The study of structure and properties for polyimide fibers which incorporate DMB with dry-jet wet -spinning of two-step process

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1. Introduction

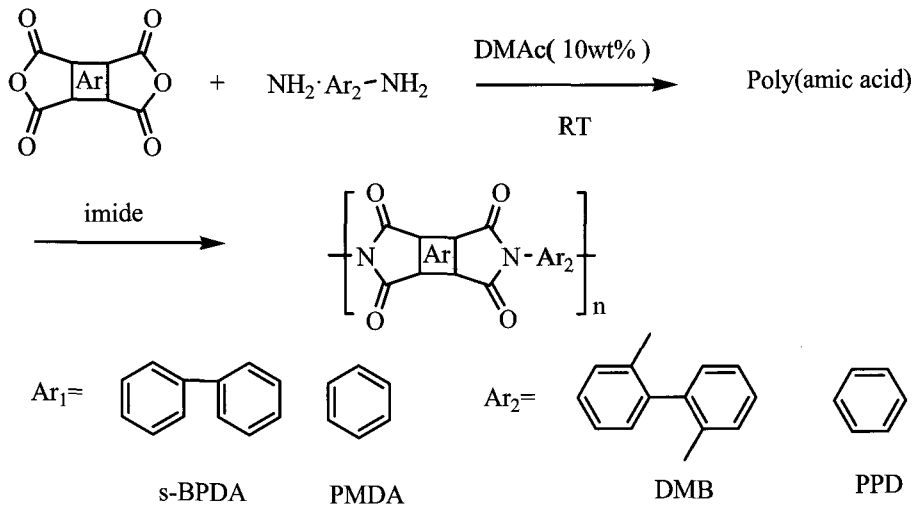
Aromatic polyimides are finding increased usage in industrial and aerospace applications due to their excellent chemical resistance, low density, radiation resistance, toughness and high temperature stability. It is very reasonable understand that polyimides are used for fiber materials because of their high performance. The polyimide fiber spinning process is divided into one-step process or two-step process on basis of the spinning solution is polyimide or poly(amic acid). The high strength and high modulus polyimide fibers were successfully manufactured with one-step process in laboratory. The DMB or OTOL is used to diamine monomer and phenols are generally used for polymer solvents to the series of fibers. Their structure –properties relationship were widely investigated by professor Stephen Z.D.Cheng with coworkers and other authors[1),2),3)]. It is a marvelous achievement that the high strength and high modulus polyimide fibers were successfully developed with one-step process, there also exists some flaws to restrict the industrial scale due to the big toxicity and odor for phenols solvent and the less choice kinds with polyimide fibers for the limitness solubility to polyimide . And the problems don't exist for the two-step process.

In this article we take two-step process for poly(amic acid) fibers and study the relationship of the fiber structure and performance ,and further analyze the fiber structure and morphology change from poly(amic acid) to polyimide, emphasis on clearly understand the influence on fiber properties due to the variation of the fiber morphology、structure、molecular chain orientation 、fiber void size and distribution in the spinning process.

2. Experimental section

2.1. Preparation of polyimide fibers

All poly(amic acid) spinning solutions were prepared via the two-step process: the synthesis of poly(a acid) followed by (scheme 1). The PAA solutions were filtered and degassed prior to use and then the PAA d were extruded through a spinneret (34 holes with measuring 0.12mm in diameter) into a air gap ,then in coagulation bath by dry-jet wet spinning. The solidify filament entered into the second and the third bath , then clustered at the fourth spool. The fibers were dried at 50℃ under vacuum for 12h, and then hea imidized and drawed at a heating furnace over 400℃.



Scheme1: Synthetic scheme of polyimide fibers with DMB

3.Results and Discussion

The main aim of this study was to know the relationship of structure and properties for polyimide fibers, and the association to properties with the change of the structure and orientation of fibers in the spinning process.We discussed the differences of the structure and properties between the DMB polyimide fibers on basis of one-step spinning process and two-step spinning process and attempted to explain the differences.

3.1. The tensile properties of DMB fibers

The tensile properties of fibers and conditions of heating-treatment were shown in table1

Table1. The tensile properties of fibers and conditions of heating-treatment

Molar ratio	Poly(amic acid) fibers			Polyimide fibers(HD)			HD condition	
	T(Cn/dtex)	E(%)	M(Cn/dtex)	T(Cn/dtex)	E(%)	M(Cn/dtex)	Temp (℃)	Draw ratio
A-1	2.02	17.4	69.7	7.90	2.90	550	530	1.37
A-2	1.85	21.5	69.3	8.30	2.70	610	530	1.57
A-3	1.45	8.52	73.5	8.70	2.38	710	530	1.65
A-4	2.40	14.1	160.6	9.30	2.07	850	550	1.32
A-5	1.71	11.2	79.3	6.10	1.92	600	560	1.08
B-1	2.03	19.1	77.8	5.00	2.21	430	480	1.18
B-2	2.18	14.0	78.2	5.60	2.58	420	490	1.10
B-3	2.15	22.4	80.3	7.10	2.67	480	490	1.18

Molar ratio : Dianhydride=BPDA, Diamine=PPD and DMB

A-1, A-2, A-3, A-4, A-5: PPD: DMB=60:40, 70:30, 80:20, 90:10, 100:0

Molar ratio b): Dianhydride=BPDA and PMDA, Diamine= DMB

B-1, B-2, B-3: BPDA: PMDA=65:35, 70:30, 75:25

T: tenacity E: elongation M: modulus HT: heat treatment

3.2. The FT-IR characterization of polyimide fibers with ATR

The IR spectra of the PAA fibers and PI fibers (as shown in Figure 1a and Figure 1b). The imidization of PAA fibers was easily observed by monitoring the disappearance of the amide-related bands and the appearance of the corresponding imide bands.In detail, the respective bands for amide I and amide II at 1650,1600 and 1314 cm^{-1} completely disappeared and conversed the typical strong imide peak at 1711(ν_s) ,1775(ν_{as}) and 1360cm^{-1}(ν_{C-N}) in the imide group at 300°C . It means that PAA

fibers were completely turned into PI fiber at this temperature.

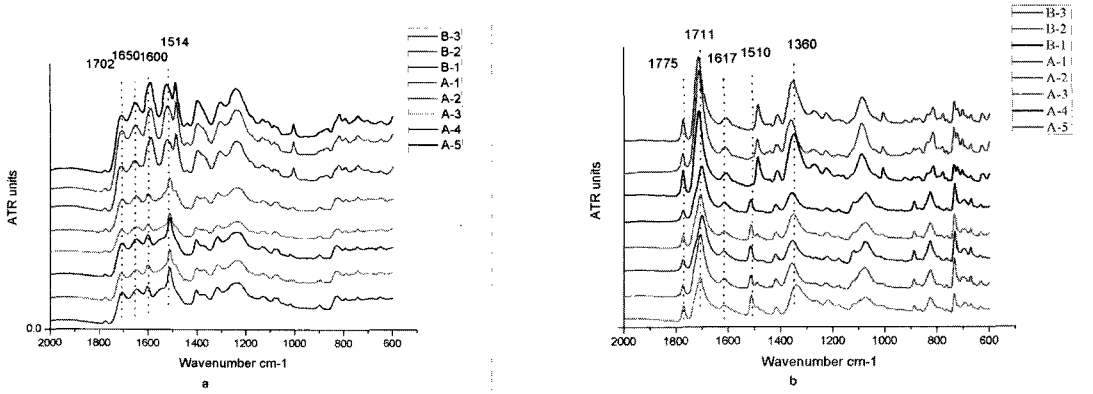


Figure1: a) FT-IR spectrum of PAA fibers b) FT-IR spectrum of heat-imidized PI fibers

3.3. Thermal properties of polyimide fibers

The thermal stability of polyimide fibers were estimated by 5%(T_5) weight loss temperature measured by a thermogravimetric analyzer(TGA) at a heating rate of 10℃/min in N_2 atmosphere . The results are tabulated in Table6 and the typical TGA curves are reproduced in Figure. The results show all PI fibers have good thermal stability, the pendent methyl of PI didn't lead to deadly thermstability loss.

Table3. The T_5 of polyimide fibers

PI fiber	B-1	B-2	B-3	A-1	A-2	A-3	A-4	A-5
T_5 /℃	483	511	491	517	522	514	533	557

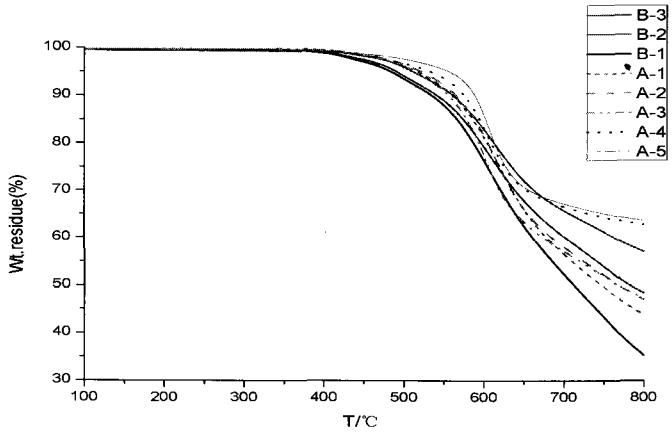


Figure2: The TGA of heat-drawing fibers

4.Conclusions

A series of PI fibers were prepared from PAA fibers with two-step process. The incorporation of DMB units in BPDA-PPD system increaseed the mechanical properties without sacrificing thermal stability.

References

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