration have appreciable impact on the decline of mechanical properties of composite.

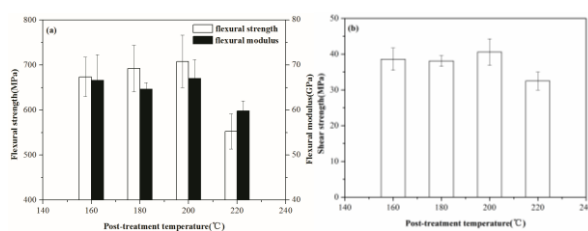


Figure 4: Flexural and shear properties of the cured PTA matrix composite at ambient temperature

The experimental results for mechanical properties of PTA matrix composites under different post-treatment time were shown in Figure 5. Figure 5 depicts that the extension of post-treatment time has insignificant influence on the mechanical properties of PTA matrix composite at room temperature and high temperature. It is found that the flexural and tensile strength retention ratio at 175 °C for PTA matrix composite postcured at 180 °C, 200 °C and 220 °C for 1h, achieved 66.93%, 62.08%, 61.66% and 60.50%, 69.26%, 60.93%, respectively, illustrating that the PTA matrix composite showed good

mechanical behavior under high temperature, and the extension of post-treatment time was uncondusive to its mechanical properties. Thus, it is enough to apply 1 h for the post-treatment time.

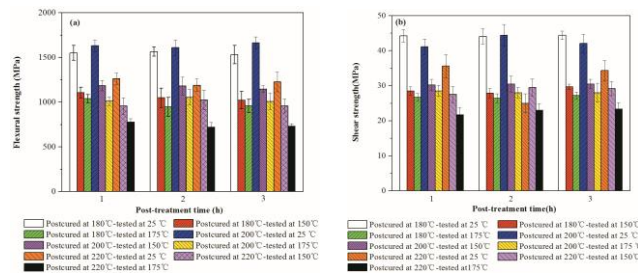


Figure 5: Flexural and shear strength of T700/PTA composite under different post-treatment time

3.4 Characterization of modified PTA resin

The FT-IR spectra of PTA resin, GO modified PTA resin and alkynyl-pendant GO modified PTA resin were represented in Figure 6. The peak in the FT-IR spectra of PTA resin is consistent with that of GO modified PTA resin except for the surface oxygenic functional groups of GO, which illustrated that there is no chemical reaction between PTA resin and GO. The surface oxygenic functional groups of GO might form hydrogen bond with the azide monomer and the triazole ring, which would conduce to the improvement of compatibility between GO and PTA resin. In comparison to PTA resin, the intensity of characteristic peak at 3133cm^{-1} and 2091cm^{-1} in the FT-IR spectra of alkynyl-pendant GO modified PTA resin increased remarkably, which implied that the alkynyl group of GO participated in the cycloaddition reactions of PTA resin. The introduction of alkynyl-pendant GO increased the intensity of characteristic peak at 2091cm^{-1} . Furthermore, the peak at 3434cm^{-1} moved to the wavenumber region with low frequency, indicating that the hydrogen bond between PTA resin and alkynyl group of GO contributed to the compatibility between GO and PTA resin insignificantly, while the reaction of alkynyl group and azide group might play a crucial part for the excellent compatibility between PTA resin and alkynyl-pendant GO.

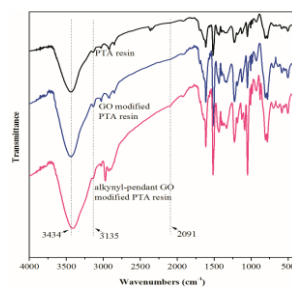


Figure 6: FT-IR spectra of PTA resin and modified PTA resin

Figure 7 presents the XPS spectrum of PTA resin, GO modified PTA resin and alkynyl-pendant GO modified PTA resin. As shown in Figure 7, the three peak (C 1s, N 1s, and O 1s) signals were detected in all the three samples (Figure 7(a)). The C 1s peak (Figure 7(b)) of the PTA resin is fitted with three components centered at 284.5, 287.8 and 285.7 eV, corresponding to the C-C and C-H bonds, C=O bonds, C-N bonds for the triazole ring respectively. Figure 7(c) shows the N 1s peak of the PTA resin fitted with three components centered at 401.3, 405.4 (N=N=N) and 402.7 (C-N) eV. The former two bands appear with a ratio 2:1, in accordance with the incorporation of an N₃ group.

Compared with C 1s peak of the PTA resin, the GO modified PTA resin exhibits two new component (C-O and COOH) due to the surface oxygenic functional groups of GO at 286.8 and 288.9 eV, respectively (Figure 7(d)). The N 1s peak for GO modified PTA resin (Figure 7(e)) is strikingly similar to that of PTA resin. It can be concluded that no chemical reaction has occurred for PTA resin and GO, and GO might form hydrogen bond with the azide monomer and the triazole ring, which coincides with the results from FT-IR determination. In comparison to C 1s peak of the PTA resin, the alkynyl-pendant GO modified PTA resin (Figure 7(f)) shows a high-intensity feature at 287.8 eV due to the O=C-NH group of alkynyl-pendant GO. In addition, these are centered at 286.8 and 288.9 eV assigned to C-O and COOH of alkynyl-pendant GO. It is important to note that the N 1s peak of the alkynyl-pendant GO modified PTA resin at 405.3 eV disappeared as the residual azide group has completely participated in the cycloaddition reaction (Figure 7(g)). The peaks are fitted with two components centered at 400.3 and 399.7 eV, which are attributable to the N-H and N-C=O of alkynyl-pendant GO. The reaction of alkynyl group of alkynyl-pendant GO with azide group contributes to the compatibility between alkynyl-pendant GO and PTA resin. Moreover, the hydrogen bond would also be conducive to their compatibility, which is consistent with the FTIR data.

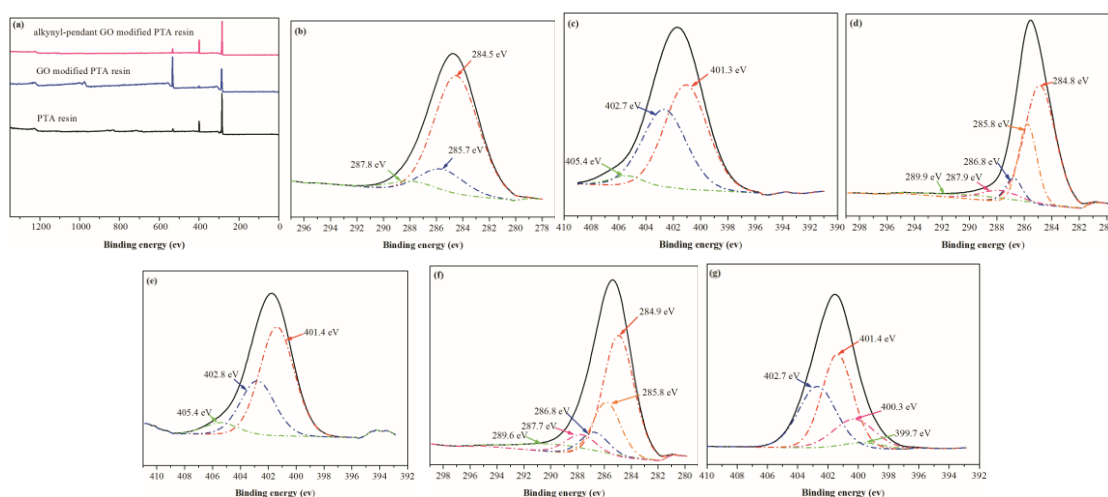


Figure 7: The whole XPS spectrum of three resins (a), characteristic C 1s (b) and N 1s (c) core line signals of PTA resin, C 1s (d) and N 1s (e) core line signals of GO modified PTA resin, and C 1s (f) and N 1s (g) core line signals of alkynyl-pendant GO modified PTA resin

3.5 Thermal properties of the T300 carbon cloth/modified PTA resin composite

As mentioned in the section 3.2 and 3.3, T700/PTA resin composite exhibits good heat resistance and high mechanical properties at room temperature and high temperature after being postcured at 200 °C for 1h. Besides, the curing degrees of PTA resin postcured at 200 °C reached 99.9%. Therefore, the T300 carbon cloth/modified PTA resin composite were cured at 80 °C for 1h, and then being postcured through 160 °C/2h+200 °C/1h to investigate the thermal property of composite.

The effect of dosage of GO on the T_g of T300 carbon cloth/PTA resin composite was shown in Figure 8. Figure 8(a) shows that the storage modulus of composite increases with improvement of quantity of GO, but the storage modulus of composite drops as the dosage of GO is above 1.0%, since the large interface interaction between GO and composite could restrict the segment movement of PTA resin. However, GO tends to form agglomerates when the dosage of GO is above 1.0%, which would

weaken the interface interaction between GO and PTA resin.

The T_g of PTA matrix composite with different dosage of GO is tabulated in Table 4. In agreement with the result of storage modulus of composite, the maximum T_g of 208.91 °C for PTA matrix composite was achieved as the dosage of GO was 1.0% (Figure 8(b)), which can be attributed to the formation of hydrogen bond between PTA resin and the homogeneous dispersion of GO in the polymer when the dosage of GO was lower than 1.0%. As a result, GO can be treated as the physical crossing point for PTA resin, and then the increase of dosage of GO would be conducive to the T_g of PTA matrix composite. Nevertheless, the aggregation of GO is harmful to the segment movement of PTA molecular restricted by GO, leading to the decline of T_g of PTA matrix composite.

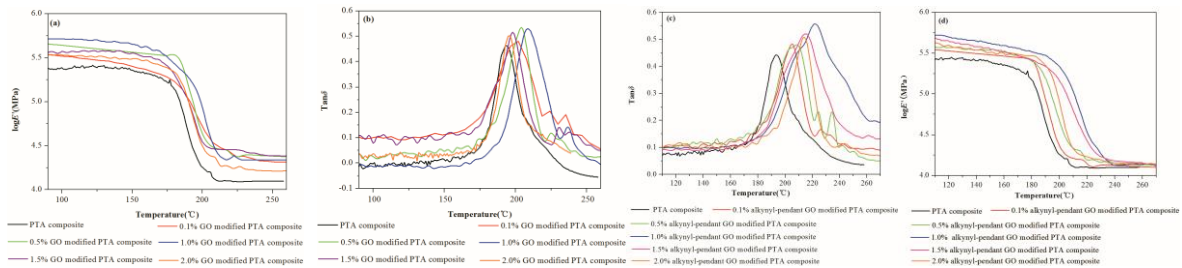


Figure 8: DMA spectrum for PTA matrix composite with different dosage of GO and alkynyl-pendant GO

Dosage (%)	T_g of GO modified PTA resin composite (°C)	T_g of alkynyl-pendant GO modified PTA resin composite (°C)
0	193.26	193.26
0.1	199.31	205.19
0.5	203.52	207.50
1.0	208.91	221.17
1.5	197.96	214.84
2.0	195.60	213.41

Table 4: The T_g of PTA matrix composite with different dosages of GO and alkynyl-pendant GO

The T_g of T300 carbon cloth/PTA resin composite influenced by the introduction of alkynyl-pendant GO on was shown in Figure 8(c) and (d). The T_g of PTA matrix composite with different concentrations of alkynyl-pendant GO is listed in Table 4. The T_g of PTA matrix composite increased with the increasing dosage of alkynyl-pendant GO, and the peak value for T_g for PTA matrix composite reached 221.17 °C when the dosage of alkynyl-pendant GO was 1.0% (Figure 8(c)), which is strikingly similar to the result of GO modified PTA matrix composite. Alkynyl-pendant GO can take part in the cycloaddition polymerization of PTA resin, and alkynyl-pendant GO can also generated hydrogen bond with PTA resin. Consequently, the promotion of alkynyl-pendant GO concentration leads to the improvement of T_g . Furthermore, the aggregation of alkynyl-pendant GO caused the decline of T_g . When the dosage of alkynyl-pendant GO was 1.0%, the improvement of T_g reached about 27.9 °C in comparison to T300 carbon cloth/PTA resin composite, which is much large than that of GO (15.7 °C), presenting the merit of alkynyl-pendant GO in the application of improving the

heat-resistance. As illustrated in Figure 8(d), the influence of alkyne-pendant GO concentration storage modulus of composite is consistent with the result of T_g . The interaction of alkyne-pendant GO and PTA resin might play a crucial role in the improvement of storage modulus of composite.

3.6 Thermal stabilities of the modified PTA resin

T300 carbon cloth/modified PTA resin composite presented good heat resistance as the dosage of GO or alkyne-pendant GO was 1.0%, and the thermal stability of modified PTA resin was investigated TG analyzer under this condition. Figure 9 shows thermogravimetric diagrams of the GO, alkyne-pendant GO and modified PTA resin under nitrogen atmosphere.

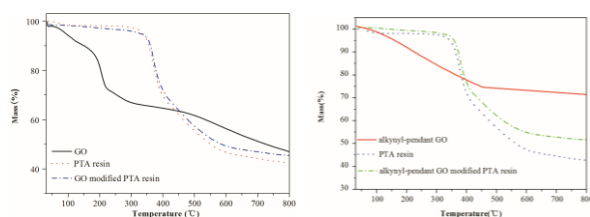


Figure 9: TG thermograms of GO, alkyne-pendant GO, PTA resin and modified PTA resin under nitrogen

As illustrated in Figure 9, the carbon yield for GO, alkyne-pendant GO and PTA resin at 800 °C was 53.17%, 70.78% and 41.79%, respectively. This result implied that alkyne-pendant GO exhibited good thermal stability than that of GO. Compared with PTA resin, the T_{d5} and carbon yields (800 °C) of PTA resin modified by GO and alkyne-pendant GO were increased to 351.8 °C, 45.76% and 355.0 °C, 52.01%, respectively. The heat insulation and physical interference play a key role in the improvement of PTA resin due to the poor heat conductivity of GO and diffusion of micromolecule interfered by lamellar structure of GO [20]. As regard to alkyne-pendant GO modified PTA resin, both the outstanding thermal stability of alkyne-pendant GO and the π - π conjugation between PTA molecule and benzene ring after carbonization of alkyne-pendant GO contribute to the good thermal stability of modified PTA resin. Compared with GO, alkyne-pendant GO presents good heat resistance and thermal stability in the improvement of PTA resin thermal properties.

3.7 Mechanical properties of the T300 carbon cloth/modified PTA matrix composite

T300 carbon cloth/modified PTA resin composites with different concentrations of GO and alkyne-pendant GO were cured at 80 °C for 4h, and then postcured through 160 °C/2h+200 °C/1h to study the mechanical property of composite. The flexural and shear properties of modified PTA matrix composites with different concentrations of GO and alkyne-pendant GO are depicted in Figure 10. The flexural and shear properties of GO modified PTA matrix composites improved considerably with the increasing GO concentration from 0% to 1.5% (w/v), but they began to decrease when GO concentration was higher than 1.5% (Figure 10(a) and (b)). The T300 carbon cloth/modified PTA resin composites with different concentrations of GO (>0) presented higher mechanical property than that of T300 carbon cloth/PTA resin composites. Since GO with good mechanical property could form hydrogen band with PTA resin and GO showed good compatibility with sizing agent including epoxy group for carbon cloth, the existence of GO resulted in the good interface between PTA and carbon cloth, and then improving the mechanical property. Nevertheless, the aggregation of GO would be a defect of composite, which can cause the stress concentration and the decline of flexural and shear strength.

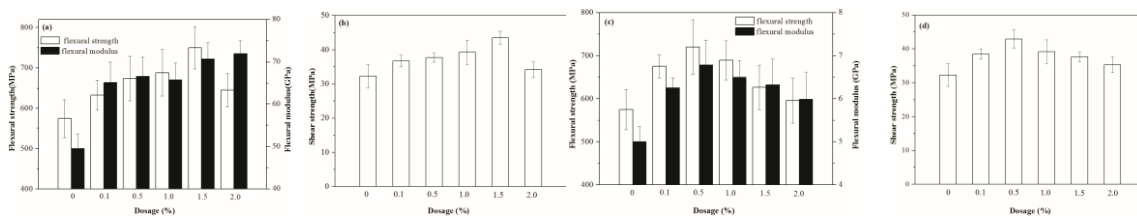


Figure 10: Mechanical properties of the T300 carbon cloth/modified PTA matrix composite

It is similar to the result of GO that alkynyl-pendant GO modified PTA matrix composites represented good mechanical property as the dosage of alkynyl-pendant GO was 0.5%, and then it began to drop down with the increase of alkynyl-pendant GO concentration. When the dosage of GO or alkynyl-pendant GO was 1.0%, the flexural and shear strength of modified PTA matrix composites in comparison to PTA matrix composite increased by 19.7%, 16.7% and 20.1%, 21.4%. In addition to hydrogen bond between PTA resin and alkynyl-pendant GO, the interaction of alkynyl-pendant GO and PTA resin as well as sizing agent including epoxy group for carbon cloth was conducive to the improvement of mechanical property. Consequently, T300 carbon cloth/ alkynyl-pendant GO modified PTA resin composites showed good thermal and mechanical properties as the concentration of alkynyl-pendant GO was 1.0% (w/v).

4 CONCLUSIONS

The increase of post-treatment temperature contributes to the improvement of T_g and flexural and shear strength for T700/PTA resin composite, while the effect of post-treatment time on the thermal and mechanical property of composite was insignificant. After being post-cured at 200 °C for 1h, the T700/PTA resin composite shows good heat resistance and high mechanical property, including the fact that the T_g of composite reached about 210 °C and the flexural and shear strength retention ratio at 175 °C for composite arrived at 62.08% and 69.26%, respectively. The compatibility between PTA resin and GO might be enhanced by the hydrogen bond interaction, while both the hydrogen bond interaction and the cycloaddition of azide and alkyne groups might contribute to the excellent compatibility between PTA resin and alkynyl-pendant GO. As the concentration of GO or alkynyl-pendant GO was 1.0%, the T_g of /PTA matrix resin composite improved 15.7 °C and 27.9 °C, respectively. Moreover, the bending strength and shear strength of composite with GO (1.0%) and alkynyl-pendant GO (1.0%) in comparison to PTA matrix composite increased by 19.7%, 16.7% and 20.1%, 21.4%, respectively. In conclusion, the introduction of alkynyl-pendant GO could make great contribution to the good heat resistance and high mechanical properties of PTA resin matrix composites at the appropriate post-treatment temperature and time, and it provide a new way to improve the thermal and mechanical property of thermosetting polymers.

ACKNOWLEDGEMENTS

This study was financially supported by the State Administration of Science, Technology and Industry of National Defence, PRC. The authors wish to thank Dr. Shuhua Chen from Xi'an Aerospace Composites Research Institute for their technical assistance.

REFERENCES

- [1] L. Xue, L.Q. Wan, Y.H. Hu, X.N. Shen, F.R. Huang and L. Du, Thermal stability of a novel polytriazole resin, *Thermochimica Acta*, **448**, 2006, pp. 147–153.

- [2] J. Kim, B.S. Yim, J.M. Kim, J. Kim, The effects of functionalized graphene nanosheets on the thermal and mechanical properties of epoxy composites for anisotropic conductive adhesives (ACAs), *Microelectronics Reliability*, **52**, 2012, pp. 595–602.
- [3] Y. Hu, Y. Luo, L. Wan, et al., 1, 3-Dipolar cycloaddition polymerization of bispropargyl ether of bisphenol-A with 4, 4'-biphenyl dibenzyl azide and their thermal analyses. *Acta Polymerica Sinica*, **4**, 2005, pp. 560.
- [4] Y. H. Luo, Y. H. Hu, L. Q. Wan, et al., Cure kinetics study of the polymerization of N, N, N',N'-tetrapropargyl-p, p'-diamino diphenyl methane with 1, 1'-bezidomethyl-4, 4'-biphenyl, *Chemical Journal of Chinese Universities*, **27**, 2006, pp. 170-173.
- [5] L. Wan, Y. Luo, L. Xue, et al., Preparation and properties of a novel polytriazole resin, *Journal of applied polymer science*, **104**(2), 2007, pp. 1038-1042.
- [6] J. Tian, L. Wan, J. Huang, et al., Synthesis and characterization of a novel polytriazole resin with low-temperature curing character, *Polymers for Advanced Technologies*, **18**, 2007, pp. 556-561..
- [7] J. Tian, L. Wan, J. Huang, et al., Preparation and properties of a new polytriazole resin made from dialkyne and triazide compounds and its composite, *Polymer Bulletin*, **60**(4)2008, pp. 457-465.
- [8] J. Tian, X. Wang, L. Wan, et al., Investigation of structure/property relationships of polytriazoles, *High Performance Polymers*, **22**(2), 2010, pp. 198-212.
- [9] D. Li, M. B. Müller, S. Gilje, et al., Processable aqueous dispersions of graphene nanosheets, *Nature nanotechnology*, **3**(2), 2008, pp. 101-105.
- [10] X.M. Yang, L.J. Ma, S. Wang, et al., “Clicking” graphite oxide sheets with well-defined polystyrenes: A new Strategy to control the layer thickness, *Polymer*, **52**, 2011, pp. 3046-3052.
- [11] J. J. Liang, Y. Huang, L. Zhang, et al., Molecular-level dispersion of graphene into poly (vinyl alcohol) and effective reinforcement of their nanocomposites, *Advanced Functional Materials*, **19**, 2009, pp.2297.
- [12] D. Cai, K. Yusoh, M. Song, The mechanical properties and morphology of a graphite oxide nanoplatelet/polyurethane composite, *Nanotechnology*, **20**(8), 2009, pp.085712.
- [13] R. Rafiq, D. Cai, J. Jin, et al., Increasing the toughness of nylon 12 by the incorporation of functionalized graphene, *Carbon*, **48**(15), 2010, pp. 4309-4314.
- [14] Y. Lin, J. Jin, M. Song, Preparation and characterisation of covalent polymer functionalized graphene oxide, *Journal of Materials Chemistry*, **21**(10) , 2011, pp. 3455-3461.
- [15] M. Fang, K. Wang, H. Lu, et al., Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites, *Journal of Materials Chemistry*, **19**, 2009, pp. 7098-7105.
- [16] Y. Cao, Z. Lai, J. Feng, et al., Graphene oxide sheets covalently functionalized with block copolymers via click chemistry as reinforcing fillers, *Journal of Materials Chemistry*, **21**(25), 2011, pp.9271-9278.
- [17] Q. Wang, T. R. Chan, R. Hilgraf, et al., Bioconjugation by copper (I)-catalyzed azide-alkyne [3+2] cycloaddition, *Journal of the American Chemical Society*, **125**(11), 2003, pp. 3192-3193.
- [18] C. Bao, L. Song, W. Xing, et al., Preparation of graphene by pressurized oxidation and multiplex reduction and its polymer nanocomposites by masterbatch-based melt blending, *Journal of Materials Chemistry*, **22**(13), 2012, pp. 6088-6096.
- [19] Y. Xiong, F. Y. C. Boey, , Kinetic study of the curing behavior of bismaleimide modified with diallylbisphenol A, *Journal of Applied Polymer Science*, **90**(8), 2003, pp. 2229–2240.
- [20] C. Zhang, L.Q. Wan, J.W. Xu, et al., Preparation and Characterization of Polytriazole/Carbon Nanotube Composites, *Chinese Journal of Materials Research*, **28**(7), 2014, pp. 555-560.