

CHARACTERIZATION OF BLEND ACRYLIC FIBER'S STRUCTURES*

QIN Jian (秦 建), LIU Zhaofeng (刘兆峰) and LI Fanting (李繁亭)

(*Man-Made Fiber Research Institute, China Textile University, Shanghai*)

ABSTRACT

The fine structures, paracrystal, porous and phase structures of blend acrylic fibers have been characterized using techniques based on X-ray diffraction, gas adsorption, density, electron and optical microscopy, mercury penetration method and IR spectroscopic analysis. The existence of a fibril-void structure, with voids and fibrils of the order of 10^2 to 10^3 Å diameter has been confirmed for the wet-spun blend fibers. It was found that the blend acrylic fiber in the present work is a kind of matrix-fibril fiber; phase separation takes place in it. Further studies about the effects of composition and sequence distribution of copolymers on structure of the blend fibers were made; and it was discovered that void volume in the blend fibers largely depends on the interface area between two polymer phases, and pore size and number on the particle size and number of the dispersing phase. An appropriate structural model about the blend fibers has been described.

INTRODUCTION

The amount and size distribution of void volume, or pore space, is related to many important fiber properties such as water retention, diffusion, and mechanical properties. It is clear that even small porosities in fibers can be important through their influence on hydrophilic properties like absorption of water and moisture, and so on. Recently, it is widely used to produce porous acrylic fibers by means of polymer blending method to improve their water retention property^[1-3]. For porous blend acrylic fiber, its structure can be divided into three levels, i.e., paracrystal, microporous and phase structures. There were many papers concerning with structure of acrylic fiber^[8-10]; but very few papers about blend acrylic fiber's structures^[11,12]. Up to now, there is no any systematic report about all of the three levels' structures of blend acrylic fibers has been published. This communication reports the results of our investigation into the fine structures of some kinds of blend acrylic fibers produced in various solvent systems. Many techniques based on X-ray diffraction, gas adsorption, density, electron and light microscopy, etc. were used and various parameters which could be used to characterize the fiber structure, such as crystallinity, orientation, density, porosity and internal surface, and so on, were obtained. Finally, an appropriate structural model of the blend acrylic fiber has been visualized.

Received September 29, 1985

* Projects supported by the Science Fund of the Chinese Academy of Sciences.

EXPERIMENTAL

Preparation of fiber samples

Two different polymers were blended and dissolved into three kinds of solvents, DMF, DMSO and NaSCN aqueous solution, to form spinning dopes, one of the polymers is a conventional acrylic copolymer containing 90.9% acrylonitrile, 8.6% methyl acrylate and 0.5% sodium methyl propenyl sulfonate; and the other is a so-called blending polymer, such as polyvinyl acetate (PVAc), polystyrene (PS), acrylonitrile-styrene copolymer (AS) and acrylonitrile-vinyl acetate copolymer (AVAc). The dopes obtained were extruded through a 700-hole (0.08mm) nozzle into a coagulation bath to form fibers. The fibers were then washed with water, drawn in a boiling water bath, and finally dried at 110°C for two hours.

X-Ray diffraction

The fiber samples were wound on aluminum sample holders in such a manner the individual strands were parallel; or the samples were cut into tiny pieces and then pressed on aluminum sample holders. Wide-angle data were obtained in transmission on a Rigaku-3015 X-ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The diffracted beam was detected with a scintillation counter and the resulting signal was exhibited on a chart recorder.

Electron microscopy

(1) Cross section:

The cross section morphology of fibers, after being frozen and broken in liquid nitrogen and then sprayed with gold, was examined with a JSM-35 SEM.

(2) Longitudinal section:

The longitudinal section morphology of fibers, after being etched with plasma and then sprayed with gold, was examined with a TSM-1 SEM.

(3) Surface morphology:

The surface of fibers, sprayed with gold, was examined with a TSM-1 SEM. The films of PAC/AS were cast from a DMF solution, immersed in butanone for 12 hours to remove AS component. The surface of the films was observed with a TSM-1 SEM after being washed with water, dried in a vacuum oven at 40°C and sprayed with gold.

Microporous structure

The micropore size distribution in the fibers was measured with a J5-70 mercury porosimeter. The pressure used ranged from 0 to 2000 atm.

The immersion density of the fibers was measured in a wetting mixture of carbon tetrachloride and $n\text{-C}_7\text{H}_{16}$, and the mercury density of the fibers was measured by the simple mercury volume method^[4].

The specific surface area of the fibers was measured by determining the amount of physically absorbed gas, measured at liquid nitrogen temperatures, and applying the BET equation.

Phase structure in blends

Phase-contrast microscope was found to be of value for studying the grosser phase structure found in blend films as well as in blend solutions. The films for observation was about 0.1 mm thick and held on the slide.

Sequence distribution of AS copolymers

Using the equations proposed by Harwood^[5], the sequence distribution parameters of AS copolymers were calculated according to the $C\equiv N$ infrared stretching frequencies of AS copolymers. IR spectra were recorded on a Perkin-Elmer 588 spectrophotometer. The samples were prepared by pressing their solutions into 0.1 mm thick films. In order to measure frequency shift accurately, IR measurements were made using $20\times$ abscissa expansion at $10\text{ cm}^{-1}/\text{min}$ scanning rate.

CALCULATED PARAMETERS

Crystallinity index

Samples on the X-ray diffractometer were rotated to average orientation effects while a 2θ scan was made from 6 to 36° . The X-ray scan was divided into "crystalline" and "non-crystalline" regions as shown in Figure 1. The ratio of the "crystalline" area to the total area was taken as the index of crystallinity shown below

$$C.I.(%) = \frac{A_1 + A_2}{A_1 + A_2 + A_3} \times 100\% \quad (1)$$

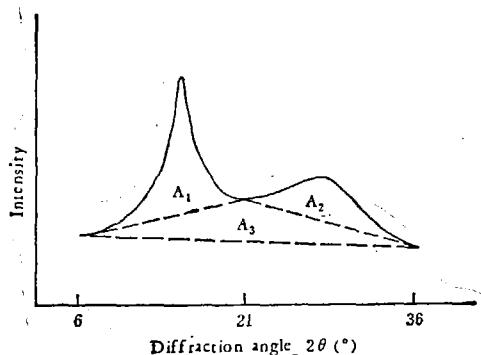


Fig. 1 X-ray diffractometer scan method for determination of crystallinity index

Orientation index

The peak at $2\theta = 16.5^\circ$ was used to determine the orientation. With 2θ set at 16.5° , an azimuthal scan was made. The width at half-maximum intensity (H) was used to calculate the orientation index ($O.I.$)

$$O.I.(%) = \left(1 - \frac{H}{180} \right) \times 100\% \quad (2)$$

Void proportion

The void proportion (*V.P.*) of the fibers was calculated from their immersion density (*d*) and mercury density (d_{Hg}) by the following equation

$$V.P.(%) = (1 - d_{Hg}/d) \times 100\% \quad (3)$$

Microporous structural parameter

The microporous structural parameters (R_p : radius of fibrils; R_s : radius of spherical pores; N_s : number of pores) were calculated with the data of specific surface area (*A*) of the fibers.

Craig^[6] assumed a kind of frame of porous structure. Several equations, which could be used to calculate the microporous structural parameters of the acrylic fiber, were obtained

$$R_p = 2/Ad \quad (4)$$

$$R_s = 3(d - d_{Hg})/Ad_{Hg}d \quad (5)$$

$$N_s = A/\zeta\pi R_s^2 \quad (6)$$

Sequence distribution parameter

Harwood^[5] proposed a parameter, run number (*R*), for characterizing sequence distribution in copolymers; *R* is the average number of monomer sequences occurring in a copolymer per 100 monomer units. The longer the number average length of one monomer, the smaller run number is. Several equations to be of value for calculating the sequence distribution parameters were derived. For AS copolymer.

$$\langle AN \rangle = \%AN/(R/2) \quad (7)$$

$$\langle S \rangle = \%S/(R/2) \quad (8)$$

$$P_{AN-AN} = (\%AN - R/2)/\%AN \quad (9)$$

where $\%AN$ and $\%S$ refer to the molar percentages of acrylonitrile and styrene units in the copolymer; $\langle AN \rangle$ or $\langle S \rangle$ refers to the number average sequence length of AN or S monomer; P_{AN-AN} is the probability of AN-AN linkage.

Shobun et al.^[7] measured the $C\equiv N$ stretching frequency shift of AS copolymers by infrared spectroscopy and found a linear relationship between the probability of AN-AN linkage and $C\equiv N$ stretching frequency ($\nu_{C\equiv N}$)

$$P_{AN-AN} = \frac{\nu_{C\equiv N} - 2234.6}{2239.6 - 2234.6} = 1/5(\nu_{C\equiv N} - 2234.6) \quad (10)$$

so, P_{AN-AN} could be obtained from the $C\equiv N$ stretching frequency shift of AS copolymers and then the other parameters, *R*, $\langle AN \rangle$ and $\langle S \rangle$, could be further calculated.

RESULTS

Paracrystal structure

The fibers derived from polyacrylonitrile containing a small amount of comonomer

(PAC fiber) have a physical structure which is very much different from other synthetic materials, such as nylon 66 or polyethylene terephthalate. The molecular conformation of PAC has been described as a helical conformation because the macromolecule of PAC is with the bulky side-group $C\equiv N$. It is generally agreed that PAC is a polymer of two-dimension or lateral order with a regular repeated distance perpendicular to the chain axis, but no order along the chain axis. The characterization on the PAC X-ray scan is that there are two diffraction peaks seated at $2\theta=16.5^\circ$ and 29.1° respectively.

Figure 2 shows the X-ray diffractometer scan results of AS copolymers. It could be seen that as the second monomer, styrene, gets more and more in AS macromolecules, the diffraction peaks at 16.5° and 29.1° become weaker and weaker. This is because the interaction between molecules has been gradually weakened and the molecular conformation has been disordered. When S monomer is higher than 45 wt% in AS copolymer, the paracrystal structure will completely disappear to become an amorphous structure. For polystyrene there are two comparatively weaker diffraction peaks at about 20° and 32° , so polystyrene is a much lower ordered polymer than PAC copolymer.

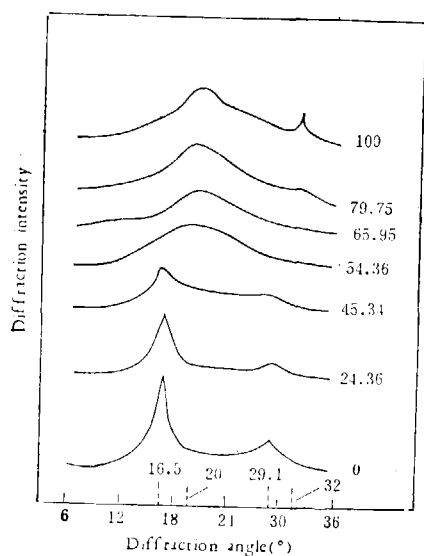


Fig. 2 Wide-angle X-ray diffraction of AS copolymers. S (wt%) in AS

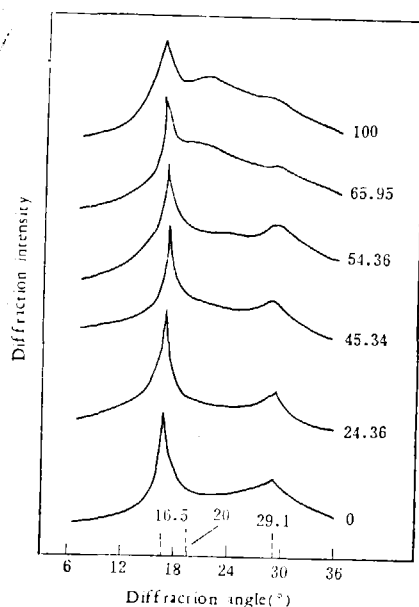


Fig. 3 Wide-angle X-ray diffraction of PAC/AS fibers. S (wt%) in AS

When two different polymers are blended and spun into textile fibers, what on earth will their crystal structure or high ordered region be? We measured a series of blend fibers of PAC and AS with X-ray diffractometer, and the results obtained are presented in Figure 3. There are no new crystalline structure formed and no ordinary one destroyed in all the PAC/AS fibers, which was mirrored that no new diffraction peaks were created and the ordinary ones did not disappear in Figure 3. The X-ray diffraction data were listed in Table 1. The

Table 1 X-ray diffraction data*

AN (wt%) in AS copolymers	Crystallinity index (%)	Orientation index (%)
100	56.8	88.2
84.25	53.6	87.4
75.64	53.7	87.9
54.66	53.9	85.0
49.71	—	83.9
45.64	52.4	83.3
40.41	—	83.3
34.05	52.8	83.9
28.52	—	83.3
20.25	51.8	81.7
11.41	—	81.1
0	49.5	78.3

* The fiber composition: PAC/AS = 90/10 wt%.

crystallinity index of the PAC/AS fibers will decrease with the increasing of S monomer in AS copolymers; that is because the order of the blend polymer (AS copolymer) becomes lower and lower. Suppose the blending polymer is totally disordered, the crystallinity index (*C.I.*) of the blend fiber, of course for the incompatible blend fiber, would be nearly equal to $w'C.I.'$ (here w' is the weight fraction of the major polymer and $C.I.'$ the corresponding crystallinity index), i.e. 51% *C.I.* for the blend acrylic fiber. In Table 1, the *C.I.* of the PAC/AS fiber gradually approach 51% as S monomer increases, which means AS copolymer is going to be totally disordered. It seems that the disordered polymer acts as a kind of "diluent" in the blend fiber to make *C.I.* low.

The changes in orientation index of the blend fibers were to be the same as those in *C.I.* (also shown in Table 1). It would be concluded that *O.I.* of the blend fibers is lower than that of ordinary acrylic fiber at the same spinning condition. When the blending polymer is a copolymer, *O.I.* of the blend fiber lowers with decreasing of AN monomer in AS copolymer. It seems to indicate that the *O.I.* in high ordered region of the blend fiber reduces after adding another polymer into PAC. Perhaps that is because the blending polymer particles dispersing in the dope have not been well stretched during spinning, so the paracrystallites with 16.5° diffraction angle in the particles are not well oriented. It was also found that the *O.I.* of the blend fiber is going to be $w'O.I.'$, i.e. 79%, just same as the change of *C.I.* discussed before.

Microporous feature

Figure 4 shows a series of electron micrographs of different acrylic fibers. There are a lot of micropores on the cross section of the blend fiber (Figure 4 A), but the PAC fiber

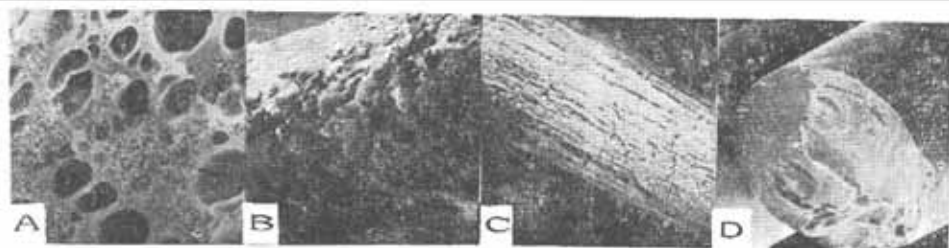


Fig. 4 The electron micrographs of the blend fibers

A Cross section of the blend fiber; B Surface morphology of the blend fiber;
C Longitudinal section of the blend fiber; D Cross section of the PAC fiber

is very different, we could hardly find any micropores in it (Figure 4 D). Otherwise, the surface of the blend fiber was also observed by electron microscopy, the difference of the structural details between blend fiber and PAC fiber is compared in Figure 4, too. On the surface of the blend fiber, many micropores and fibrils can be found, it is much coarser than the surface of PAC fiber (see Figure 4 B and D). The reason why the blend acrylic fibers can absorb and hold large quantity of water is that they have many pathes to let the water enter them easily and have much free volume inside to hold it. The microporous structure is to be the most important characterization of the blend acrylic fiber's structures. In order to find out the shape of the micropores in fiber axis direction, we etched the surface of the blend fiber with plasma and then observed it, the result is photographically shown in Figure 4 C. The micropores seem to be cylinderlike and well-oriented in the direction of the fiber axis.

Electron microscopy cannot be used to measure directly the void or fibril size since there is an unavoidable influence during preparation of the samples, which causes the apparent size of a void to change, so it is reasonable to quantitatively calculate micropore radius and void proportion in porous fiber. Using equations concerned before, the average pore size, number of voids, fibril radius and void proportion were calculated for the PAC/AS fibers with measurable surface area or densities and are presented in Table 2. The void proportion and surface area were found to be higher for the blend fibers than for the PAC fiber, which is in

Table 2 Porous structural parameters for PAC/AS blend fibers*

AN(wt%) in AS	d (g/cm ³)	d_{Hg} (g/cm ³)	A (m ² /g)	R_p (Å)	R_s (Å)	$N_s \times 10^{14}$ (pores/g)	V.P. (%)
100	1.1704	0.998	0.23			0.85	14.7
75.64	1.1456	0.749	12.73	1370	1089	0.85	34.6
54.66	1.1420	0.686	19.34	906	903	1.89	39.9
45.64	1.1528	0.596	28.03	620	867	2.77	48.3
34.05	1.0936	0.524	46.71	392	638	9.13	52.1
20.25	1.1328	0.770	10.90	1620	1145	2.99	32.0
0	1.1639	0.870					25.3

* The blend fibers contain 6 wt% AS copolymer.

agreement with the results obtained by electron microscopy. Moreover, the larger the void proportion of the blend fibers, the more the number of voids and the smaller the average pore size are.

A further investigation about pore size distribution in the blend fibers had been made. Using a mercury porosimeter, the pore size distribution of the several blend fibers was easily obtained shown in Figure 5, it is evident to see that the pore size distribution is much wider in the blend fibers than in the PAC fiber; the diameter of all pores in PAC fiber seems to be less than $100 \text{ \AA}$, but most of pore size in the blend fibers is larger than $100 \text{ \AA}$, which is within the range of 100 to $1000 \text{ \AA}$.

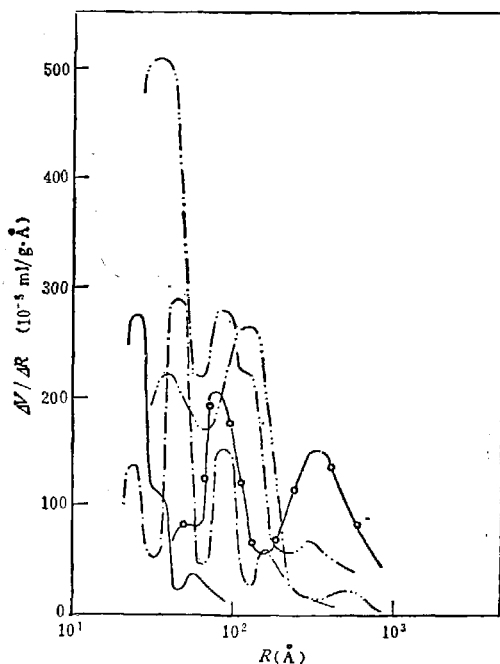


Fig. 5 The pore size distribution in the blend fibers
 — PAC; — · — PAC/PVAc (85/15); — · — PAC/AS (94/6);
 PAC/AVAc (90/10); — ○ — PAC/PS (94/6).

Phase texture and separation

Two kinds of polymer, in incompatible polymer blends, gather in respective domain to form heterogeneous polymer system. Heterogeneous polymer blends, in contrast to conventional polymer, have a different structure which brings about a lot of unique properties. For bicomponent polymer blend, phase texture largely depends on interaction between two kinds of macromolecules.

A change from non-phase separation to phase separation in PAC/AS blend films was photographed in Figure 6 by means of phase-contrast microscope. The blend film is homogeneous when AS copolymer is with less than 15.75 wt % styrene; on the contrary, the blend films, in which AS contains more than 15.75 wt % styrene, are heterogeneous and phase separation takes place in them. Furthermore, the films trend towards coarser texture, when AS

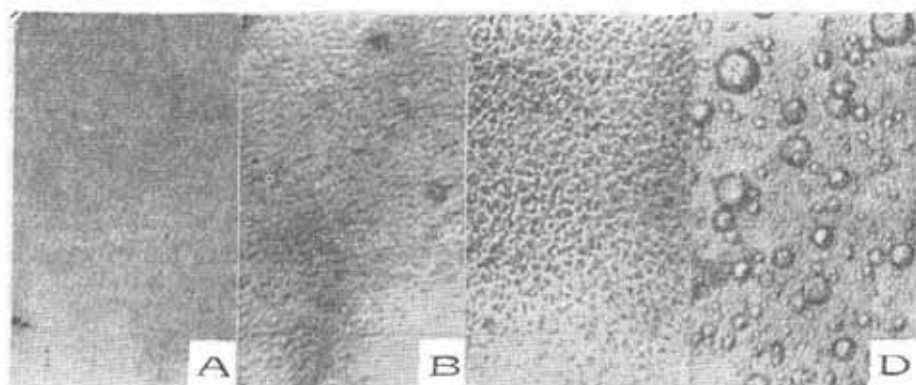


Fig. 6 Phase separation of PAC/AS (50/50) blend films (200 $\times$)

AS composition AN/S (wt%): A 84.25/15.75;

B 75.64/24.36; C 45.64/54.36; D 0/100.

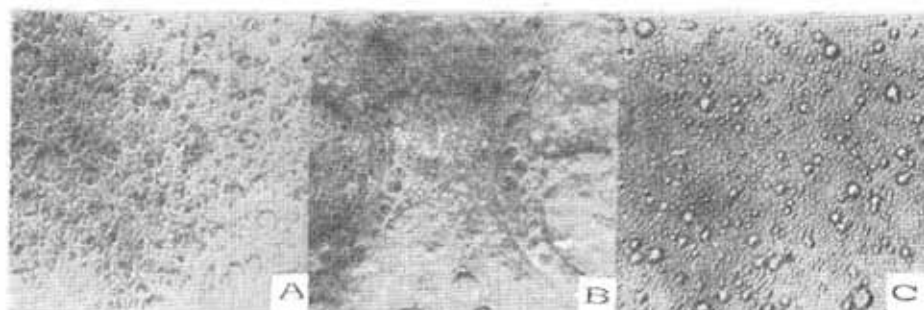


Fig. 7 Change in dispersibility of dispersing phase in PAC/AS (50/50) blend solution dissolved in DMF (200 $\times$)

AS composition AN/S (wt%): A 75.64/24.36; B 45.64/54.36; C 34.05/65.95.



Fig. 8 Electron micrograph of PAC/AS film coagulated in water

gains more and more S monomer, and finally they become fully phase separated in which the interfaces appear to be very distinct like a view seen in oil-in-water emulsion. That is because compatibility is poorer and poorer. From Fig. 7 we could see the change in dispersibility of disperse phase with polymer blend solution. Permeability between two phases seems to be weakened as styrene component in AS gets more and more; PAC/AS blend in A is a kind of permeable network, but in C, AS disperses in PAC phase as droplets, and disperse state in B is a combination of A and C, i.e., a transition point.

There are many micropores in the blend fibers, so formation of the micropores is closely related to polymer blending. It is the most interesting to find out where the pores are formed in the blend fiber. Figure 8 vividly shows that the pores are formed on the interface of two polymer phases, which means phase separation is an important factor for micropore formation. In incompatible polymer blends phase separation can produce a lot of interface and the interface would cause the micropores. Surely, microporous structure will largely depend on the compatibility and phase texture.

DISCUSSIONS

Description of the blend fiber's morphological structure

In order to describe the blend acrylic fiber's morphological structure, it is very useful to visualize an appropriate structural model. From the structural results presented before, we could imagine a model to describe the structures of the blend fiber. In the blend fiber, two kinds of polymers are incompatible and gather in respective domain, which means phase separation. It is a kind of matrix-fibril fiber. In each polymer domain, the polymer remains its own crystal structure; crystalline regions do not interfere with each other, so the crystallinity index of the blend fibers is nearly equal to the combination of each component. Microporous structure is the most important structural feature of the blend acrylic fibers. The micropores, formed on the interfaces between two polymer domains, appear to be well oriented in the direction of the fiber axis and elongated in the same direction to be cylinderlike; further, we could conclude that pores in the blend fibers is not isolated but penetrable according to the results from mercury porosimeter and specific surface area test.

Effect of AS composition on structure of PAC/AS fibers

Added a certain amount of different composition AS copolymers into PAC polymer to obtain a series of polymer blends, spun them into blend fibers, in which there were different amount of micropores. The void proportion (*V.P.*) and density of the PAC/AS fibers varies with the composition of AS copolymers. The effects of AS composition on *V.P.* and density

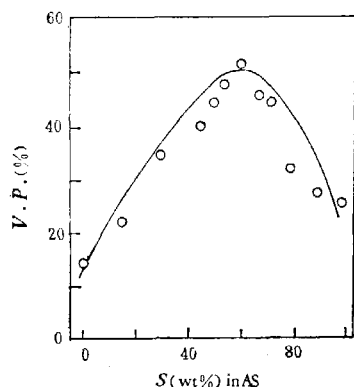


Fig. 9 Effect of AS composition on *V.P.* of PAC/AS (94/6) fibers

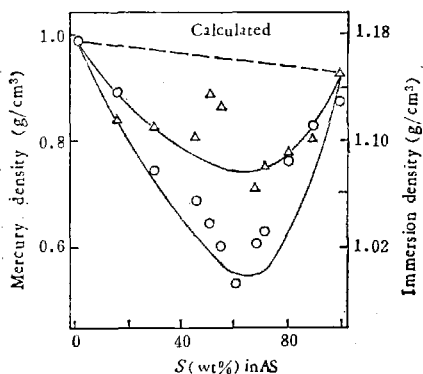


Fig. 10 Effect of AS composition on densities of PAC/AS fibers
—○— M.D.; —△— I.D.

are shown in Figure 9 and Figure 10. There were a maximum of *V.P.* in Figure 9 and a minimum of mercury density (*M.D.*) in Figure 10, at the extreme position, AS composition AN/S equale about 34/66 wt %, that is about 50/50 mol %. It indicates that PAC/AS blend fiber will have maximal porous volume if acrylonitrile and styrene in AS copolymers are near half-and-half. It was very interesting as shown in Figure 10 that a minimum of immersion density (*I.D.*) was observed. There were three reasons: first of all, there are sealed pores in the blend fiber and the more the total pore volume, the more the sealed pores are; secondly, there is low-density amorphous region in the interface between two polymer phases; finally, the density of copolymer itself is not equal to the combination of its own monomers. That is why the *I.D.* of the PAC/AS fibers is not equal to the result contributed proportionally by each component, the latter is calculated and shown in Figure 10 as dotted line.

It was well known that phase structure of bicomponent blend largely depends on interaction between two kinds of polymers, furthermore, for copolymer blend on its composition. Phase domain size is related to its composition too. The relation between phase structure (or porous structure) of PAC/AS fibers and AS composition is listed in Table 3. We could conclude from it that, (1) the smaller the particle size of dispersed AS phase in blends, the larger the *V.P.* of the PAC/AS blend fiber is; (2) phase separation takes place in all porous blend fibers, so it is an important condition to form pores in the blend fiber. The reason why the *V.P.* of the blend fiber is not linearly related to AS composition will be discussed below.

Table 3 Relation between phase structure (or porous structure) of PAC/AS fibers and AS composition

AN(wt%) in AS polymer	Phase separation in PAC/AS films	<i>V.P.</i> (%) of the blend fibers	Particle size(μm) in PAC/AS films*	Compared results**
100	—	14.7	—	—
84.25	one phase	19.3	—	—
75.64	two phases	34.6	20	+
45.64	two phases	48.3	16	+
34.05	two phases	52.1	10	+
0	two phases	25.3	18	+

* From micrographs of PAC/AS (50/50) solution films in DMF.

** '+' stands for porous fiber with higher than 20% *V.P.*;

'-' stands for poreless fiber with lower than 20% *V.P.*

Effect of AS sequence distribution on structure of PAC/AS fibers

According to Harwood's equations^[5] and AS infrared spectroscopy, the sequence distribution parameters are given in Table 4. There is a slight decrease in $\text{C}\equiv\text{N}$ stretch frequency with increasing styrene content of AS copolymer; the existence of styrene monomer in AS, which weakens the coupling between nitrile groups and thins the density of electron cloud around nitrile bonds, makes $\text{C}\equiv\text{N}$ stretching frequency decrease. Figure 11 indicates the effect

Table 4 Sequence distribution parameters of AS copolymers

AN (mol%)	$\nu_{C\equiv N}(\text{cm}^{-1})$	P_{AN-AN}	R	$\langle AN \rangle$	$\langle S \rangle$
100	2239.6	1.00	—	—	—
85.90	2239.4	0.96	6.87	25.00	4.10
70.29	2238.6	0.84	22.49	6.25	2.64
62.23	2237.5	0.58	26.14	4.76	2.89
50.33	2235.5	0.18	41.27	2.44	2.41
33.26	2234.8	0.04	31.93	2.08	4.18

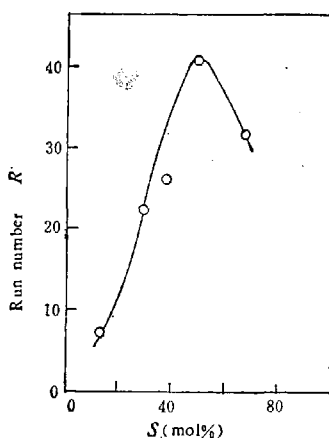


Fig. 11 The run numbers related to the S content in AS

of AS composition on its run number (R). R is a parameter to characterize the sequence distribution in copolymers. The larger the R , the more evenly the two kinds of monomers can be distributed in the macromolecular chain. When AN monomer and S monomer in AS copolymer are half-and-half, run number reaches maximal value. Figure 11 seems to be similar to Figure 9, from which we could imagine there are some internal relations between them. The relation between run number of AS copolymers and porous structural parameters of PAC/AS blend fibers is illustrated in Figure 12. It is seen that the void proportion, radius and number of micropores are linearly related to run number, in which $V.P.$ and N_s are in direct proportion to R and R_s is in inverse proportion to R ; that is, the more even the sequence distribution of AS copolymers, the larger the $V.P.$, the more the N_s and the smaller the R_s of the PAC/AS blend fibers are. The reason why R is linearly related to $V.P.$, N_s and R_s is how finely the dispersing particles of AS copolymer can be dispersed in PAC polymer. Thus, we treated PAC/AS blend films with butanone to remove the dispersing AS particles, and then observed the left void size and number by means of electron microscope. The micrographs obtained are presented in Figure 13 and the particle size of AS phase is listed in Table 5. The AS particles become smaller in size and more in number when its run number gets larger and larger, it is quite similar to the result shown in Figure 12. An explanation was given below.

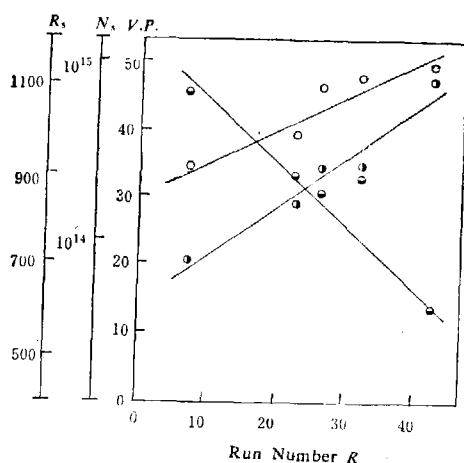


Fig. 12 Relation between structural parameters of PAC/AS fibers and run number of AS copolymers

—○— $V.P.$ (%); —●— N_s (pores/g); —○— R_s (Å).

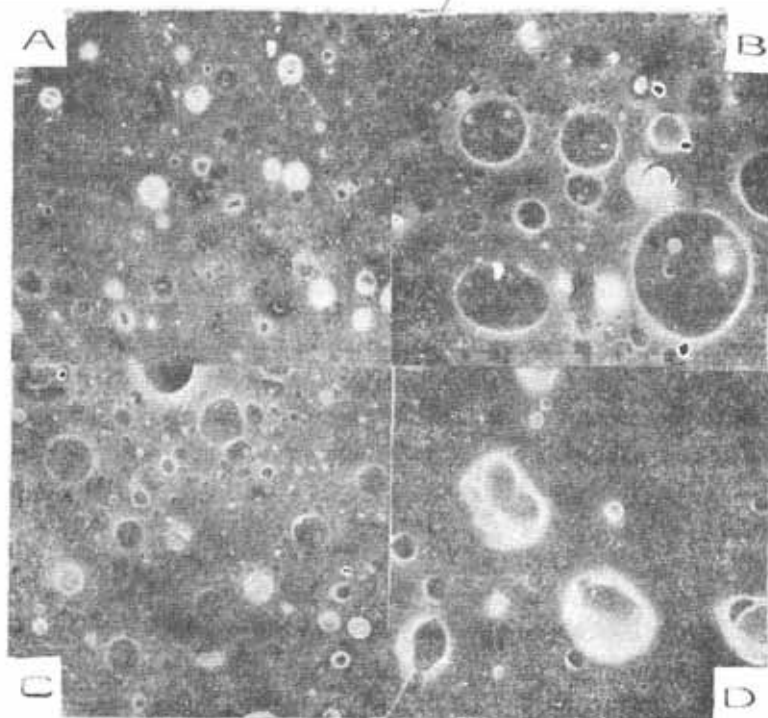


Fig. 13 Electron micrographs of PAC/AS (90/10) films treated with butanone (1500 $\times$)
 AS composition AN/S (wt%): A 54.66/45.34; B 45.64/54.36;
 C 34.05/65.95; D 0/100.

The interaction between AS and PAC macromolecules is very even and strong if AS has an even sequence distribution, which causes the AS particles relatively steady and difficult to gather together in blend solution; conversely, the interaction is very uneven and weak if AS

Table 5 Particle size and number of dispersing AS phase in PAC/AS blend films

AN(mol% in AS)		Large micropore		Small micropore	
		Size (μm)	Number	Size (μm)	Number
70.29	22.49	1.6	Few	—	None
62.23	26.14	5.0	Many	0.7	A great many
50.33	41.27	2.5	Many	0.7	A great many
0	0	4.0	Few	—	None

has an uneven sequence distribution, which causes the AS particles very unsteady and easy to agglutinate. That is, the more even the sequence distribution of AS copolymer, the finer the AS particles are. Under a certain blend ratio, it would have more dispersing particles and larger interface area to disperse finely than rough, which makes the coagulated blend fiber have larger void volume, more pore number and smaller pore size. Because the micropores are seated at the interface and around the dispersing particles, the void volume in the blend fibers largely depends on the interface area, and the pore size and number on the particle size and number of the dispersing AS domain. It is the internal relation between porous and phase structures that we have expected to present in this work.

Acknowledgment The authors would like to express appreciation to Mr. Yang Mingyuan and Ms. Mao Pingjun of the China Textile University for their helpful advice and assistance.

REFERENCES

- [1] Lennox-Kerr, P., *Text. Inst. Ind.*, **1981**, 19 (3), 83.
- [2] Fukui, T. and Sekiguchi, T., *Sen-I Gakkaishi*, **1980**, 36, 8, p. 313.
- [3] Komatsu, G. and Bukyo, S., *Jpn. Res. Assn. Text. End-Uses*, **1982**, 23 (9), 359.
- [4] 张安秋、陈寅生、刘念宁, 合成纤维 (*Synthetic Fibers*), **1980**, 4, 9.
- [5] Harwood, H.J. and Ritchey, W.M., *J. Polymer Sci.*, **1964**, B2, 601.
- [6] Craig, J.P.; Knudsen, J.P. and Holland, V.F., *Textile Res. J.*, **1962**, 32 (6), 435.
- [7] Sboun, O.; Miyazaki, K.; Shinku, K. and Shimada, H., *Kobunshi Kagaku*, **1972**, 29 (326), 388.
- [8] Bell, J.P. and Dumbleton, J.H., *Textile Res. J.*, **1971**, 41 (3), 196.
- [9] Knudsen, J.P., *Textile Res. J.*, **1963**, 33 (1), 13.
- [10] Lindenmeyer, P.H. and Hosemann, R., *J. Appl. Phys.*, **1963**, 34, 42.
- [11] 秦建、刘兆峰、毛萍君、李繁亭, 高聚物材料科学与工程 (*Polymer Materials Science and Technology*), **1985**, 1 (1), 44.
- [12] 李繁亭、肖长发、杨明远、刘兆峰、毛萍君, 纺织学报 (*Journal of China Textile Engineering Association*), **1982**, 3 (11), 645.