Study on the Light Stability of Poly(*p*-phenylenebenzobisoxazole) Fiber†

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AJC-15722

Although poly(*p*-phenylenebenzobisoxazole) (PBO) fiber has outstanding mechanical performances and thermal stability but its application was hindered seriously due to low light stability. Thus, main aim in present work is to increase the light stability of PBO fiber. Four means, such as reacted sol-gel means, mixed sol-gel means, silane sol-gel means and physical adhesion means, were performed for light stabilizers to adhere on the surface of PBO fiber. The experimental results indicate that the PBO fibers processed by reacted sol-gel means exhibit flat surface without obvious particle accumulation. Contrasted with those fibers processed by other three means, these fibers show better light stability. After 130 h of light irradiation, the mechanical tensile strength of the fibers processed by reacted sol-gel means is still over 75 % of strength of unaged fiber and the strength is much higher than the aged original fibers whose strength is *ca.* 40 % of that of unaged original fiber.

Keywords: Reacted sol-gel means, Mixed sol-gel means, Ferrocenecarboxylic acid.

INTRODUCTION

As one of the lyotropic rigid rod-like liquid crystalline polymers *via* a dry-jet wet-spinning technique, poly-*p*-phenylenebenzobisoxazole¹ (PBO) can be spun into the strongest commercialized organic fiber with ultra-high and mechanical performance and thermal stability, for which it can be used as composite material in many fields and²⁻⁹. According to test, the mechanical tensile strength, tensile modulus and LOI of PBO fiber (naming as zylon in commerce) are 5.8, 270 and 68 GPa¹⁰, respectively, which is commercially produced by Toyobo Co in Japan in 1998. It is a real fly in the ointment that the mechanical strength of PBO fiber and would obviously decrease after light irradiation. According to the results reported by Toyobo, both AS and HM fibers lose 65 % of their strength after six-month exposure at Ohtsu, Japan, or after 500 h exposure in a Xenon light weatherometer¹⁰. Therefore, it is imperative to improve the UV-visible light aging-resistant performance of PBO fiber.

In recent years, several studies have been reported on the light stability of PBO fibers. Humidity, moisture, acidic environments¹¹, UV-visible radiation, residual phosphoric acid¹² and folding¹³ result in degrading PBO fiber with a great loss of mechanical properties. To increase the light stability of PBO

fibers, Walsh *et al.*¹⁴ introduced UV-visible light blocking coatings and they found out that the light stability of carbon black-coated PBO fibers did not increase and. Hindered amine light stabilizer (HALS) shows a marginal stabilization effect¹⁵. In contrast to above the light stabilizers, the light stability of the fibers were increased after they were immersed in ferrocene solution, which was a kind of reversible redox reagents^{16,17}. In addition, iodide compounds, cupric compounds or their mixtures, which can undergo reversible electron transfer, are also effective in increasing the light stability of PBO fibers.

Han *et al.*¹⁸ investigated the kinetics of PBO thermal degradation using TG/DTG measurements and found the degradation kinetic model followed the mechanism of random scission of weak bonds of PBO molecule. Fu *et al.*¹⁹ studied degradation mechanism of PBO under neutral and acidic conditions, corresponding results indicated that the degradation occurred through the ring opening presenting in the PBO molecule chain to some extent because of the incomplete polymerization and chain scission of the benzoxazole ring, so they proposed a new degradation mechanism that hydrolysis occurred primarily in the *o*-hydroxy amide linkage of the open ring¹⁹ in the early and middle stages. Song *et al.*²⁰ also investigated the effect of oxygen and moisture on the light aging of PBO fibers and found that the photoaging contained two developmental stages,

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

where the physical and the chemical aging were the dominating factors, respectively. The surface of PBO fibers is flat and almost no polar groups on the surface, so the adhesion of light stabilizers by van der Waals force are not very effective and light stability of PBO fibers are not increased obviously. Song *et al.*¹ improved the adhesion by the coordination bond and further the light stability of PBO fibers was increased obviously.

The light stability of PBO fibers can be increased considerably if the UV stabilizers cover uniformly and effectively the fiber surface. In this study, a new means called reacted sol-gel (RSG) was used to increase the adhesion of light stabilizers on the surface of PBO fiber that *via* sol-gel means the silane coupling agent reacted with UV stabilizer adhered on the surface of PBO fibers. This means is advantageous because UV stabilizers can cover uniformly and effectively the surface of fibers without exfoliation. Further more, the aging-resistant properties of PBO fibers treated in UV stabilizer solutions (physical absorption, PA), silane sol-gel means (SSG), reacted sol-gel and sol-gel mixed with UV stabilizer (MSG) were investigated and contrasted with each other. Mechanical properties and microstructures of unprocessed and processed PBO fibers were investigated in the experiments.

EXPERIMENTAL

Poly-*p*-phenylenebenzobisoxazole was prepared in the laboratory and the preparation means is reported²¹. Before light irradiation, the mechanical tensile strength of PBO fiber was 3.8 GPa. The other experimental reagents, including light stabilizer (ferrocene carboxylic acid), hydrophobic agent phenyltrimethoxysilane (Ph-TMS) and silane coupling agent Y-(2,3-epoxypropoxy) propyltrimethoxysilane (KH560), were purchased from J & K Technology Ltd. The molecular structure of these reagents is shown in **Scheme-I**.

Scheme-I: Synthesis of UV stabilizer-reacted-silicon coupling agent (URS)

Sample preparation: Five kinds of samples were prepared as follows to find out effect of processing means on the light stability of PBO fiber.

Reacted sol-gel fiber sample (by reacted sol-gel means): Reacted sol-gel means is to comprise the synthesis of the silane coupling agent KH560 reacted with the UV stabilizer (UV stabilizer-reacted-Silane coupling agent, URS) and then reacted sol-gel fiber samples were prepared *via* the sol-gel means. First, we prepared URS in DMF at 100 °C for 24 h (**Scheme-I**).

Then, in the catalysis of ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$), the organo-silicon sol mixed with URS (mole ratio of URS: KH560:Ph-TMS = 1:9:2.2) was prepared by the hydrolytic condensation of silane coupling agents in DMF at 27 °C for 9 h and the mass concentration of sol in DMF is 5 % in the present study. Subsequently, PBO fiber thread was soaked into prepared sol for 3 min; the same operation was performed again. Finally, the soaked fibers were dried in the vacuum drying oven at 80 °C for 24 h and in the oven at 130 °C for 10 min, respectively, subsequently to get reacted sol-gel fiber sample required.

The characterizations of synthesis of UV stabilizer-reacted-Silane coupling agent (URS) were as follows:

There is one ethylene oxide unit at one end of molecular chain of silane coupling agent KH560 and ferrocene carboxylic acid contains one carboxyl, so the latter has been utilized as a ring-opening agent to react with KH560 for preparation of UV stabilizer-reacted-silane coupling agent (URS). The reaction route is illustrated in **Scheme-I**. The reaction, which took place in DMF at 100 °C, was carried out through a ring-opening reaction between KH560 and ferrocene carboxylic acid using DMP-30 as a reaction promoter. The FTIR spectrums before and after the reaction show that the absorption of the ethylene oxide group of KH560 in the raw materials appears at 911.5 cm^{-1} and the absorption disappears in the FTIR spectrum after the reaction. It will not occur for ethylene oxide groups to open rings and auto-polymerize at 100 °C and apart from the carboxyl in the ferrocene carboxylic acid there are no groups which can promote the ethylene oxide group to open rings. Furthermore, the FTIR spectrums before and after the reaction show that the absorption of the $\text{Si-OC}_2\text{H}_5$ group appears at 1105-1104 cm^{-1} , which indicates that the $\text{Si-OC}_2\text{H}_5$ group exists in the raw materials and the reaction products and further confirms that the $\text{Si-OC}_2\text{H}_5$ groups of KH560 in the raw materials don't change after the reaction. Moreover, The FTIR spectrums before and after the reaction reveal that the absorption of the C-OH group in the reaction products appears at 3372.5 cm^{-1} , but the absorption doesn't exist in the FTIR spectrum before the reaction. So it can be concluded that URS is obtained through ring-opening reaction between KH560 and ferrocene carboxylic acid.

Mixed sol-gel fiber sample (by mixed sol-gel means): Apart from the silane coupling agent KH560 mixed with UV stabilizer (UV stabilizer-mixed-Silane coupling agent, UMS), mixed sol-gel means is identical to reacted sol-gel means.

Organo-silicon sol-gel fiber sample (by organo-silicon sol-gel means): PBO fiber samples treated in organo-silicon sol-gel means (SSG fiber sample) were prepared and the preparation conditions were in accordance with the second step in reacted sol-gel means.

Physical adhesion fiber sample (by physical adhesion means): PBO fiber samples treated by soaking in ferrocene carboxylic acid/DMF solution (PA fiber sample) were prepared and the mass concentration of the solution is 5 %. PBO fiber was soaked into the solution for 3 min and the same operation was done again, then the soaked fibers were dried in the vacuum drying oven at 80 °C for 24 h to get physical adhesion fiber sample required.

Original fiber sample: Original fiber sample, as a comparison sample, was also prepared.

Light aging: With an SN-500 xenon lamp, the light aging test of the fibers was done and light intensity, wavelength range, relative humidity and temperature of the lamp is 1100 W m^{-2} , 280-800 nm, 65 % and 54°C respectively.

Measurements: The structure of the silane coupling agent reacted with UV stabilizer (URS) was confirmed using IR spectrometer (Thermo Electron Corporation, Model NLCOLET5700) at wavenumbers ranging from $4000\text{--}500 \text{ cm}^{-1}$.

The TGA tests of all samples were carried out using Thermo Gravimetric Analyser (DSC1 1600HT) in N_2 at temperatures ranging from $0\text{--}800^\circ\text{C}$ (heating rate: $20^\circ\text{C min}^{-1}$).

The chemical composition analyses of all samples were performed by energy-dispersive X-ray spectrometry (EDS, Model: EDAX APOLLO X). The relative quantifications were done by fixing the acceleration voltages (15 KV) and data acquisition conditions.

With an electronic yarn strength tester whose model is YG020B, the mechanical performances of the fibers were tested. Strength of the fibers was got from the average value of at least 35 samples. With scanning electron microscopy (SEM) whose model is TS5136MM, the surface of the fiber was observed.

RESULTS AND DISCUSSION

Effect of processing means on light aging of the fiber:

The effect of processing means on the light aging of PBO fiber was found out by putting five kinds of processed fibers including reacted sol-gel fiber, mixed sol-gel fiber, organo-silicon sol-gel fiber, physical adhesion fiber and original PBO fiber in a xenon lamp. By means of the linkage between reactive groups in UV stabilizer and silane coupling agent, UV stabilizer in reacted sol-gel fiber adhered on the surface of PBO fiber *via* sol-gel means, whereas UV stabilizer in mixed sol-gel fiber did so by mixing with silane coupling agent in sol-gel means. The silicon gel film on the surface of organo-silicon sol-gel fiber was prepared by hydrolyzing and concentrating of silane coupling agent in sol-gel means. The preparation of physical adhesion fiber involved physical adhesion. Fig. 1 shows the mechanical strength -light irradiation time curves of the fibers. It can be seen that the effect of reacted sol-gel means on increasing the light stability of PBO fiber is the most obvious in the four means in spite of the significant losses of the tensile strength for all the treated fibers after 130 h of UV exposure. For the untreated PBO fiber, at the first 40 h, the tensile strength retention is only 60 % and this value decreases slowly to 39.8 % after 130 h exposure. After aging for 130 h, the mechanical strengths of reacted sol-gel and mixed sol-gel fibers are still above 60 % of strength of unaged fiber and the strengths are much higher than that of unprocessed fibers. Moreover, the mechanical strength of organo-silicon sol-gel and physical adhesion fibers is a little higher than that of unprocessed fibers after 130 h of light aging.

Fig. 2 shows the surface of original and processed fibers after the 130 h light aging. It is seen clearly that the surface of original fibers is smooth and compact with well-oriented microfibrils, while the surface of the aged original fibers is damaged severely, where defects and voids increase, even large area skin peeling appears.

Fig. 1. Tensile strength for original and treated fibers as a function of photo aging time

In Fig. 2, after UV radiation, some microfibrils have been peeled from the surface of physical adhesion fiber and organo-silicon sol-gel fiber and some cracks appear on their surfaces, which indicate that the adhesion of light stabilizers by immersing means has limited effect on increasing the light stability of the fibers, so does for the organo-silicon sol-gel means. However, the adhesions of light stabilizers through reacted sol-gel and mixed sol-gel means are very effective on increasing the light stability of the fiber, despite a few of UV stabilizer particles agglomerate on the surface of mixed sol-gel fiber. Although the cross-sectional microstructure of fibers penetrated by UV light was not determined, as-spun PBO fiber exhibits a core-shell structure. The shell with about $0.2 \mu\text{m}$ in thickness has fewer voids and a higher degree of order than these of core region²². Degradation of small extent at the fiber surface results in changing remarkably in cross-sectional area available to bear load and loss of a fairly small proportion of the fiber shell region may disproportionately have a significant effect on the strength of fiber²⁶.

Fig. 2. SEM photographs of (a) unaged original fiber, (b) original, (c) physical adhesion, (d) organo-silicon sol-gel, (e) mixed sol-gel, (f) reacted sol-gel fibers after 130 h of photo aging

Difference among reacted-sol-gel, mixed-sol-gel and physical adhesion means: The fibers processed by reacted sol-gel and mixed sol-gel means have better light stability than the fiber processed by adhesion means. TG curves of all kinds of fibers were got to find out the reason for above the difference and which are indicated in Fig. 3.

Fig. 3. Thermogravimetric analyses of the fibers

In Fig. 3, curve (e) shows that visible weight loss appears in ferrocene carboxylic acid due to sublimation when the system temperature exceeds 150 °C. Compared with original fiber [curve (a)], it can be seen that slight weight loss appears in PA fiber (physical adhesion fiber, curve (d)), which is caused by physical adhesion of light stabilizer (ferrocene carboxylic acid). Curve (c) indicates that due to being hindered by the silane coupling agent gel layer on the surface of the fiber, little weight loss caused by ferrocene carboxylic acid appears in MSG fiber (mixed sol-gel fiber) under 250 °C. Great weight loss rate appears in mixed sol-gel fiber at more than 250 °C and the weight loss in mixed sol-gel fiber is considerable when the system temperature is up to 500 °C, which is due to gasification and decomposition of the silane coupling agent gel layer on the surface of the fiber and ferrocene carboxylic acid mixed with the gel layer. Compared curve (b) and curve (c), it can be seen that the weight loss in reacted sol-gel fiber is identical to that in mixed sol-gel fiber under 496 °C, but the weight loss in mixed sol-gel fiber is greater than that in reacted sol-gel fiber when the system temperature exceeds 496 °C, which can be caused by the different existing forms of ferrocene carboxylic acid in mixed sol-gel and reacted sol-gel fiber. In other words, ferrocene carboxylic acid mixed with silane coupling agent in mixed sol-gel fiber, whereas ferrocene carboxylic acid reacts with silane coupling agent in reacted sol-gel fiber. The contrast result also shows the weight loss in reacted sol-gel fiber is greater than that in mixed sol-gel fiber when the system temperature exceeds 766 °C, which suggests the content of ferrocene carboxylic acid in reacted sol-gel fiber is more than that in mixed sol-gel fiber.

To further confirm the conclusions above, the energy-dispersive X-ray (EDS) spectra for the surface products of original fiber, physical adhesion fiber, organo-silicon sol-gel fiber, mixed sol-gel fiber and reacted sol-gel fiber are performed and corresponding results are shown in Fig. 4.

Fig. 4. Surface element compositions of the fibers

The spectrum in Fig. 4a shows the predominant elements of original fiber are carbon and oxygen represented by two visible EDS peak intensity. Apart from carbon and oxygen, iron element is presented in Fig. 4b with weak peak intensity, which indicates that a spot of ferrocene carboxylic acid has adhered on the surface of physical adhesion fiber. In comparison with Fig. 4a, silicon element in Fig. 4c shows obviously peak intensity, in addition, higher content of oxygen element is tested. The observed result confirms that the silane coupling agent gel layer has been got by hydrolysis and condensation of the silane coupling agent on the surface of organo-silicon sol-gel fiber. On the basis of Fig. 4c, iron element is presented in Fig. 4d-e with lower peak intensity, which indicates that ferrocene carboxylic acid has adhered on the surface of mixed sol-gel and reacted sol-gel fiber by mixing or reaction with silane coupling agent, respectively. Compared Fig. 4d-e, it can be seen that the content of silane and iron on the surface product of reacted sol-gel fiber is higher than that in mixed sol-gel fiber, which is coincident with the TGA results.

Mechanism of reacted sol-gel means: With the intense absorbance of UV-visible light^{23,24} and inhibition of the photo-reaction of PBO by electron donation¹⁴⁻¹⁶, ferrocene and its derivants can be used effectively as light stabilizer for PBO fiber. In the present work, *via* reacted sol-gel means, URS (UV light stabilizer (ferrocene carboxylic acid)-reacted-silane coupling agent) adheres closely and uniformly on the surface of reacted sol-gel fiber. Moreover, with its hydrophobicity, silane coupling agent gel layer can reduce the hygrothermal degradation of PBO fiber availably^{25,26}. So the aging-resistant performance of reacted sol-gel fiber is better than that of the original fiber, physical adhesion fiber, organo-silicon sol-gel fiber and mixed sol-gel fiber.

Conclusion

In this study, three means, reacted sol-gel means (reacted sol-gel means), mixed sol-gel means (mixed sol-gel means) and physical adhesion (PA means), were studied for light stabilizer to adhere (ferrocene carboxylic acid) on the surface of PBO fiber. Furthermore, organo-silicon sol-gel means (organo-silicon sol-gel means) was also studied with a contrast to above the three means. The light aging results reveal that the surface of PBO fiber processed by reacted sol-gel means is flat without obvious particle accumulation. The light stability of these fibers is increased obviously contrasted with those fibers processed by mixed sol-gel means, organo-silicon sol-gel means and physical adhesion means. The light stability of mixed sol-gel fibers is also increased to some extent, despite obvious particle accumulation on the surface of the fibers. Organo-silicon sol-gel means and physical adhesion means can slightly increase the light stability of the fibers. It is concluded that on the basis of the reaction of light stabilizer with silane coupling agent, *via* sol-gel means, light stabilizer adhered closely and uniformly on the surface can reinforce effectively the aging-resistant performance of PBO fiber.

ACKNOWLEDGEMENTS

The authors express their gratitude to the Shanghai Natural Science Foundation (12ZR1407900) and China Scholarship Council (CSC) for their financial support. This project is also supported by the National Natural Science Foundation of China (NSFC). Contract grant number is 50973028.

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