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Paper

Fabrication of novel wave-transparent HMPBO fibres/BADCy laminated composites

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The method of "impregnation-winding-lamination-compression molding" is performed to fabricate novel wave-transparent high modulus poly (*p*-phenylene-2, 6-benzobisoxazole) fibres/bisphenol A cyanate ester resins (HMPBO fbires/BADCy) laminated composites. And the "two-step approach" of methanesulfonic acid/γ-glycidoxy propyl trimethoxy silane (MSA/KH-560) is also proposed to functionalize the HMPBO fibres' surface. Results reveal that KH-560 has grafted on the HMPBO fibres' surface successfully. And functionalized HMPBO fibres/BADCy laminated composite possesses better ILSS & flexural strength, lower ε & tanδ, and higher heat-resistance index & T_g. The ILSS and flexural strength of the functionalized HMPBO/BADCy laminated composite is increased to 53.7 MPa and 753.7 MPa, respectively. The corresponding ε and tanδ is decreased to 2.93 and 0.00097, respectively. And the corresponding heat-resistance index and T_g is increased to 219°C and 236°C, respectively. Functionalized HMPBO fibres/BADCy laminated composite displays potential application in radomes and antenna system of aircrafts.

Introduction

Cyanate ester (CE) resins possess superior dielectric properties (dielectric constant of 3.0-4.0 and dielectric loss of 0.005-0.010), which reveal good stability in a wide range of temperature and electric field frequency [1-4], better than other thermosetting resins, such as epoxy resin, polyimide and bismaleimide, etc., Furthermore, CE resins possess excellent high-temperature mechanical properties, very low water-adsorption, good heat & humidity resistance, preferable dimensional stabilitiy and an epoxy-like processability, etc., and have been widely applied in aerospace, electronics, insulations, adhesives and other areas [5-8].

Poly (*p*-phenylene-2, 6-benzobisoxazole) (PBO) fibres possess light weight, superior dielectric properties (dielectric constant of 3.0 and dielectric loss of 0.001), outstanding specific tensile strength & modulus, excellent thermal stability, and good chemical & flame resistance [9-13], far exceeding other organic fibres. PBO/polymer advanced structural composites show promising applications in aerospace, navigation, bulletproof materials and reinforced materials [14-15].

However, due to PBO fibres' low surface activity and chemical inertia, the interfacial adhesion of PBO fbres/polymer matrix is poor, which restricts PBO fibres' application in the high-performance composites. Work by Lu and coworkers[16-17] has also shown that the surface functionalization of carbon fibres can effectively improve the interfacial adhesion properties of the carbon fibres/polymeric matrix composites. Given that, the surface functionalization of PBO fibres is also an effective method to increase interface interaction between PBO fibres and polymer matrix. Recently, different functionalized methods have been proposed to improve the interfacial adhesion between PBO fibres and polymer matrix, including chemical treatment [18], plasma treatment [19], enzymatic treatment [20], γ-ray irradiation treatment [21], discharge treatment [22-23], polyhedral oligomeric silsesquioxanes (POSS) molecule [24], and the combination treatment of several methods [25].

In our previous work, the methods of polyphosphoric acid/absolute alcohol [26], γ-glycidoxy propyl trimethoxy silane (KH-560) [27], γ-aminopropyl triethoxy silane (KH-550) [28], oxygen plasma/POSS [29] and methanesulfonic acid/KH-550/POSS [30], have been adopted to functionalize the surface of PBO fibres. Results indicated that polar groups have been successfully introduced on the PBO fibres' surface and the interfacial adhesion of PBO fibres to polymer matrix has also been improved effectively. Compared with the latter two methods, the former three methods are more applicable to funcationalize the lots of PBO fibres, much easier for the fabricate the PBO fibres/polymer matrix laminated composites.

In our present work, the method of "impregnation-winding-lamination-compression" is performed to fabricate novel wave-transparent high modulus poly (*p*-phenylene-2, 6-benzobisoxazole) fibres/bisphenol A cyanate ester resins

(HMPBO fibres/BADCy) laminated composites And the "two-step approach" of methanesulfonic acid/γ-glycidoxy propyl trimethoxy silane (MSA/KH-560) is also proposed to functionalize the surface of HMPBO fibres, to effectively improve their interfacial adhesion to BADCy matrix. In addition, the influences of HMPBO fibres' surface functionalization on the mechanical properties, dielectric properties and thermal stabilities of the HMPBO fibres/BADCy laminated composites are also investigated. This paper is part of a large project on the development and preparation of novel wave-transparent polymeric composites with light weight, thermal insulation and high load-bearing capacity, which display potential application in radomes and antenna system of aircrafts, promising to replace present wave-transparent composites of glass fibres/BADCy, quartz fibres/BADCy and/or kevlar fibres/BADCy composites.

Materials and Methods

Materials

Bisphenol A cyanate ester (BADCy) resins are purchased from Jiangdu Wuqiao resin Factory (Jiangsu, China); Epoxy resins are received from Wuxi Resin Factory of Blue Star New Chemical Materials CO., Ltd (Jiangsu, China); High modulus poly (*p*-phenylene-2, 6-benzobisoxazole) (HMPBO) fibres, with trade name Zylon^{TM}, are purchased from Toyobo Co. Ltd. (Osaka, Japan); γ-aminopropyl triethoxy silane (KH-560) is supplied by Nanjing Shuguang Chemical Group Co., Ltd (Jiangsu, China); Methanesulfonic acid (MSA) is received from Chengdu Kelong Chemical Co. Ltd.(Sichuan, Chian); Absolute ethanol (EtOH), acetone and formaldehyde are all received from Tianjin Ganglong Chemical Group Co., Ltd. (Tianjin, China).

Purification of BADCy

BADCy is dissolved in acetone and evaporated under 40°C to obtain the saturated solution, followed by cooled to room temperature and kept for 3 hr. Then the solid is filtered out from the liquid. The steps above are repeated for three times to obtain white crystals, followed by ground into powders and dried for 24 hr in a vacuum oven at 40°C. Finally, the purified white dry BADCy powders are obtained.

Surface funcationalization of HMPBO fibres

HMPBO fibres are firstly immerged in EtOH and formaldehyde for 24 hr at room temperature for each step, then washed by distilled water, and finally dried at 100°C in a vacuum oven for 24 hr; The obtained HMPBO fibres are then soaked in 60 wt% MSA/distilled water solutions for 12 hr at 60°C under ultrasonic vibration, and then washed by distilled water; The obtained HMPBO fibres and KH-560/EtOH/distilled water solutions (1/50/50, wt/wt/wt) are reacted for 6 hr at 70°C (pH ≈ 9), followed by ultrasonic vibration at the set temperature & power (100W, 50°C) for another 2 hr. Finally, the MSA/KH-560 functionalized HMPBO fibres are washed by EtOH and distilled water, and dried at 120°C for 24 hr.

Fig.1 shows the general fabrication process of MSA/KH-560 functionalized HMPBO fibres.

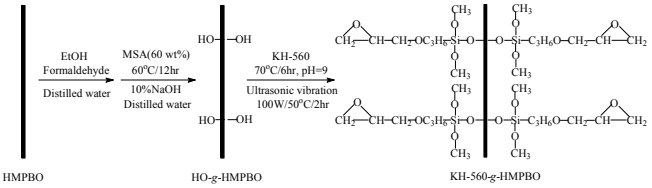

Fig.1 General fabrication process of MSA/KH-560 functionalized HMPBO fibres.

Fabrication of the HMPBO fibres/BADCy composites

Mixtures of BADCy/epoxy resin (19/1, wt/wt) are heated to 150°C and prepolymerized for 4 hr, then cooled to below 100°C, followed by adding excessive acetone and appropriate dibutyltin dilaurate to obtain the prepreg glue. The dried HMPBO fibres are then immerged in the prepreg glue above, followed by filament winding, and then HMPBO/BADCy mixtures are laminated and moulding pressed at 10 MPa as the technology of 160°C/1 hr+180°C/2 hr+200°C/5 hr, followed by post-curing in vacuum oven at 220°C/2 hr.

Characterization

Thermo-gravimetric analyses of samples are performed using a thermoanalyzer (STA 449F3, Netzsch Group, Germany) in the temperature range of 40-900°C with a heating rate of 20K/min under argon atmosphere; Dynamic mechanical analyses (DMA) of samples are performed using DMA/SDTA861e (Mettler-Toledo Co. Switzerland) at 5°C/min at 1 Hz; Scanning electron microscope (SEM) morphologies of samples are analyzed by VEGA3-LMH (TESCAN Corporation, Czech Republic); The flexural strength and the interlaminar shear strength (ILSS) of samples are measured by Electron Omnipotence Experiment Machine SANS-CMT5105 (Shenzhen New Sansi Corp., China) according to standard ASTMD 7264-2007 and ASTMD 2344-2000, respectively. The dielectric constant and dielectric loss of samples are measured using high frequency Q instrument (QBG-3D) and dielectric constant detector (S914) from Aiyi Electronic Equipment Co. Ltd. (Shanghai, China).

Results and discussion

Analysis and characterization on HMPBO fibres

Fig.2 shows the entire XPS scanning spectra of native HMPBO fibres and functionalized HMPBO fibres. According to **Fig.2**, various elements contents can be calculated and listed in **Table 1**.

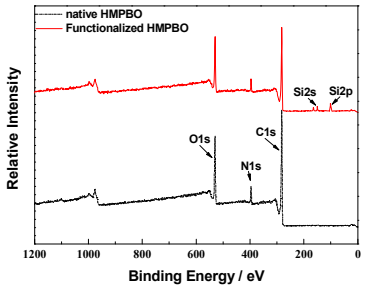

Fig.2 XPS scanning spectra of native HMPBO and functionalized HMPBO fibres

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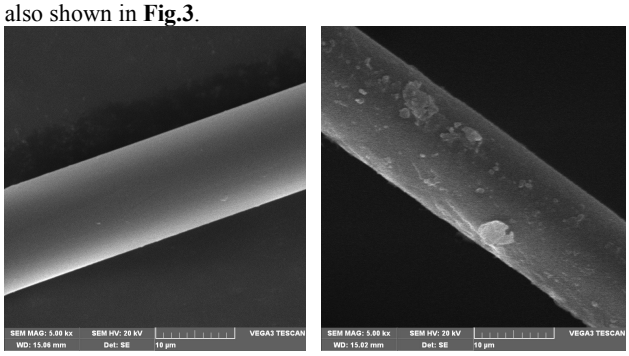
Table 1 Concentrations of various elements on HMPBO surface

HMPBO samples	Concentrations of elements/%			
	C	O	N	Si
Native HMPBO fibres	79.35	14.02	6.63	--
Functionalized HMPBO fibres	71.27	18.04	7.26	3.43

There are carbon, oxygen and nitrogen elements on the native HMPBO fibres' surface. After the surface functionalization, the corresponding C1s peak, O1s and N1s peaks are all changed at different levels, due to the contribution of KH-560 molecular. Meanwhile, the appearance of Si2p and Si2s peaks in **Fig.2** further confirm that KH-560 has covered on the HMPBO fibres' surface successfully. And the corresponding SEM morphologies of native HMPBO fibres and functionalized HMPBO fibres are also shown in **Fig.3**.



(a) Native HMPBO fibres (b)Functionalized HMPBO fibres

Fig.3 SEM morphologies of native HMPBO fibres and functionalized HMPBO fibres

The surface of native HMPBO fibres is smooth (**Fig.3a**). After the surface functionalization, the surface of HMPBO fibres becomes coarser, and there are several white substances adhering to HMPBO fibres' surface (**Fig.3b**), which is ascribed to KH-560 molecule grafting on the HMPBO fibres' surface (Also proved in **Table 2**).

Table 2 The elements and contents of white substances on the functionalized HMPBO fibres surface

Element	Weight/%	Atom/%
C	36.01	43.39
O	61.16	55.33
Si	2.83	1.28
Total	100.00	100.00

Mechanical properties of the HMPBO fibres/BADCy composites

Fig.4 shows the mechanical properties of the HMPBO fibres/BADCY composites.

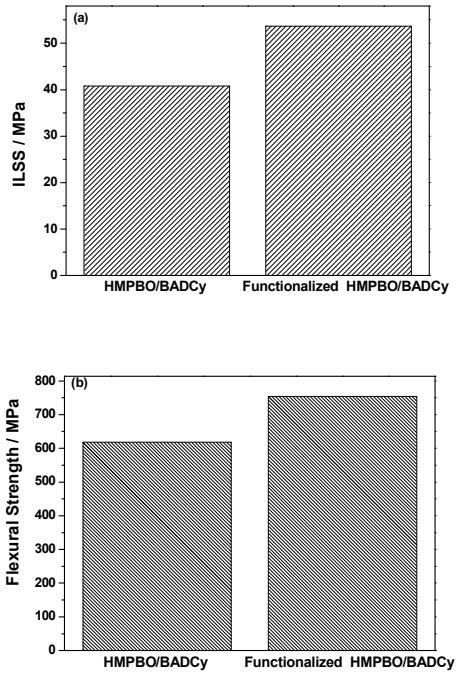
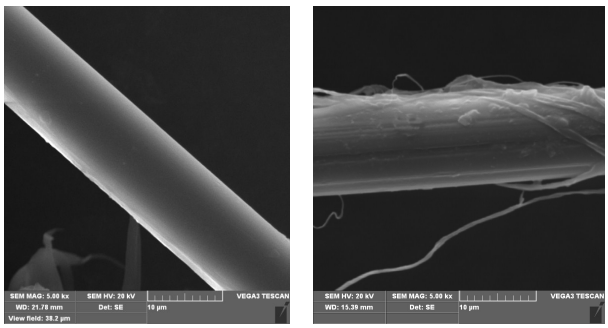


Fig.4 The mechanical properties of HMPBO fibres/BADCy composites

Compared with native HMPBO fibres/BADCy composite (40.8 MPa for ILSS and 618.1 MPa for flexural strength), the corresponding ILSS (53.7 MPa) and flexural strength (753.7 MPa) of functionalized HMPBO fibres/BADCy composite is increased by 31.6 percent and 21.9 percent, respectively.

The reason can be attributed that, after the surface functionalization, the introduction of hydroxyl and epoxy polar groups on the surface of functionalized HMPBO fibres can react with the active groups of BADCy matrix, which can contribute to the improvement of interfacial compatibility of HMPBO fibres/BADCy matrix. Thus the interfacial adhesion between HMPBO fibres and BADCy matrix is also enhanced, finally the mechanical properties of the HMPBO fibres/BADCy composite are further increased accordingly. The corresponding SEM morphologies of the HMPBO fibres/BADCy micro-composites after single fibre pull-out test are shown in **Fig.5**. After single fibre pull-out test, there is much more BADCy matrix remaining on the surface of functionalized HMPBO fibres than that of native HMPBO fibres, which further proves that functionalized HMPBO fibres possess much larger interfacial adhesion to BADCy matrix than that of native HMPBO fibres. Thus the functionalized HMPBO fibres possess better friction with BADCy matrix accordingly.



(a) Native HMPBO fibres (b)Functionalized HMPBO fibres

Fig.5 SEM morphologies of the HMPBO fibres/BADCy micro-composites after single fibre pull-out test

Dielectric properties of the HMPBO fibres/BADCy composites

The dielectric properties of the HMPBO fibres/BADCy composites are shown in **Table 3.**

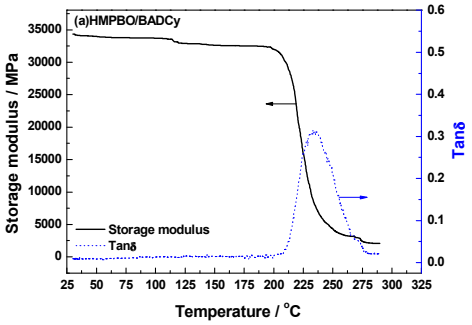
Table 3 Dielectric properties of the HMPBO fibres/BADCy composites

Samples	ε	tanδ
Native HMPBO fibres/BADCy	3.11	0.0016
Functionalized HMPBO fibres/BADCy	2.93	0.00097

Compared with native HMPBO fibres/BADCy composite (3.11 for dielectric constant, ε and 0.0016 for dielectric loss tangent, tanδ), the corresponding ε and tanδ of functionalized HMPBO fibres/BADCy composite is decreased to 2.93 and 0.00097, respectively. After the surface functionalization, the interfacial compatibility between functionalized HMPBO fibres and BADCy matrix are improved effectively, and the corresponding interfacial polarization of HMPBO fibres/BADCy and voidages inner HMPBO fibres/BADCy composite system are synchronously decreased, thus to decrease the ε and tanδ of the HMPBO fibres/BADCy composite.

Thermal properties of the HMPBO fibres/BADCy composites

Fig.6 shows the DMA curves of the HMPBO fibres/BADCy composites.



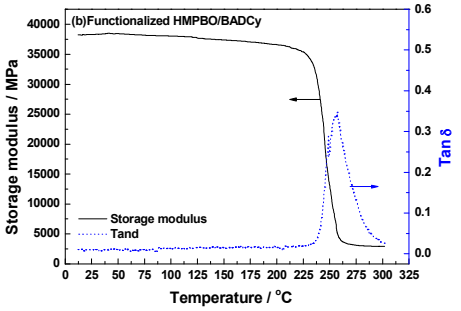


Fig.6 DMA curves of the HMPBO fibres/BADCy composites

HMPBO fibres/BADCy composites possess high shorage modulus & excellent heat resistance, and the corresponding glass transition temperature (T_g) of native HMPBO fibres/BADCy composite and functionalized HMPBO fibres/BADCy composite is 214°C and 236°C, respectively. It can be deduced that the surface functionalization of HMPBO fibres can improve the T_g of the composite effectively. The reason is that surface functionalization of HMPBO fibres can improve the interfacial adhesion between HMPBO fibres and BADCy matrix, finally to increase the T_g of the HMPBO fibres/BADCy composite.

TGA curves of the HMPBO fibres/BADCy composites are presented in **Fig.7**. And the corresponding characteristic thermal data of the HMPBO fibres/BADCy composites are listed in the **Table 4**.

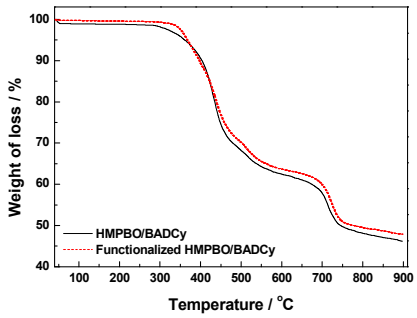


Fig.7 TGA curves of the HMPBO fibres/BADCy composites

Table 4 Thermal data of the HMPBO fibres/BADCy composites

Samples	Temperature/°C			Heat-resistance index*/°C [31]
	5	30	50	
Native HMPBO fibres/BADCy	361	480	745	212
Functionalized HMPBO fibres/BADCy	367	501	778	219

The weight loss of the HMPBO fibres/BADCy composite is 1 percent at the beginning of the experiment (0-280°C), the moment is mostly due to the loss of absorbed water and other small molecule volatilization. The weight loss reaches 37 percent over the range of 280-590°C, the moment can be contributed that the BADCy matrix fuses, chars and decomposes. And the weight loss of the HMPBO fibres/BADCy composite is 54 percent till 900°C, which is mainly acribed to the decompose of HMPBO fibres at high temperatures.

The corresponding weight loss temperatures of the functionalized HMPBO fibres/BADCy composite are all increased at the same stages (weight loss of 5%, 30% and 50%). When the weight loss

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is 50 wt%, the corresponding heat decomposing temperature of functionalized HMPBO fibres/BADCy composite is increased from 745°C to 748°C, and the corresponding heat-resistance index is also increased from 212°C to 219°C. It suggests that functionalized HMPBO fibres/BADCy composite possess better thermal stability than that of native HMPBO fibres/BADCy composite. The reason is that better efficient combination between functionalized HMPBO fibres and BADCy matrix can further increase the thermal stability of the HMPBO fibres/BADCy composite.

Conclusion

XPS and SEM-EDS analysis confirm that KH-560 has grafted on the HMPBO fibres' surface successfully after the surface functionalization by MSA/KH-560. HMPBO fibres/BADCy composites possess outstanding mechanical properties, excellent dielectric properties & good thermal stabilities, and the surface functiaonalization of HMPBO fibres can further improve the mechanical properties, dielectric properties and thermal stabilities of the HMPBO fibres/BADCy composites, by improving interfacial compatibility of HMPBO fibres/BADCy matrix. Compared with those of native HMPBO fibres/BADCy composite, functionalized HMPBO fibres/BADCy composite possesses better ILSS & flexural strength, lower ε & tanδ and higher heat-resistance index & T_g. The corresponding ILSS (53.7 MPa) and flexural strength (753.7 MPa) of functionalized HMPBO fibres/BADCy composite is increased by 31.6 percent and 21.9 percent, respectively. The corresponding ε and tanδ of functionalized HMPBO fibres/BADCy composite is decreased to 2.93 and 0.00097, respectively. The corresponding heat-resistance index is increased from 212°C to 219°C, and the corresponding T_g is increased from 214°C to 236°C. Functionalized HMPBO fibres/BADCy laminated composite displays potential application in radomes and antenna system of aircrafts, promising to replace present wave-transparent composites of glass fibres/BADCy, quartz fiberes/BADCy and/or kevlar fibres/BADCy composites.

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