Thermal Properties and Chemical Changes in Blend Melt Spinning of Cellulose Acetate Butyrate and a Novel Cationic Dyeable Copolyester

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ABSTRACT: A novel cationic dyeable copolyester (MCDP) containing purified terephthalate acid (PTA), ethylene glycol (EG), 2-methyl-1,3-propanediol (MPD), and sodium-5-sulfo-isophthalate (SIP) was synthesized via direct esterification method. The chemical structure of modified cationic dyeable polyester (MCPD) was confirmed by FTIR and ^{1}H-NMR. The thermal properties of MCDP and cellulose acetate butyrate (CAB) blends with different blend ratios were investigated by DSC. The results revealed that MCDP and CAB were immiscible polymer blends, and the glass transition temperature of CAB in blend fibers was higher than that of CAB in blend chips because of the strengthening hydrogen bonding. The chemical changes of MCDP and CAB in blend melt spinning were analyzed. It was found that the thermal hydrolysis reaction of ester side groups of CAB occurred in blend melt spinning, which resulted in that the acid gas was produced and the hydroxyl group content of CAB was increased. Furthermore, the moisture absorption of blend fibers was improved about three times than pure MCDP fiber even after washing 30 times. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2487–2495, 2010

Key words: copolyester; cellulose acetate butyrate; fiber; blend melt spinning

INTRODUCTION

Poly(ethylene terephthalate) (PET) fiber has many outstanding properties for textile and clothing applications. Despite the great success, it exhibits limitations in certain properties such as dyeability, moisture absorption, pilling resistance, and etc. Many copolymers, in which a small amount of a third component is added to PET in an effort to improve on the properties of PET resins, have been investigated for fiber applications.[1–3] Sodium sulfonate-containing PET is known for long time and was originally commercialized by DuPont as textile fibers with improved dyeability to cationic dyes, but it also limited by the high melt viscosity resulted from the ionic aggregates effect of sodium-5-sulfo-isophthalate (SIP).[4,5] Therefore, we synthesized a novel cationic dyeable copolyester (MCDP) by adding 2-methyl-1,3-propanediol (MPD) into sulfonate-containing PET. MPD, as a smallest branched aliphatic diol, can reduce the crystallizability of modified polyester effectively.[6] Shwartz and coworkers[7] revealed that the modified polyester containing MPD has well spinnability and commercial values. No prior studies

of both MPD and SIP added to PET could be found. In our work, we found that MPD can reduce the ionic aggregates of SIP[8,9] and further enhance the dyeability of modified polyester fiber because of the irregular molecular structure of MPD. More details about synthesis, characterization, and dyeability of MCDP will be introduced elsewhere.

In this article, we report a modification method by using of cellulose acetate butyrate (CAB) to improve the moisture absorption of MCDP. It is well known that CAB is one of the most important thermoplastic cellulose esters derived from natural polymers.[10] In the last few years, various studies[11–15] have been performed on the blends of CAB with other polymers in general attempt to use the high glass transition temperature (T_g) or the molecular stiffness of CAB,[16] to compensate the weakness of other polymers, and to develop materials with friendly environmental conditions. For these studies, all of the articles were interested in the miscibility, thermal property, crystallizability and super-molecular structure of the blends. However, CAB often discolors and suffers loss of physical properties due to the poor thermal stability during melt processing.[17] The chemical changes of CAB in blend melt process which affect on the performance of blends have received very little attention. Therefore, the purpose of this article is to study the thermal properties and chemical changes in blend melt spinning. On the

basis of the experimental results, the mechanism of chemical changes of CAB during blend melt spinning is discussed. Meanwhile, the moisture absorption of MCDP fiber is well improved by blending with CAB.

EXPERIMENTAL

Materials

MCDP copolyester was synthesized via purified terephthalate acid (PTA; Yizheng Chemical Fibers Corp., China), ethylene glycol (EG; Yangzi Petrochemical Corp., China), MPD (Lyondell Chemical Corp., USA), and SIP (Yangzhou Huitong Corp., China).

CAB was purchased from Acros Chemical Corp., USA. The butyryl and acetryl were 35–39 wt % and 12–15 wt %, respectively.

Synthesis of MCDP copolyester

MCDP copolyester was synthesized by direct esterification method. The esterification of PTA, EG, and MPD (feed molar ratio: diacids/diols = 1/1.4; MPD/EG = 10/90) was reacted at 180–240°C for 1.5–2 h in the presence of antimony triacetate as catalyst, water being removed by distillation at atmospheric pressure. Then the SIP (feed molar ratio: SIP/ PTA = 3/97) was added to esterification product before condensation reaction. The subsequent polycondensation was carried out at 260–275°C for 1–1.5 h under a vacuum of less than 1 torr. Finally, MCDP copolyester was obtained. The intrinsic viscosity of MCDP was 0.486 dL/g as measured at 25°C using phenol/tetrachloroethane (3 : 2, w/w) as a mixing solvent.

Preparation of MCDP/CAB blend fibers

First, MCDP and CAB were mixed with a certain proportion and dried under vacuum at 110°C for 12 h. The blends were extruded and chipped by using Thermo Hakke EUROLAB-16 corotating twin-screw extruder. The temperature, the rotation rate, and the processing period were 250°C, 85 rmp, and 2 min, respectively. Different component samples are coded in Table I.

Then, the MCDP/CAB blend chips were dried by heating under vacuum at 110°C for 12 h. The blend melt spinning experiment was performed using ABE spinning equipment. All the MCDP/CAB blend chips, along with MCDP and CAB chips, were spun with the same temperature settings; the temperature zones 1, 2, 3, and 4 (spinneret) in the spinning equipment were 265, 295, 300, and 280°C, respectively. Unfortunately, the MCDP/CAB blend filaments, except for the C5 and C10 blend filaments,

TABLE I
Sample Code of Different CAB/MCDP Weight Ratio

No.	CAB (wt %)	MCDP (wt %)	Sample code
1	0	100	MCDP
2	5	95	C5
3	10	90	C10
4	15	85	C15
5	30	70	C30
6	50	50	C50
7	100	0	CAB

were hardly wound onto a bobbin at any given take-up velocity due to the immiscible of MCDP and CAB. Only the as-spun fibers extruded from the spinneret can be obtained. The C5 and C10 filaments were subjected to the posting-spinning drawing experiments by using Barmag two-stage drawing equipment with total draw ratio $R = 4$, the first and second stage temperature settings of two-stage drawing equipment were 80 and 160°C, respectively.

Measurement and characterization

FTIR analysis was done on Nicolet 8700 IR spectrometer. All the spectra were collected in transmittance through KBr pellet.

The characterization of MCDP was determined by ^{1}H-NMR spectrometer (using Bruker Avance400). The MCDP sample was dissolved in a mixture of deutero-chloroform/deutero-trifluoroacetic acid (3 : 1, v/v), and tetramethylsilane was used as an internal standard. The structure of CAB was analyzed by ^{13}C-NMR. The CAB sample was dissolved in deutero-chloroform. The center peak of deutero-chloroform was used as an internal standard.

The thermal properties were investigated with a PerkinElmer Diamond DSC under a N_2 atmosphere. Every sample was heated from 40 to 300°C at a heating rate of 20°C/min.

Pyrolysis-Gas Chromatography/Mass Spectrometry (py-GCMS) studies were carried out via using Shimadzu GC/MS-QP2010 system with a pyrolysis unit (Frontier Laboratories Ltd.). The sample was pyrolyzed at 300°C. The products were separated on a DB-5MS column and identified through comparison of their EI+ mass spectra with Nist 107, Wiley, and NBS electronic libraries.

Thermogravimetric/infrared spectroscopic (TG-IR) analysis was performed using a Netzsch TG 209F1 in conjunction with a Nicolet 8700 spectrometer. Each sample was accurately weighted 5.0 mg. The temperature was raised with 20°C/min from 40 to 300°C and held at 300°C. The volatile gaseous products were identified by IR spectrophotometer and recorded at each 5-min intervals.
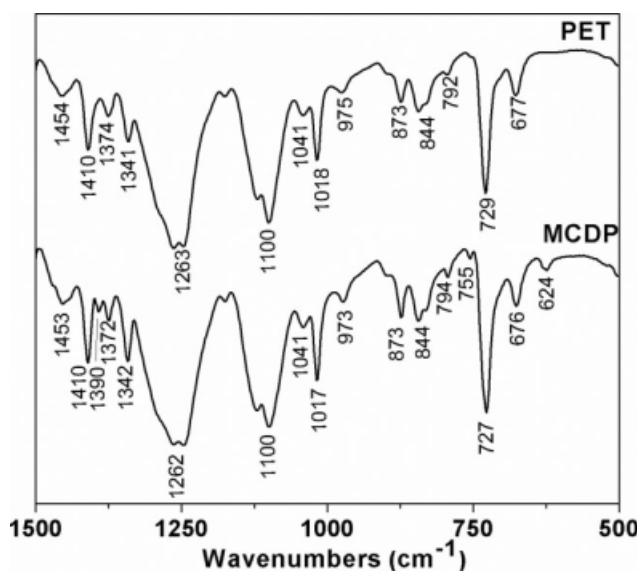
Figure 1 The FTIR spectra of PET and MCDP.

All the samples were sputter coated with a thin layer of gold for scanning electron microscopic (SEM) observations via using a HITACHI S3000N SEM.

Moisture absorption of blend fibers was measured after deoiling and drying. The fiber was kept at 25°C, 65% RH for 48 h, and weighted (w_1/g). Then after balancing at 100°C for 48 h in vacuum baking oven, it was again weighed (w_2/g). Moisture absorption (M) can be calculated according to this formula[18]:

$$M(\%) = \frac{w_1 - w_2}{w_1} \times 100\% \qquad (1)$$

The dyeability of blend fibers was carried out using a laboratory scale dyeing machine (Atlas Linitest Plus). One gram of the sample was placed in a 2% owf Cationic Red GRL dyebath of a liquor ratio 50 : 1 and was dyed at 100°C for 1 h. The commercial cationic dyeable polyester fiber (CDP; SIP content: 3 mol %) was also dyed at same condition for comparison. The dye uptake value was determined by the absorbance of each dyebath solution before and after the dyeing via using a PerkinElmer Lambda 35 UV/visible scanning spectrophotometer. The dye uptake (D) was calculated by the follow equation,[19] where A_0 and A are the absorbance of the dyebath before and after dyeing, respectively.

$$D(\%) = \frac{A_0 - A}{A_0} \times 100\% \qquad (2)$$

Mechanical properties of blend fibers were determined by using Shimadzu AGS-500ND universal material testing machine. Length between two hold-

ing jigs was 200 mm and drop rate was 200 mm/min at room temperature.

RESULTS AND DISCUSSION

Characterization of MCDP copolyester

The FTIR spectra of the MCDP and PET are shown in Figure 1. Most absorption bands of MCDP were similar to the PET homopolymer, as well as a certain absorption bands belong to MCDP. Particularly, the absorption peaks at 624 cm^{-1} and 755 cm^{-1} were attributed to benzene ring of SIP units, and at 1390 cm^{-1} was attributed to free methyl of MPD units. The FTIR analysis indicates that the MPD and SIP were polymerized into MCDP copolyester.

The ^{1}H-NMR spectra of MCDP can also confirm the results above (Fig. 2). The chemical shifts of protons of SIP were H_1 (9.02 ppm) and H_2 (8.93 ppm), and those of MPD appeared at H_5 (4.88 ppm), H_6 (2.65 ppm) and H_7 (1.29 ppm), respectively. The chemical compositions of MCDP were determined from the relative integration areas of these proton peaks. The calculated results were listed in Table II. It shows that the SIP unit content in MCDP was very close to the SIP feed ratio, whereas the MPD unit content was a slighter rich than MPD in the feed ratio. This result might come mainly from the following reason.[20,21] MPD has a relatively high boiling point) (212°C) than that of EG (197°C).

Thermal properties changes in blend melt spinning of CAB and MCDP

The moisture absorption of MCDP fiber is very poor due to lacking of hydrophilic groups. To deal with
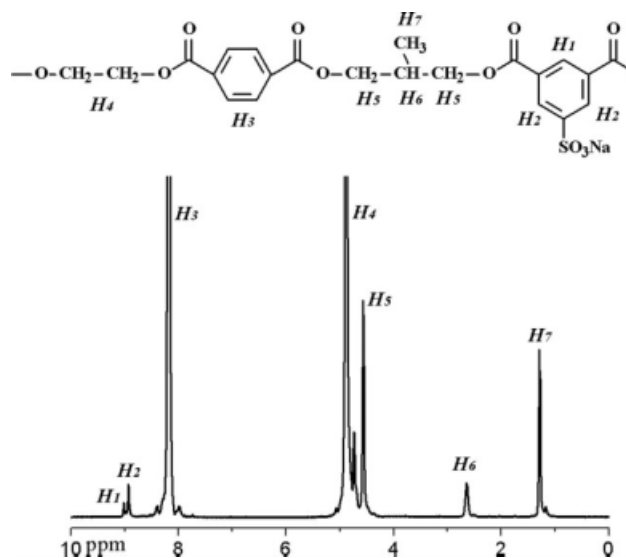

Figure 2 ^{1}H-NMR spectra of MCDP. The peaks in ^{1}H-NMR spectra coded were represented different hydrogen in MCDP molecular structure.

TABLE II
Feed Molar Ratio and Relative Ratio Calculated from ^{1}H-NMR

	Feed molar ratio	Relative ratio calculated from ^{1}H-NMR
MPD/EG	10/90	10.83/89.17
SIP/PTA	3/97	2.96/97.04

this problem, the CAB was added into the MCDP fiber via using blend melt spinning. Surprisingly, the moisture absorption of MCDP/CAB blend fiber was well improved even adding a small amount of CAB. Moreover, it was interesting to find that the gas acid smell escaped in actual MCDP/CAB blend melt spinning process. These phenomenons imply that some chemical changes occurred in the blend melt spinning. For this concern, we first investigated the thermal properties changes of MCDP/CAB blend chips and their as-spun fibers via using DSC analysis. The as-spun fibers extruded from spinneret were quickly submerged in ice-water to prevent further chemical changes during cooling process. All the results have been summarized in Table III.

Seen the DSC results of blend chips in Table III, CAB and MCDP have their own T_g in the blend chips, which was similar to the T_g of pure CAB and pure MCDP. The T_m's of MCDP in the blend chips kept constant with composition. The measured ΔH_m's of MCDP were decreased as MCDP content reduced, as shown in Figure 3. It was found a good linear relationship with an R^2 value of 0.9874. The T_m's of CAB blend chips were increased slightly and the measured ΔH_m's of CAB were increased with rising CAB content (Fig. 3). It is easily noticed that the measured $\Delta H_m'$s of MCDP or CAB were affected by the weight fraction significantly. If the ΔH_m were corrected to include the weight fraction using the formula:

$$\Delta H_m^* = \frac{\Delta H_m}{w} \quad (3)$$

where w is the weight fraction. The results show that the corrected ΔH_m^*'s of MCDP were tend to identical, whereas the corrected ΔH_m^*'s of CAB were still differ markedly. It can be assumed that the interaction between of CAB and MCDP were very poor, and the MCDP component attains the same level of crystallinity regardless of the amount of CAB. The different corrected ΔH_m^*'s value of CAB, which might be explained that the original crystallization structure of CAB in blend chips was significantly affected by the chemical reaction occurred in heating process.

For the DSC results of as-spun fibers, it can be clearly seen that T_g's of CAB in as-spun fibers were always higher than that of CAB in blend chips, and

TABLE III
Measured T_g, T_m, and ΔH_m value, and Calculated ΔH_m^* and T_g Value for Blend chips and As-Spun fibers

Sample code	Blend chips								As-spun fibers					
	MCDP				CAB				MCDP			CAB		
	T_g (°C)	T_m (°C)	ΔH_m (J/g)	$\Delta H_m^{*\,a}$ (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_m^* (J/g)	T_g (°C)	T_m (°C)	ΔH_m^* (J/g)	T_g (°C)	T_m (°C)	$T_{g\,\mathrm{cal}}{}^{b}$ (°C)
MCDP	74.6	212.9	1.24	1.24	/	/	/	/	74.6	212.2	0.56	/	/	/
C5	74.3	212.5	1.18	1.31	128.2	168.1	0.25	5.01	74.1	212.4	0.61	129.0	/	77.7
C10	75.1	212.7	1.13	1.25	128.2	168.3	0.79	7.16	73.2	212.8	0.59	129.5	/	80.7
C15	74.5	212.2	1.17	1.38	128.5	168.3	1.07	7.94	74.6	212.9	0.51	132.2	/	83.8
C30	74.2	212.9	0.95	1.35	128.1	168.7	3.07	10.24	73.5	212.6	0.65	132.6	/	93.0
C50	74.6	212.9	0.66	1.32	127.9	168.8	6.14	12.29	74.8	212.9	0.57	133.0	/	105.3
CAB	/	/	/	/	128.6	168.8	13.32	13.32	/	/	/	135.9	/	/

a ΔH_m^* value is corrected to include the weight fraction in blends.
b $T_{g\,\mathrm{cal}}$ value is calculated by Fox equation.
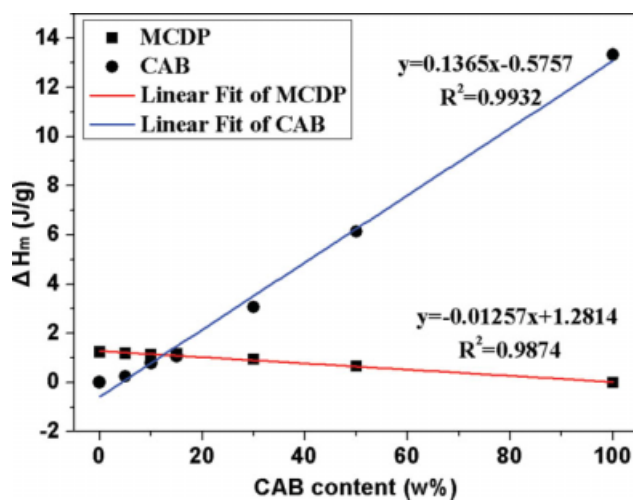
Figure 3 The plot of relationship between ΔH_m and content for MCDP and CAB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the T_g's of CAB in as-spun fibers were increased with CAB content rising. In contrast, the T_g's of MCDP in as-spun fibers were still constant. It is evident that the CAB occurred chemical changes in blend melt spinning, which perhaps enhanced the intermolecular hydrogen bonding among the hydroxyl groups in CAB. Furthermore, the T_g's of CAB in as-spun fibers were seriously increased by the strong hydroxyl bonding. In the DSC scan of as-spun fibers, the melting peak of CAB totally disappeared in as-spun fibers, indicating that no further crystallization took place in CAB during heating. The T_m's and corrected ΔH_m^*'s of MCDP in as-spun fibers still maintain constant with composition.

The DSC results in Table III also demonstrate that all the as-spun fibers existed obvious two T_g. If CAB is completely miscible with MCDP, we could calculate the theoretical single T_g value by Fox equation[22] as follows:

$$\frac{1}{T_{g\text{Blend}}} = \frac{w_{\text{CAB}}}{T_{g\text{CAB}}} + \frac{w_{\text{MCDP}} \sum_{a}^{b}}{T_{g\text{MCDP}}} \quad (4)$$

where w is the weight fraction, the subscripts "blend", "CAB," and "MCDP" indicating value of the blend fibers, CAB and MCDP fibers, respectively. However, neither the T_g's of CAB nor the T_g's of MCDP obtained from DSC had a tendency to the calculated T_g's value or depend on composition of blends, which suggests that CAB was immiscible with MCDP.
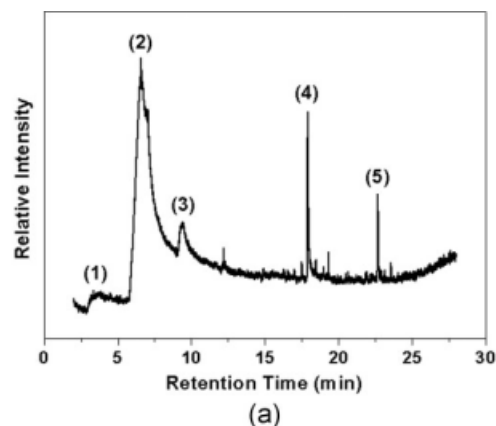
From above discussion, the conclusion can be drawn that the interaction between MCDP and CAB were poor due to the immiscible blends; the thermal properties of CAB were changed markedly by the

chemical reaction occurred in blend melt spinning, whereas that of MCDP were seldom affected.

The chemical changes in blend melt spinning of MCDP/CAB

To gain insight with regard to the chemical changes in blend melt spinning, the gaseous products of CAB were analyzed by using py-GCMS at 300°C (simulating the spinning temperature). Figure 4 shows that the volatile gaseous products of CAB at the spinning temperature were butyric acid, butyric anhydride, acetic acid, and unknown complex compound. The majority of the products were butyric acid and butyric anhydride, which accounted for 94% of all. This result might come mainly from the reasons as follows. On the one hand, the content of butyrate in CAB is higher than that of acetate in CAB. One the other hand, butyrate having more methylene units than acetate, the electron density of the oxygen atom in the butyrate is greater than that of acetate. The ester bond in butyrate is more favorably to react, which results in a relatively high content of butyric acid and butyric anhydride in gaseous products.

To probe the chemical changes further, The CAB was extracted from C5 blend chip and C5 blend fiber by dissolving in acetone, and then examined by the ^{13}C-NMR spectra, respectively. Compared

Figure 4 (a) Chromatograms obtained from CAB; (b) EI mass spectrum, molecular structure, name and relative intensity of volatile pyrolysis gaseous products of CAB.
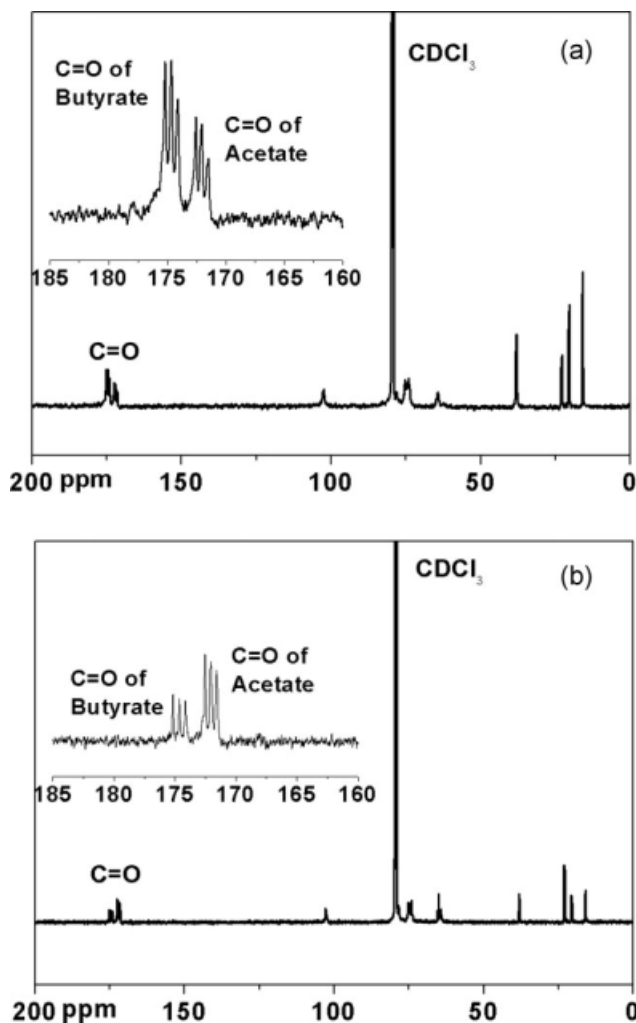
Figure 5 (a) ^{13}C-NMR spectra of CAB extracted from C5 blend chip; (b) ^{13}C-NMR spectra of CAB extracted from C5 blend fiber. The inset shows carbonyl carbon region of 185~160 ppm.

Figure 5(b) with Figure 5(a) spectra, it can be found that no peaks disappeared or new peaks emerged, especially in the region 60–110 ppm, which represents the carbon atoms in anhydroglucose units, indicating that the backbone of CAB kept stable in blend melt spinning. From the carbonyl carbon region 180–170 ppm for acetate and butyrate,[23,24] it is obviously noted that the content of butyrate was higher than that of acetate of CAB in blend chip, whereas the content of butyrate was lower than that of acetate of CAB in blend fiber, proving that most of chemical reaction occurred on butyrate ester side groups.

The hydroxyl groups of CAB and MCDP extracted from C5 blend chip and C5 blend fiber were also examined by using FTIR spectra, respectively. Seen in Figure 6, CAB in blend chip exhibited an apparently single peak with the maximum 3462.7 cm^{-1}, which may be assigned actually to a mixture of absorbance free and from intramolecularly hydrogen

bonded hydroxyl groups.[25] After blend melt spinning, the hydroxyl absorption peak of CAB in blend fiber was shifted to low wavenumbers at 3447.8 cm^{-1} which can be associated with intermolecular hydrogen bonding.[25] The new peak displayed at 3750.1 cm^{-1} due to moisture uptake, becoming pronounced with the increase of hydroxyl content of CAB. The hydroxyl absorption peaks of MCDP in blend chip and blend fiber were centered at 3432.0 cm^{-1} and 3432.2 cm^{-1}, and seldom be changed before and after melt spinning. It can be easily explained that the ester bond in MCDP was relatively stable compared with CAB due to the conjugation effect of benzene ring.

Based on the above study, it can be assumed that the chemical reaction of CAB occurred in blend melt spinning was the thermal hydrolysis reaction, which results in that the acid gas was produced and the hydroxyl group content of CAB was increased. Seen in Figure 7(a), the CAB backbone is composed of repeat glucose unit. Every glucose unit contains random acetate ester, butyrate ester, and hydroxyl groups. As an example for butyrate ester, the proposed mechanism of the thermal hydrolysis reaction of CAB in blend melt spinning is shown in Figure 7(b). It is easy to understand that the blend chips always contain water moisture due to the hydrophilicity of hydroxyl groups in CAB. Under the blend melt spinning condition, the carbonyl carbon react more favorably with water molecular which lead to the chemical scission of ester bond in CAB. Finally, the ester bond scission created carboxyl acid and hydroxyl groups.
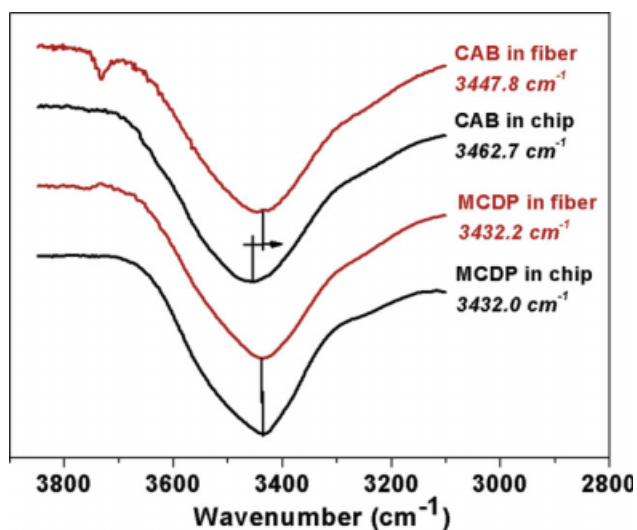

Figure 6 The hydroxyl stretching region in the FTIR spectra of CAB and MCDP extracted from C5 blend chip and C5 blend fiber. The peak maximums are indicated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
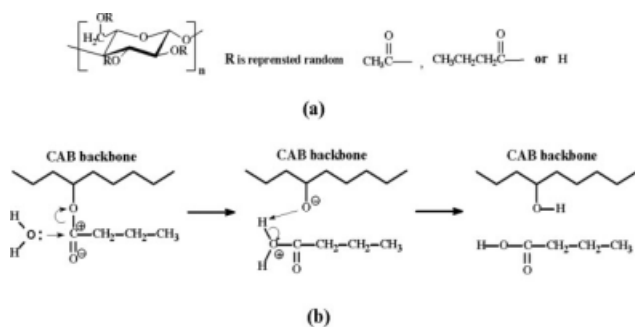
Figure 7 (a) Structure of CAB; (b) a proposed mechanism of thermal hydrolysis reaction of CAB in blend melt spinning.

Because the most of gaseous products escaped in blend melt spinning were acid gas which containing carbonyl group, the dynamic changes of the thermal hydrolysis reaction can be indirectly investigated from the changes of carbonyl infrared absorbance at 1783 cm^{-1} (coded as $A_{carbonyl}$) by using TG-IR analysis. From Figure 8, except for pure MCDP, the $A_{carbonyl}$ of other samples were gradually increased with the time extension, suggesting thermal hydrolysis reaction occurred on more and more ester groups in CAB. Compared the $A_{carbonyl}$ of different blend samples, it was found that the higher CAB content in blends, the stronger carbonyl absorbance. The thermal hydrolysis reaction was seriously affected by the weight fraction. Figure 8 also clearly shows that the $A_{carbonyl}$ increased sharply from 15 to 20 min, which indicates that the thermal hydrolysis reaction rate arrived at maximum. It was in good agreement with the phenomena observed in actual MCDP/CAB blend melt spinning. The spinning stability of MCDP/CAB blends got worse while the spinning time exceed 15 min, because the large number of escaped acid gas were seriously decreased the stability of the blends melt flow.
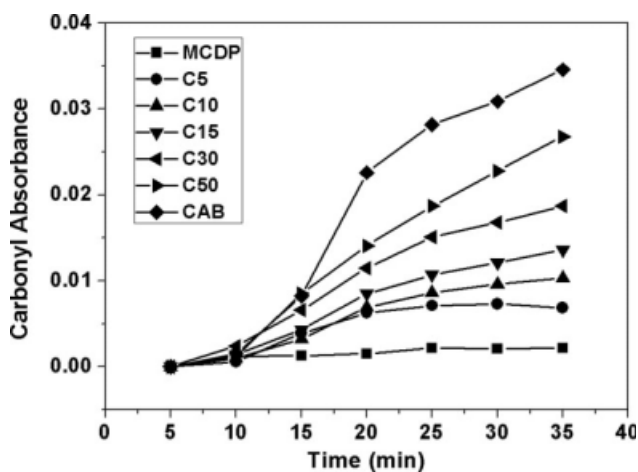

Figure 8 Carbonyl absorbencies of gaseous products of CAB/MCDP blend chips with different time.

Moisture absorption, mechanical properties, dyeability, and morphology of CAB/MCDP blend fibers

Figure 9(a,b) shows the SEM images of pure MCDP fiber and C5 blend fiber. To enhance contrast for image analysis, both of the samples were treated by submerging in acetone, and the CAB phase was etched due to dissolving in acetone. As seen in Figure 9(a), the surface of pure MCDP fiber was still smooth after treated by acetone. In contrast, the surface of C5 blend fiber exhibited lots of microvoids ranged from 0.1 to 1 μm, proving the immiscible of CAB and MCDP.

The moisture absorption of C5 and C10 blend fibers, as well as MCDP and CAB fibers, are shown in Table IV. Compared with the MCDP fiber, the moisture absorption of C5 blend fiber was improved more than three times. The theoretical estimate of blend fiber's moisture absorption value was calculated from the moisture absorption of pure MCDP and pure CAB as the following formula:
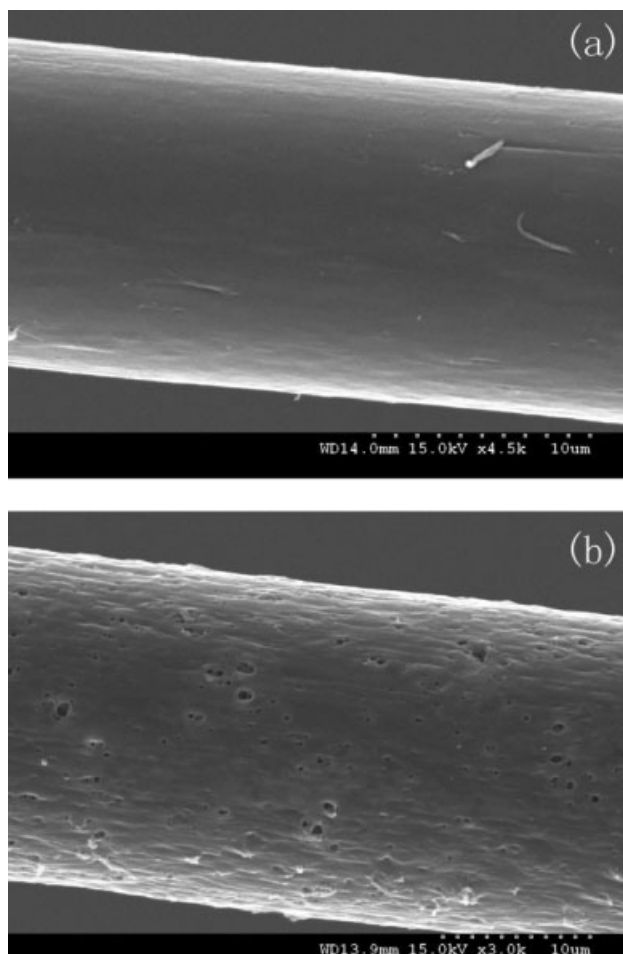

Figure 9 (a) SEM image of MCDP fiber treated with acetone; (b) SEM image of C5 fiber etched with acetone.

TABLE IV
Measured and Calculated Moisture Absorption for MCDP, CAB, and CAB/MCDP Blend Fibers

	MCDP	C5	C10	CAB
M (%)	0.56	1.88	2.03	4.75
M_T (%)	0.56	0.77	0.87	4.75

$$M_T(\%) = M_{CAB} \sum_a^b w_{CAB} + M_{MCDP} \sum_a^b w_{MCDP} \quad (5)$$

where M_{CAB} is 4.75%, M_{MCDP} is 0.56% measured in laboratory. It is found that the actual moisture absorption of blend fibers was much higher than the value of theoretical estimate. The reason might be explained that the hydroxyl content of fiber was increased by the thermal hydrolysis of CAB, and finally improved the moisture absorption of blend fibers.

To investigate the washing resistance property, the blend fibers were washed several times according to AATCC test method 124-2006.[26] Each washing cycle was conducted in a commercial washing machine set on a normal wash for 35 min. The machine was filled with water at 35°C and about 4 g/L detergent. Table V presents the moisture absorption of C5 and C10 blend fibers with different washing times. Although the moisture absorption of C5 and C10 blend fibers were slightly decreased with increasing the washing times, the decrease extent was tend to the balance. After washing 30 times, the moisture absorption of C5 and C10 blend fibers were still improved about three times compared with MCDP fiber.

The SEM image of C5 blend fiber unwashed shown in Figure 10(a) was clearly illustrated that the CAB domain existed on the fiber surface. However, the C5 blend fiber after washing 30 times was became rough and appeared some microvoids on fiber surface displayed on Figure 10(b). These results indicate that partial CAB broke off from the fiber surface after washing, which is the possible reason leading to the decrease of moisture absorption.

TABLE V
Moisture Absorption of C5 and C10 Blend Fibers after Different Washing Times

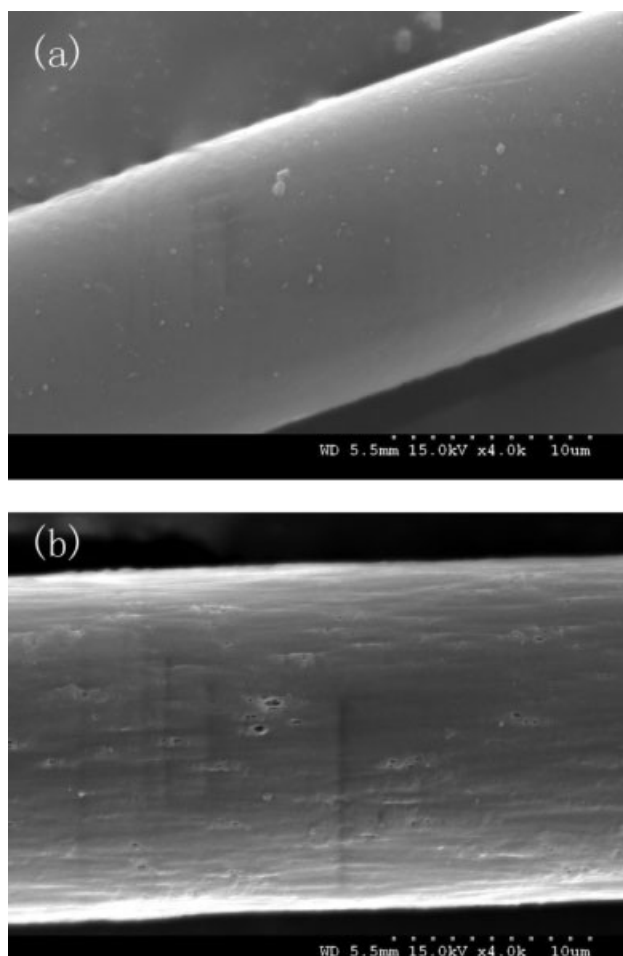|	M (%)	
Washing times	C5	C10
0	1.88	2.03
10	1.79	1.92
20	1.63	1.78
30	1.58	1.72

Figure 10 (a) SEM image of C5 fiber unwashed; (b) SEM image of C5 fiber after 30 washed times.

The dyeability of blend fibers is shown in Table VI. The dye uptake value of MCDP fiber is obviously higher than CDP fiber with the same SIP content. It might be explained that the crystallizability of polyester molecular chains was inhibited by the introduction of MPD,[6] which leads to the dyestuff molecular can be easily diffused into the MCDP molecular chains and combined with the SIP group. The dye uptake value of blend fibers was slightly decreased as CAB content increased, but was still close to the MCDP fiber, suggesting that the dyeability of blend fibers was also very good. The theoretical estimate dye uptake value of blend fiber was calculated using the following formula:

TABLE VI
Measured and Calculated Dyeability for CDP, MCDP, CAB, and CAB/MCDP Blend Fibers

	CDP	MCDP	C5	C10	CAB
D (%)	78.6	91.5	91.1	89.7	52.6
D_T (%)	/	91.5	89.6	87.6	52.6

TABLE VII
Mechanical Properties of CAB/MCDP Blend Fibers

	MCDP	C5	C10
Breaking strength (cN/dtex)	2.22	1.89	1.56
Breaking elongation (%)	32.3	31.7	33.8

$$D_T(\%) = D_{CAB}w_{CAB} + D_{MCDP}w_{MCDP} \qquad (6)$$

where D_{MCDP} is 91.5%, D_{CAB} is 52.6%. The result clearly shows that the actual dye uptake value of blend fibers was higher than the theoretical estimate value. It was probably explained as due to the phase separation structure of blend fibers, which is benefit to the dyestuff molecular diffuse to the inner structure of blend fibers.

As seen from Table VII, the breaking elongation of C5 and C10 blend fibers were almost same as pure MCDP fiber. The breaking strength of C5 and C10 blend fibers were lower than pure MCDP fiber, but still above 1.5 cN/dtex. It illustrates that the blend fibers can also suitable for the requirements of textile.

CONCLUSIONS

Novel cationic dyeable copolyester containing SIP and MPD was first synthesized by direct esterification method, which was supported from the evidence of the FTIR and ^{1}H-NMR results. Moreover, the content of MPD units in MCDP was higher than feed molar ratio. The thermal hydrolysis reaction of CAB occurred in CAB/MCDP blend melt spinning, mainly to the butyrate ester side groups of CAB, which results in that the acid gas was produced and the hydroxyl group content in CAB was increased. The changes of thermal properties of CAB before and after blend melt spinning indicate that the hydrogen bonding of CAB was significantly increased. Furthermore, the moisture absorption of MCDP/CAB blend fibers was improved about three times than MCDP fiber even after washing 30 times. The blend fibers also have a good dyeability similar to the MCDP fiber, and the mechanical prop-

erties of blend fibers were suitable for the requirements of textile.

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