New disperse dyeing method of poly(*p*-phenylene benzobisoxazole) fiber pretreated with polyphosphoric acid

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Abstract−Poly(*p*-phenylene benzobisoxazole) fiber is considered as a high-performance fiber because of its high strength and excellent thermal and chemical stability. It has been used in industrial reinforcement, body armor and military camouflage. But the application of poly(*p*-phenylene benzobisoxazole) fiber used for protective clothing is limited because it is difficult to dye with conventional dyeing processes. In this work, a carrier dyeing method with disperse dyes was first used to dye the fiber after a pretreatment with polyphosphoric acid. The effects of the carrier structure and dyeing conditions on the color strength of dyed samples were investigated. In addition, the crystallinity and orientation degree of the poly(*p*-phenylene benzobisoxazole) fibers before and after pretreatment with phthalimide and benzyl benzoate were measured by X-ray diffraction and velocity-oriented test, respectively. The results suggested phthalimide and benzyl benzoate, as carrier, could effectively promote disperse dyeing of the PBO fiber pretreated with polyphosphoric acid. Meanwhile, the optimal conditions for the carrier dyeing were obtained, that is, concentration of carrier 4%, dyeing temperature 150 °C and time 120 min. By way of the carrier dyeing, the K/S value of dyed sample and the percentage of dye exhaustion were greatly improved, while the crystalline structure and orientation degree of the pretreated samples hardly changed. Furthermore, the decreases of the tensile strength and the limiting oxygen index of dyed poly(*p*-phenylene benzobisoxazole) sample were very little, and the color fastness was also satisfactory.

Keywords: PBO Fiber, Dyeing, Disperse Dye, Carrier

INTRODUCTION

As a popularly used semi-crystalline high performance fiber, poly (*p*-phenylene benzobisoxazole) (PBO), whose structural unit is listed in Table 1, is reported to exhibit the highest modulus and tensile strength among all commercial synthetic polymer fibers. It can be used as reinforcement in advanced composites and has great potential applications in aerospace, the military and general industry [1-3]. The excellent mechanical and thermal properties and the chemical stability stem from the structure of PBO fiber, *i.e.*, the rigid chain in the structural unit, a high level of crystallinity and a high degree of chain orientation along the fiber axis [4,5].

PBO fiber is hydrophobic and its macromolecular chains are arranged densely and do not contain any active groups that can combine with conventional dye molecules [6,7]. This makes the dyeing and printing of PBO fiber very difficult, which limits applications of PBO fiber in some special areas such as the military camouflage. Similar to the dyeing property, compatibility problems of PBO with other polymers have puzzled academia and industry. Therefore, since the invention of PBO fiber, many researchers continuously have made progress in the field of PBO surface modification, based on the need as reinforced materials [8-13].

In our previous researches [14,15], polyphosphoric acid (PPA) was employed to pretreat the PBO, and then the pretreated PBO fiber was dyed with disperse dyes by using the conventional method of high temperature-pressure dyeing. Meanwhile, the thermodynamics and kinetics of the disperse dye on the PBO fiber pretreated with PPA were studied. The results showed that the equilibrium adsorption isotherm of the disperse dye on the pretreated PBO fiber was a Langmuir-Nernst mixed Model. The adsorption of disperse dyes on the pretreated PBO fiber is an exothermic process, and the diffusion process basically accords with a pseudo first-order kinetic model. Although the pretreated PBO fiber can be dyed with disperse dyes with good color fastness and without significant loss in tensile strength and flame-retardant property, the color strength (K/S value) of the dyed PBO is not enough to satisfy the requirements of military camouflage and some special industries. So we need a more effective method to dye PBO fiber.
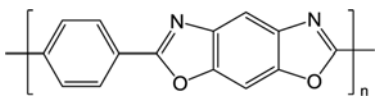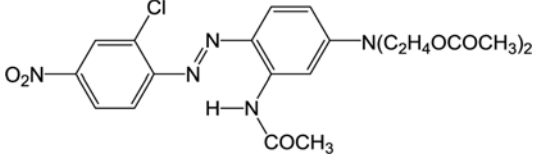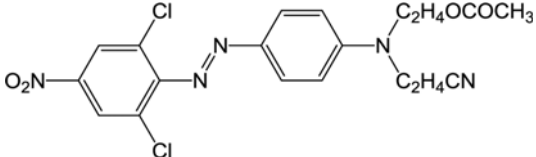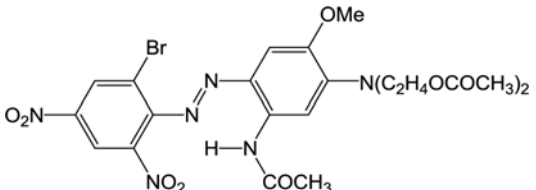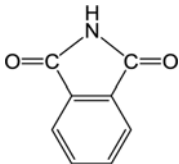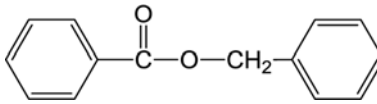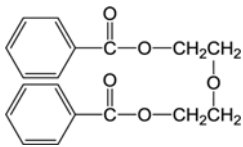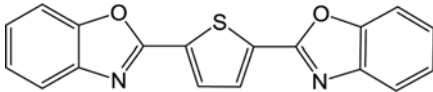
The term 'carrier' has been defined by earlier researchers as a type of accelerant, particularly used in the dyeing or printing of hydrophobic fibers with disperse dyes [16]. Carriers are thought to be absorbed by fibers through polar and non-polar interactions. Based on the classical carrier dyeing theory, the procedure of promoting dyeing of carrier contains two continuous steps. In the 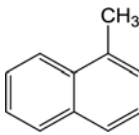first step, the carrier is adsorbed on the synthetic fiber and diffuses into the fiber. This function is help to the disperse dye diffusion in the fiber due to its plasticization, which can effectively increase the distance between macromolecules. In the second step, the carrier mol-

Table 1. Structure of the fiber, dyes and carriers used

Category	Commercial/C.I. generic name	Structure
Fiber	Poly(p-phenylene benzobisoxazole)	
Disperse dye	C.I. Disperse Red 225	
	C.I. Disperse Yellow 30	
	C.I. Disperse Blue 79	
Carrier	Phthalimide	
	α-Methylnaphthalene	
	Benzyl benzoate	
	Diethylene glycol dibenzoate	
	2,5-Di(benzo[d]oxazol-2-yl)thiophene (Fluorescent brightener EBF)	

ecules gradually desorb from the fiber and the dye molecules are adsorbed on the fiber synchronously. This step is a control procedure because it can ultimately determine the amount of dye on dyed fiber. Salvin [17] postulated that carriers replace fiber-fiber interactions with more readily breakable fiber-carrier bonds, which can sequentially permit the polymer chain to move easily and promote more free volume available in the fiber. As a result, the glass transition temperature (T_g) and dyeing transition temperature (T_d) of the fiber may be expected to be decreased during the carrier dyeing process, and the diffusion rate of dyes and the dye exhaustion to be increased [18,19]. Therefore, carriers could be used in

the coloration of synthetic fiber, for example, for acrylic, PVC and polyphenylene sulfide fibers with cationic dyes [19-23], and for polyester and triacetate fibers with disperse dyes [24-26].

In addition to our previous researches [14,15], the results related to PBO fiber dyeing had never been published. In the present study, for further improving disperse dyeing process, five organic substances with different structures (Table 1) were first used as carriers in the dyeing of PBO fiber with disperse dyes to increase the dyeability of PBO fiber. The color strength (K/S value), tensile strength and dyeing fastness of dyed samples and the percentage of dye exhaustion were measured and compared under different dyeing con-

ditions. Moreover, the effect of carriers on the flame retardant property and the supramolecular structure of PBO fiber was analyzed to evaluate the possibility of this carrier dyeing process used for PBO fiber with disperse dyes.

EXPERIMENTAL

1. Materials

Poly(*p*-phenylene benzobisoxazole) fiber (PBO fiber), free of fluorescent brightener, was used in this study which came from Chenguang Chemical Industry Institute (Chengdu, China) and the filament diameter was 21.9 μm. To remove the oil and chemicals clung on the fiber, it was scoured with acetone and then with ethanol at room temperature for 20 min, respectively, and repeatedly washed with hot and cold deionized water and dried under laboratory conditions. Three commercial disperse dyes and five carriers of phthalimide, *α*-methylnaphthalene, benzyl benzoate, diethylene glycol dibenzoate and 2,5-di(benzo[*d*]oxazol-2-yl)thiophene, listed in Table 1, were used without further purification. Polyphosphoric acid (PPA), sodium dithionite, sodium carbonate, sodium acetate, acetic acid, acetone and ethanol were analytical grade.

2. Pretreating and Dyeing

The fiber bundles were dipped in the heated PPA liquid at temperature 65 °C for 2 min. Then the specimen was rinsed with flowing water for ten minutes, and was dipped in 10 g/L sodium carbonate aqueous solution. Finally, the fiber bundles were rinsed repeatedly with hot and cold deionized water and dried under laboratory conditions[14].

All samples were dyed in a laboratory dyeing machine (Ahiba Nuiance, Datacolor International, Switzerland), and the exhaustion dyeing process and the bath composition are depicted in Fig. 1. Then the dyed samples were washed with 3 g/L sodium dithionite and 1 g/L sodium carbonate aqueous solution at 80 °C for 10 min at material-to-liquor ratio 1:30, rinsed with hot and cold deionized water three times, respectively, and dried under laboratory conditions[26].

3. Measurements of Color Strength of Dyed Sample

The fiber bundles to be tested were evenly wrapped on an opaque plastic sheet in both the horizontal and vertical directions, whose length, width and thickness was 2 cm, 2 cm and 0.1 cm, respectively. The reflectance of the dyed specimen was measured by reflectance spectrophotometry (Spectra Flash SF600, Data Color Co.) under a D_{65} illuminant using 10° standard observer [14]. From the reflectance values (R) at the maximum absorption wavelength (λ_{max}) for each dye, the corresponding color strength (K/S) values of the samples were calculated by using the Kubelka-Munk equation (see Eq. (1)). The color strength (K/S value) is used to indirectly characterize the concentration of dye fixed on fiber or fabric surface, which is a semi-quantitative description of color depth of the dyed sample [27]. The K/S value was obtained by the average of five tests.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{1}$$

where K is the absorption coefficient of the substrate, S is the scattering coefficient of the substrate and R is the reflectance of the dyed fabric at λ_{max}.

4. Measurements of Dye Exhaustion

Based on the Lambert-Beer Law, the determination of dye bath concentration (g/L) contained two main steps. First, the absorbance of the dye bath was tested on Shimadzu UV-2401PC UV/Visible spectrophotometer at the maximum absorption wavelength (λ_{max}) of the dye solution. Second, the concentration was acquired by referring the measured absorbance to the corresponding standard concentration-absorbance curves of the three kinds of dyes. The testing solution was composed of H_2O and N,N-dimethyl formamide, of which the volume ratio of these two constituents was 1 : 1, and the pH value of the mixed solution was adjusted to 6.0±0.2 with dilute acetic acid solution [28]. The percentage of the dye exhaustion on PBO (%E) was calculated using Eq. (2):

$$\%E = 1 - \frac{C_2}{C_1} \times 100 \tag{2}$$

where C_1 and C_2 are the concentrations of a dye in the dye bath before and after dyeing of PBO, respectively [14].

5. Flammability Analysis

The flame-retardant test of all samples was carried out by measuring the limiting oxygen index (LOI) value on a flammability tester (S.C. Dey, Kolkata) as per the standard ASTM D 2863-77 [29] procedure for self-supported samples. The minimum concentration of oxygen required in the oxygen-nitrogen gas environment just sufficient to sustain the flame for 30 s was used for calculating the LOI value according to the following formula [30,31]:

$$LOI = \frac{\text{volume of oxygen}}{\text{volume of nitrogen} + \text{volume of oxygen}} \times 100 \tag{3}$$

6. X-ray Diffraction Analysis

To determine crystallinity, the integral area distribution method was used, which is suitable for a polymer having a limited number of crystalline peaks in its X-ray diffraction pattern I=f(2θ). In this way, the sharp diffraction peak(s) of the crystalline region could be differentiated from the scattering of the amorphous region. That is, after the background scattering had been deducted from the XRD pattern, the total diffraction area under the curve (S_o), and the area of crystalline portion in the XRD pattern (S_k), were integrated. The crystallinity (K) is calculated as [32,33]:

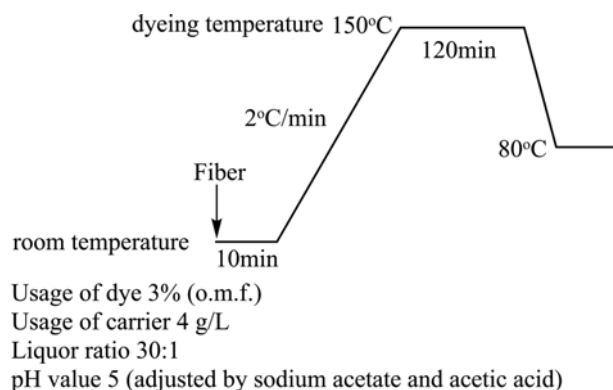$$\%K = S_k \times 100 / S_o \tag{4}$$

Fig. 1. Exhaustion of dyeing method.

7. Measurements of Degree of Orientation

Because the moisture content of a fiber greatly affects test results on the degree of orientation, the samples were laid under conditions of constant temperature and humidity (25 °C, RH 60%) for 24 hours before the test. An SOT-II velocity-oriented tester (Shandong Laizhou Electronic Instrument Co., Ltd., China) was used as test instrument. Both ends of the fiber were fixed on the tester, and the appropriate tension was applied to the test sample. After the sound wave through the fiber bad become stable, the value of sonic speed on the display was recorded. Ten measurements for each sample were averaged to determine the value of sonic speed [34,35].

8. Measurement of Tensile strength and Color Fastness

The tensile strength of filaments was tested at 100 mm/min (25 °C, RH 60%) according to BISFA-2004 *Testing Methods for Polyester Filament Yarns* [36] using a YG001A fiber electronic strength tester (Textile Instrument Ltd., China). For dyed samples before and after washing or light irradiation, the washing fastness and light fastness were tested, expressed as CIELAB color difference (ΔE) according to ISO 105-C02 (1989) [37] and ISO 105-B02 (1994) [38] respectively [39].

RESULTS AND DISCUSSION

1. Effect of the Different Carriers on the K/S Value of the Dyed Sample

The effect of the different carriers on the color strength (K/S value) of dyed PBO fiber with three kinds of disperse dyes is shown in Fig. 2. The K/S values of all dyed samples increased with the dyeing temperature, and when the temperature was equal to or higher than 140 °C, the increase of K/S value of each dyed fiber became faster. In all of the five carriers used, the dyed samples with phthalimide and benzyl benzoate had higher K/S values and significant upward trend than the three others. The results indicated that the PBO fiber could hardly be colored with disperse dyes at temperature less than or equal to 130 °C. The repeat unit of PBO polymer contains a benzene ring and a benzobisoxazole ring, a typical rigid chain structure [1]. Without enough thermal energy at relatively low temperatures, the movement of chain segment of PBO could hardly occur, so it was difficult for the dye molecule to diffuse into the fiber. This result was similar to previous studies [14] in spite of carriers being used in the dyeing.

The carriers, except for fluorescent brightener EBF, are usually used to dye polyester fabrics through a special carrier dyeing process in which the lower dyeing temperatures than usual can be employed. Fluorescent brightener EBF was selected as a carrier here because of the similarity between the structure of EBF and the PBO chain unit. The mechanism of carrier dyeing is based on the structural similarity either between the fiber and the carrier, or between the dye and the carrier involved. The former is correlative to the plasticization of the fiber and the latter the solubilization of the dye. So the carrier in the process can promote the adsorption and diffusion of dye molecules into the fiber, and as a result that the dye
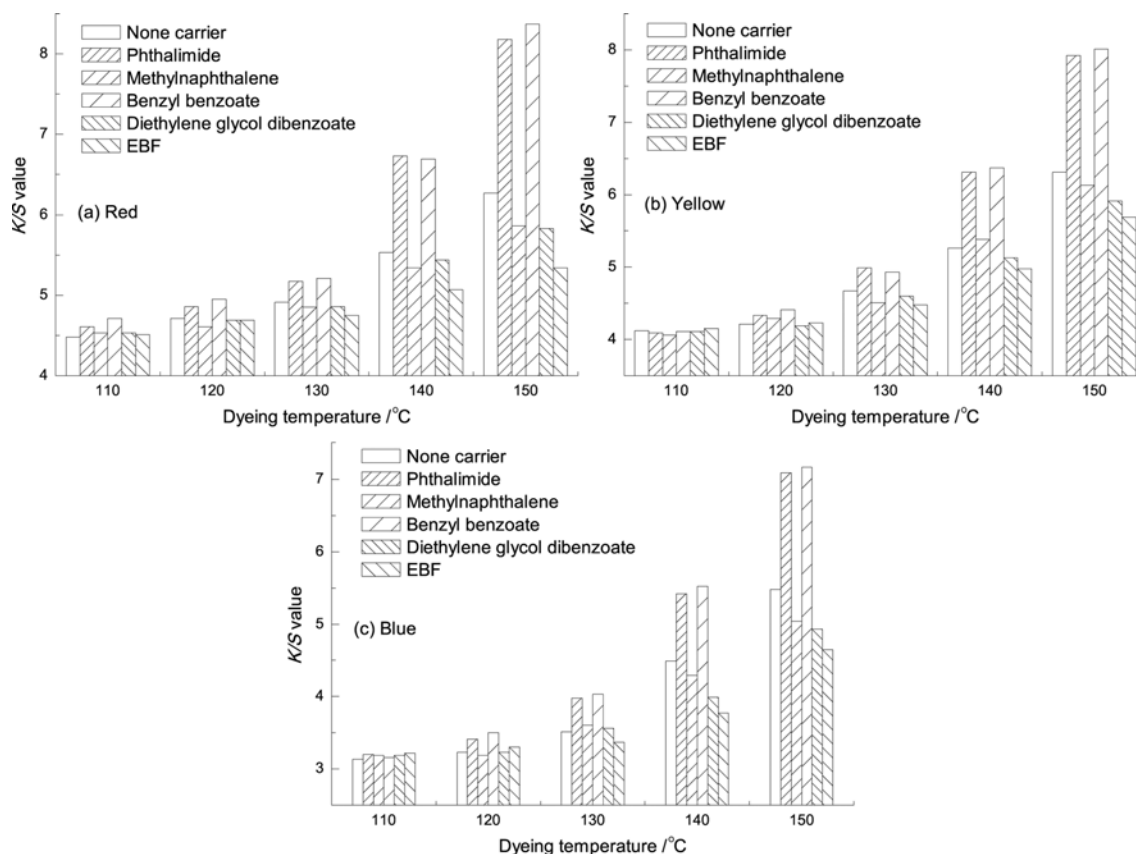

Fig. 2. Effect of the different carriers on the K/S value of the samples dyed with three disperse dyes.

uptake is improved [40]. The K/S values in Fig. 2 show that only phthalimide and benzyl benzoate had perceptible acceleration of disperse dyeing of the PBO fiber, especially at higher temperatures. However, the K/S values of the other dyed samples were hardly improved, and even lower in the case of EBF.

Phthalimide, methylnaphthalene and EBF, among the five carriers, have a fused ring or fused-heterocycle structure similar to the benzobisoxazole unit of PBO [40]. For phthalimide, it was true for all the dyes used in the carrier dyeing at elevated dyeing temperatures. However, there was no evident increase in the K/S value in the process used with methylnaphthalene and EBF. The opposite effect on the dye-uptake occurred, especially for the EBF system, as shown in Fig. 2, where the K/S value was even lower than the corresponding control sample. The unconventional result suggested that EBF molecules actually prevent to dye molecules adsorb on the fiber from the dye bath. For this phenomenon, a rational explanation could be that the molecular size of EBF was larger than phthalimide (see Table 1), which could have larger affinity between EBF molecules and the fiber. As a result, the carrier EBF adsorbed on the fiber surface was not easily desorbed and replaced by dye molecules. As for methylnaphthalene, its naphthaline nucleus was obviously different from benzobisoxazole of PBO fiber, so the affinity between them could be ignored.

On the other hand, both diethylene glycol dibenzoate and benzyl benzoate have the structure of benzene derivatives which is similar to the three dyes used. When this type of carrier was applied, it could be expected that the affinity between the carrier and the dye was relatively large and the carriers could carry them into the fiber to be dyed. Compared with benzyl benzoate, diethylene glycol dibenzoate did not show any accelerating effect on the dyeing, as shown in Fig. 2. Among the reasons, the difference between the ether linkage in diethylene glycol dibenzoate and the macromolecular unit of PBO was very obvious. The addition of diethylene glycol dibenzoate almost did not help the plasticization of PBO fiber, which was not different from the effect of diethylene glycol dibenzoate in disperse dyeing process of polyester.

From the results and discussion above, both benzyl benzoate and phthalimide could effectively improve the dyeability of the PBO fiber, which had moderate molecular size and hydrophobicity, and whose structural similarity with the fiber and dyes used was also relatively modest. Therefore, the novel carrier dyeing proved to be feasible. And the effect of the carriers on the dyeing property and structures of the fiber was discussed as below.

2. Effect of the Dyeing Conditions on the Dyeability of PBO Fiber

Temperature generally plays a key role in dyeing processes of synthetic fibers or fabrics with disperse dyes, especially in PBO dyeing procedures [14]. Based on dyeing thermodynamics theory, a higher temperature is not beneficial to the increase of the dye uptake (or the equilibrium adsorption capacity) for general dyeing processes. The data in Figs. 2 and 3, however, show that the K/S values and the dye exhaustion (%E) significantly increased with the temperature rising. This demonstrated that the dyeing temperatures in our experiment were lower than the optimal temperature for PBO fiber dyeing. Below 140-150 °C, the rigid chain segment of PBO was still in the "frozen" state and the disperse dye failed to sufficiently diffuse into the fiber. It can be expected that the dye
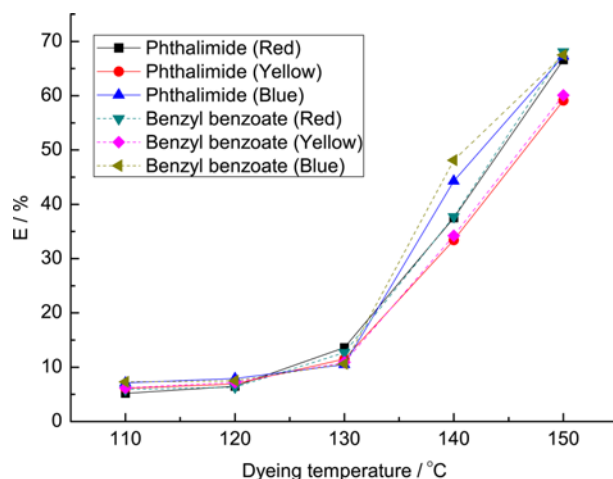

Fig. 3. Effect of dyeing temperature on the dye exhaustion on PBO fiber.

uptake would be much higher if the dyeing temperature was to be further increased. Limited to the existing conditions, unfortunately, we could not obtain a higher dyeing temperature than 150 °C. Therefore, these results imply that the dyeing process was not controlled by the thermodynamics but by the kinetics at the existing dyeing temperatures. This is also our intention to select the appropriate carriers used in PBO fiber dyeing process.

The effect of the concentration of carriers on the K/S value of dyed samples and the percentage of the dye exhaustion (%E) after the dyeing process of PBO fibers pretreated with PPA were shown in Fig. 4(a) and 4(b), respectively. It can be seen from these curves that both the K/S value and %E increased with the addition of benzyl benzoate and phthalimide up to 4 g/L, and then declined gradually or remained unchanged with further increasing the carrier concentration. The two carriers in a concentration range obviously improved the dyeing property, which may result from the plastici-
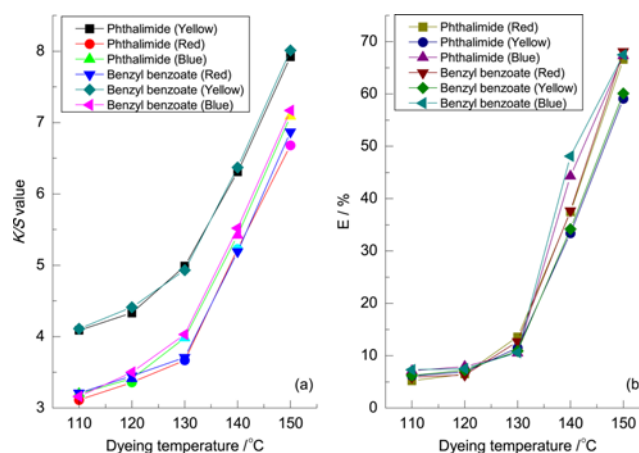

Fig. 4. Effect of carrier concentration on the K/S value of the dyed samples and the dye exhaustion on PBO fibers (None-carrier condition: K/S value of dyed samples with red, yellow and blue dyes was 4.77, 6.31 and 5.48 respectively; %E of dyed samples with red, yellow and blue dyes was 56.63, 51.05 and 54.21, respectively.).
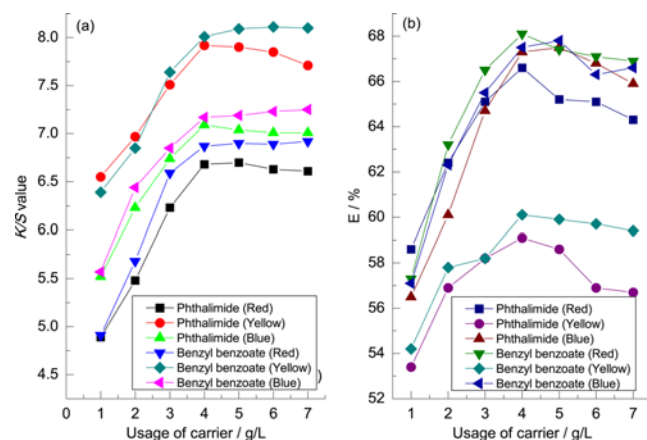
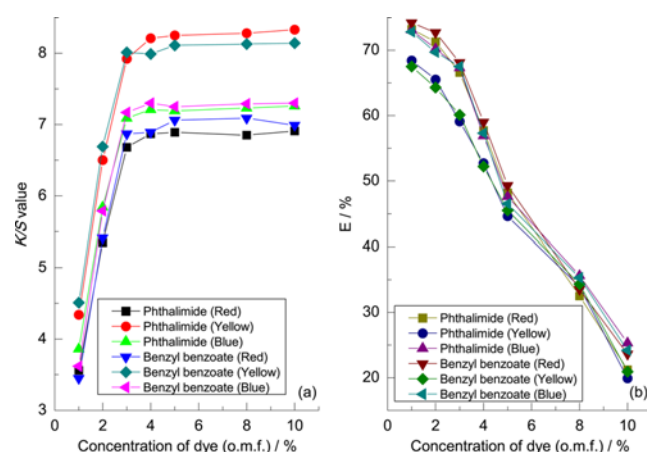**Fig. 5. Effect of dyeing time on K/S value of the dyed samples and the dye exhaustion on PBO fibers.**

Fig. 6. Effect of dye concentration on K/S value of the dyed samples and the dye exhaustion on PBO fibers.

zation of carriers on the PBO fiber or the solubilization on the dyes, or from their combination. Once the usage of carrier exceeded a certain concentration, such as 4 g/L here, the carrier adsorbed on the fiber could be saturated, so that no more dyeing sites (surface or free volume of the fiber) on the fiber could be available to accept the dye molecules.

Fig. 5 indicates that the K/S values of all the dyed samples and the %E rapidly increased with prolonging dyeing time up to 120 min, and then the growth tended to slow down. This means that,

during the dyeing time of 120 min, the carrier dyeing process could nearly reach the kinetic and thermodynamic equilibrium, which was similar to conventional dyeing processes of other synthetic fibers, such as polyphenylene sulfide fibers [26].

Fig. 6 shows the effect of the dye concentration on the K/S values of the dyed samples and the %E. The K/S values of dyed fibers rapidly rose to 6.7-8.1 with increasing the dye concentration to 3% and then almost leveled off. Accordingly, the %E slowly fell to 60-69% at dye concentration of 3% and then rapidly fell down with the further increase of the dye concentration. So, a dye concentration of 3% could be considered to be the optimal dye concentration. When the dyeing process operated at 3% dye concentration without carrier, the K/S values and %E were 5.5-6.3 and 55-58%, respectively [14]. By comparing the data before and after adding carrier, the two parameters in carrier dyeing method were evidently higher. Therefore, the carrier dyeing method is suitable for dyeing of PBO fiber with a highly dense supramolecular structure.

3. Effect of the Carriers on the Flame Retardant Property of PBO Fiber

Limiting oxygen index (LOI) value is widely used to measure the flammability of polymers and to investigate the effectiveness of fire retardants [30,31]. The effects of the carriers on the flame retardant property of original, pretreated and dyed PBO fiber are shown in Table 2. The data in Table 2 indicate that the LOI values of all samples after carrier dyeing were lower than that of before dyeing. Although the dyed fiber was repeatedly washed with deionized water, dyes and a small amount of carriers were still attached on the fibers. Both the dyes and carriers are combustible, so the flame retardant property of the dyed fibers was reduced. But the LOI values of all dyed fibers were still far higher than the oxygen content in atmosphere (27%), which meant that the dyed PBO fibers with these two carriers were still regarded as good flame-retardant materials.

4. Effect of the Carrier on the Supramolecular Structure of PBO Fiber

In Fig. 7, the X-ray diffractograms of the original and dyed PBO fiber via carrier dyeing are compared. The XRD patterns of all treated samples were very similar to the original sample and the patterns had almost the same diffraction angle, which indicated that the basic crystals of the fiber did not substantially change during the pretreatment with PPA and the two carriers. To further clarify the changes of the crystallinity, the diffraction peak area was calculated and the exact crystallinity was listed in Table 3. Owing to the etching and swelling of PPA and plasticization of carrier, the crystalline structure of the fiber was destroyed successively, and the de-

Table 2. Effect of usage of carrier on limiting oxygen index (LOI) of original, pretreated and dyed fiber

| Samples[a] | LOI/% | | | | | | | | | | |
| | None carrier[b] | Phthalimide | | | | | Benzyl benzoate | | | | |
		1	2	3	5	7	1	2	3	5	7
Original	67	65	65-66	66	66	65-66	65-66	65	65	66	65-66
Pretreated with PPA	70	65	64-65	64-65	64	64	65-66	65	65	65	65-66
Dyed	55	55-56	56	55	55-56	55	56	55	55-56	55	55

[a]Carrier treating condition: pH 5, liquor ratio 30 : 1, treating at 150 °C for 120 min
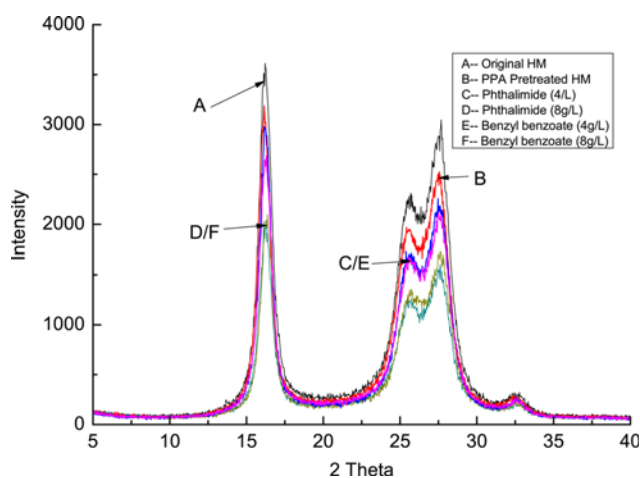[b]The results refered to Ref 14

Fig. 7. X-ray diffraction patterns of untreated and treated fibers with carriers.

Table 3. Degree of crystallinity of original, pretreated and dyed fibers with carriers

Samples[a]	Degree of crystallinity/%
	HM
Original fiber	93.15
Pretreated fiber with PPA	87.09
Phthalimide (4/L)	85.93
Phthalimide (8/L)	83.98
Benzyl benzoate (4/L)	86.06
Benzyl benzoate (8/L)	85.12

[a]Carrier treating condition: pH 5, liquor ratio 30 : 1, treating at 150 °C for 120 min

crease became more obvious with increasing the usage of carriers. The carrier-dyed sample using phthalimide had lower crystallinity than that with benzyl benzoate, which meant a stronger plasticization effect of phthalimide on the fiber. This was consistent with the effect of the carrier structure on dyeing properties above.

The anisotropy of sonic wave propagation in a fiber is the basic principle of measuring the orientation degree of fiber by sonic velocity. Thus, a larger value of sonic speed corresponds to a higher degree of orientation of the fiber [14,34,35]. In Fig. 8, the sonic speed values of the fibers treated with PPA and carriers are lower than that
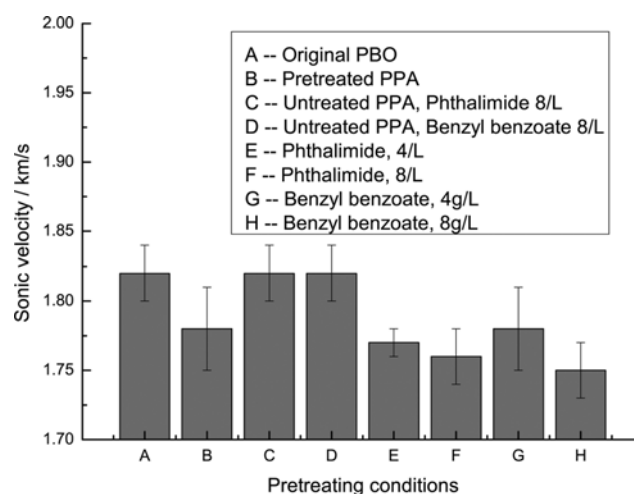

Fig. 8. Effect of treatment process on the degree of orientation of PBO.

of the original sample. And it decreased with increasing the concentration of carrier. The result is consistent with the influencing factors on the crystallinity, because any factor that can reduce the regularity of the fiber could decrease the orientation degree, as well as the crystallinity of the fiber. But, the negative effect of the carrier dyeing on supramolecular structure was very limited, which was similar to the pretreatment of PBO fiber by polyphosphoric acid [14]. And the results were also consistent with the classical theory of the carrier dyeing [16,18,26,41,42].

5. Effect of the Dyeing Process on the Tensile Strength and Fastness of Dyed Fiber

The values of tensile strength of PBO fibers dyed with three different disperse dyes are presented in Table 4. The tensile strength and the elongation at break decreased after the pretreatment with PPA. The dense surface layer of PBO fiber was destroyed by the etching of polyphosphoric acid [14]. Although the crystallinity of the dyed fiber lightly decreased, the plasticization was relatively mild and uniform, and the amorphous region formed during the dyeing process was also small and dispersed, which did not bring significant defects on the surface of dyed fibers. Thus the decrease of tensile strength was very limited.

Compared to the color changes of dyed samples before and after washing and light irradiation, the color fastness of the dyed fibers was presented indirectly in color changes of dyed fibers, listed in

Table 4. Tensile Strength of Dyed PPS fabrics with three different disperse dyes

Sample		Tensile strength/GPa	Elongation at break/%	Loss of strength/%
Original fiber		4.69	2.3	N/A
Pretreated fiber		4.52	2.1	3.63
Disperse Red 225	Phthalimide	4.48	2.2	4.48
	Benzyl benzoate	4.51	2.1	3.84
Disperse Yellow 30	Phthalimide	4.50	2.1	4.05
	Benzyl benzoate	4.50	2.1	4.05
Disperse Blue 79	Phthalimide	4.51	2.0	3.84
	Benzyl benzoate	4.49	2.0	4.26

Table 5. Fastness properties of dyed PBO fabrics with three different disperse dyes[a]

Samples		Washing fastness[b]				Light fastness[c]			
		ΔE	ΔL	ΔC	Δh	ΔE	ΔL	ΔC	Δh
Disperse Red 225	Phthalimide	0.794	0.271	−0.733	−0.139	1.793	−1.462	−0.913	−0.495
	Benzyl benzoate	0.821	0.289	−0.757	−0.133	1.811	−1.530	−0.845	−0.473
Disperse Yellow 30	Phthalimide	0.919	0.702	−0.532	−0.261	2.304	−1.930	−1.220	−0.312
	Benzyl benzoate	0.915	0.693	−0.554	−0.222	2.577	−2.210	−1.290	−0.306
Disperse Blue 79	Phthalimide	0.844	0.431	-0.684	−0.241	2.646	−2.207	−1.320	−0.624
	Benzyl benzoate	0.844	0.440	−0.679	−0.239	2.714	−2.254	−1.338	−0.703

[a]Dyeing condition: pH 5, liquor ratio 30 : 1, dyeing at 150 °C for 120 min
[b]Fading fastness
[c]Exposure time 20 hours

Table 5. The washing fastness was mainly affected by the change of color hue, and the light fastness was mostly influenced by the change of color brightness [14].

Under the existing dyeing conditions, for the PBO fiber with high crystallinity and orientation degree, dye molecules only adsorbed and aggregated on the fiber surface or in the surface layer, in general. And the dyes could not easily diffuse into the interior of the fiber. So that the dyes could be easily scoured off by washing or faded by light irradiation. However, the color differences (ΔE) of dyed fibers before and after tests were in the ranges of 0.71-0.92 for washing and 1.8-2.8 for irradiation, respectively, corresponding to the grey scale level 4-5 and 3-4 for washing fastness and light fastness respectively (Instrumental assessment of change in color for determination of grey scale rating, ISO, 1996, 105-A05). These results are commercially acceptable.

CONCLUSIONS

The PBO fiber was dyed with disperse dyes using benzyl benzoate and phthalimide as the carriers. The results indicated that the carrier dyeing method could effectively improve the dyeability of PBO fiber. The structural similarity between the fiber and carrier, such as phthalimide, or between the dyes and carrier, such as benzyl benzoate, would possibly play a key role in promoting the color strength of dyed PBO fiber. At the highest practicable temperature 150 °C, the optimal concentration of carrier 4 g/L, and dyeing time 120 min would be beneficial to increasing the K/S value of dyed sample and the percentage of dye exhaustion. Insignificant changes of crystallinity and orientation degree of the PBO fiber were found in the carrier dyeing process. Furthermore, the macroscopic properties of dyed samples, such as flame retardant property, the tensile strength and dyeing fastness, could meet the requirements of special industry and military camouflage protection.

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