Microvoid Formation of Acrylic Copolymer (PAC)/Cellulose Acetate (CA) Blend Fibers

It is well known that the hydrophilic properties of synthetic fibers will be greatly modified if they contain numerous microvoids inside.[1-4] For acrylic fibers, polymer blend technique has been used to produce porous and water absorbing acrylic fibers in the recent years. We prepared the porous water absorbing acrylic blend fibers by means of wet-spinning method.[5] However, the studies on the mechanism of microvoid formation in blend acrylic fibers are very few. In this paper we wish to report the mechanism of microvoid formation in the acrylic copolymer (PAC)/cellulose acetate (CA) blend fibers by the characteristics of microvoids and phase structure in the blend fibers.

EXPERIMENTAL

The PAC is a acrylic copolymer containing 90.9% acrylonitrile, 8.6% methyl acrylate, and 0.5% sodium allyl sulfonate and M_w of 72,000. The CA is DP of 219.4 and combined acid of 54.82%. We mixed the blends in certain ratio, and then dissolved the blends into dimethylformamide (DMF) as the dopes. Spinning was proceeded with the dopes through a nozzle into a coagulation bath. The as-spun fibers were then washed with water, dried by dry ice freezing, as well as drawn in a boiling water bath and finally dried at 105°C for 2 h.

The microvoid content and microvoid size distribution of the fibers were measured with a Carlo Erba Model-225 mercury porosimetry in the range 0 to 2000 atm.

The cross section morphology of fibers was observed with a JSM-35 scanning electron microscope (SEM).

The storage modulus E', loss modulus E'' and loss tangent tan δ were measured with a Rheovibron DDV-II at frequency 110 Hz and heating rate 2°C/min in the 0 to 250°C range.

The composite model filaments with a shear/core ratio about 50/50 and diameter 1.2–1.5 mm was obtained by a normal wet-spinning process. The interfacial structure between skin and core on the cross section of the model filaments was observed with a body microscopy and a phase contrast microscopy.

RESULTS AND DISCUSSION

Table I shows the changes of mercury absorbed in the as-spun, drawn and dried PAC and PAC/CA (90/10, wt) blend fibers. It is evident to see that even if after drawing and drying, there were also numerous microvoids in the blend fiber. In general, microvoids are bound to form in the as-spun fiber because of solidification and phase separation of the spinning dope system during the coagulation and formation of PAC fibers,[6,7] the diameters of microvoids are 200–400 Å or so, those become finer and longer after drawing.[8] Hence, the total microvoid content in the primary swelled fiber is less than that in the as-spun fiber. The microvoids in primary swelled fiber close and disappear along with the routine heat treatment (that is, drying and heat set), so that the microvoids are few and very small in the heat treated fibers.

TABLE I
Changes of Mercury Absorbed (mL/g Fiber) During Fiber Formation

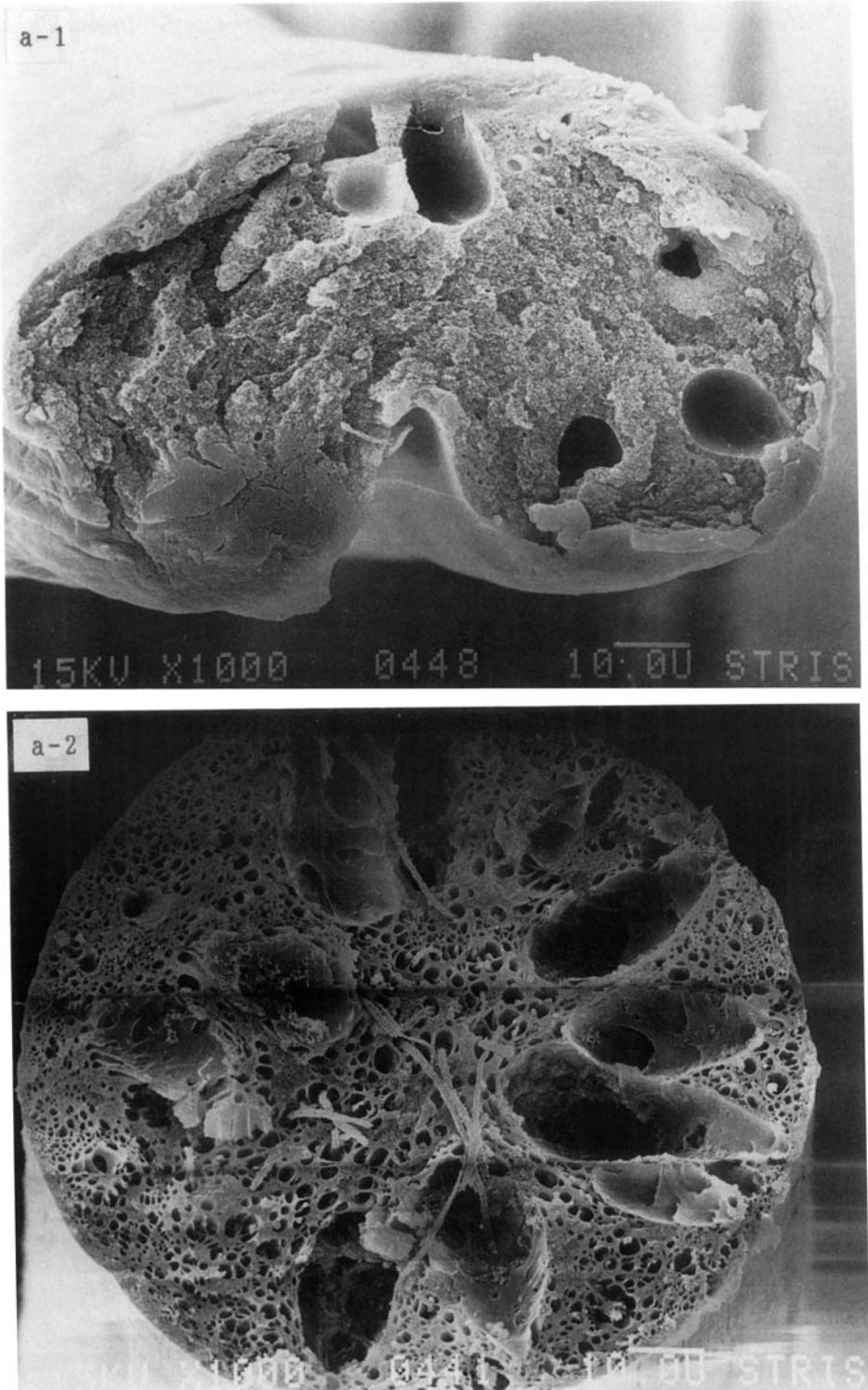| Fiber	As-span	Drawn × 5.0	Dried
Acrylic fiber (V_1)	0.58	0.35	0.12
Blend fiber (V_2)	1.10	1.00	0.80
(V_2/V_1) × 100 (%)	189.66	285.71	666.67

Fig. 1.   Scanning electron micrographs of the fibers. a-1: PAC, a-2: PAC/CA (90/10) for as-spun; b-1: PAC, b-2: PAC/CA (90/10) for drawn × 5.0 and dried.

Fig. 1. (Continued from the previous page.)

Figure 1 shows a series of electric micrographs of fibers. The cross section of the PAC as-spun fiber is not circular (Figure 1.a-1). That is because when the flux of spinning dope enters into the coagulation bath, a rigid skin will be immediately formed in general wet spinning condition with a organic solvent. Further, the shrinkage of the cross section will lead to noncircular shape. There are a great number of microvoids with the size of hundreds to thousands Å that most of them are
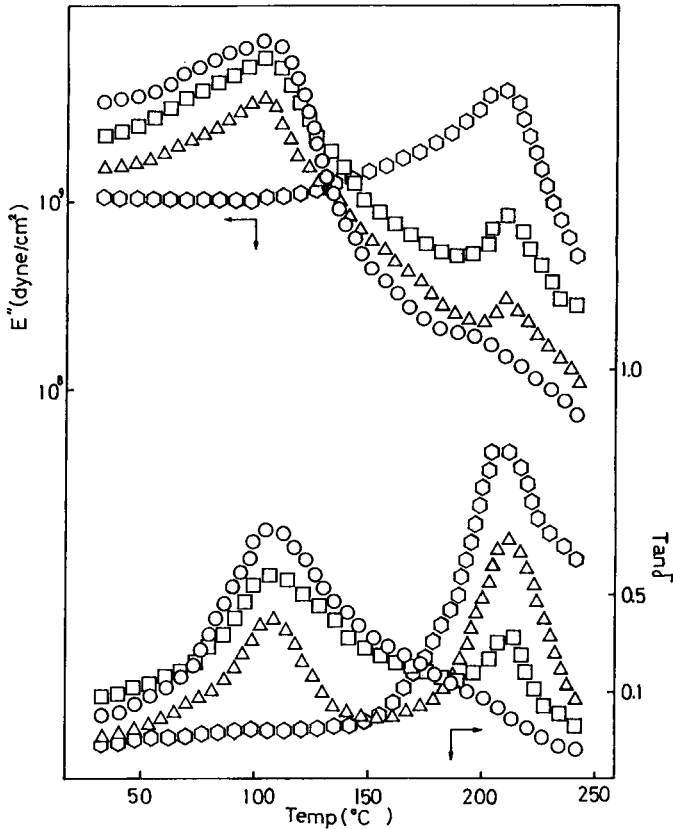
Fig. 2.   Dynamic mechanical properties of the fibers after drawn × 5.0 and dried: PAC (○), PAC/CA = 90/10 (□), PAC/CA = 70/30 (△), CA (○).

connected with each other in the blend fiber, so that with a soft, deformable layer the resulting shrinkage can still retain to circular cross section (Figure 1.a-2). After drawing and heat treatment, there are also many microvoids as well many capillaries or cracks that can be observed on the surface of the blend fiber (Figure 1.b-2) besides the fibrils as in the PAC fiber (Figure 1.b-1).

Figure 2 shows the dynamic mechanical spectra of the fibers. In the tan δ-T and the E''-T curves, there are two comparatively evident damping peaks at about 110°C and 210°C, those positions hardly change with the variation of two components in the blend fibers and correspond to those of the pure PAC and CA. This shows that the molecular chains of two components diffuse into
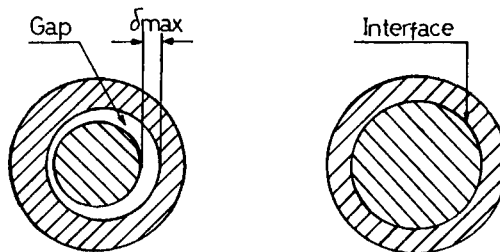

Fig. 3.   Scheme of gap formation at the interface of skin/core model filament: (a) skin/core = PAC/CA, (b) skin/core = CA/PAC.

Skin/core (50/50)	Drying condition	Characteristic of interface
PAC/CA	untreated	a clear interface, no gap
PAC/CA	air dry 5 min	a distinct gap at interface
PAC/CA	air dry 30 min	a very distinct gap at interface
PAC/CA	105°C dry 15 min	a very distinct gap at interface
CA/PAC	untreated	a clear interface, no gap
CA/PAC	air dry 5 min	a clear interface, no gap
CA/PAC	air dry 30 min	a clear interface, no gap
CA/PAC	105°C dry 15 min	a clear interface, no gap

each other to a rather small extent and do not sufficiently interact with each other, so that they retain own glass transition. That is, phase separation takes place in it.

Furthermore, we used a model spinning equipment to spin the skin/core composite filaments. For the sake of convenient observation and comparison, the max.gap width δ_{max} at the interface of two phases is taken as the cross section parameter of the filaments shown in Figure 3.a. We found that an evident gap appears at the interface of two phases through solidification and drying when the skin is PAC and the core CA. However, the interface of two phases can be seen on the cross section of the filament but no apparent gap comes into view as shown in Figure 3.b if the skin is CA and the core PAC. Table II shows the effects of drying conditions on the interfacial structure of the skin/core filaments. It is clear that as for the model filament, several drying conditions are all unable to produce a gap at the interface of two phases when CA is skin; but it is easy to cause a distinct gap after solidification, washing (or no washing) and drying when PAC is skin, which can be seen clearly even without microscope. Figure 4 shows the dynamic curve of the gap variation in the solidified PAC/CA (skin/core) filament during drying at room temperature. This result shows that it is different in the deswelling, solidification and shrinking properties between the phases of PAC and CA. Figure 5 shows that after drying at room temperature, the diameter of PAC filament decreases only 5% or so, but that of CA decreases over 20%, about 4 times of the former. Hence, it can be induced that the difference of shrinkages between the phases of PAC and CA leads to the gap at the interface of two phases. From the results it is clear that forming many microvoids in the blend fibers, if they may cause phase separation and the shrinkages of their gels, it is necessary to take the polymer with greater shrinkage as dispersing phase and the other as continuous phase.
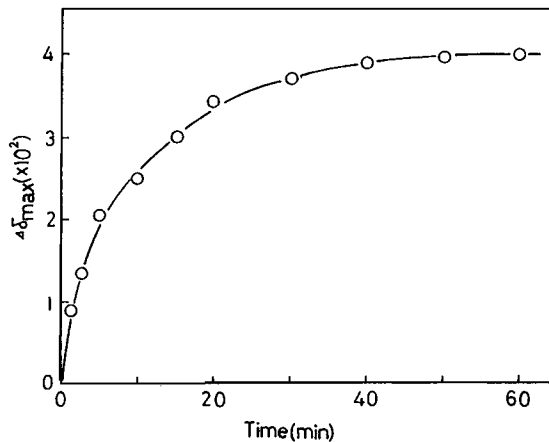

Fig. 4.   Dynamic curve of the gap variation in the skin/core (PAC/CA) filament during drying at room temperature.
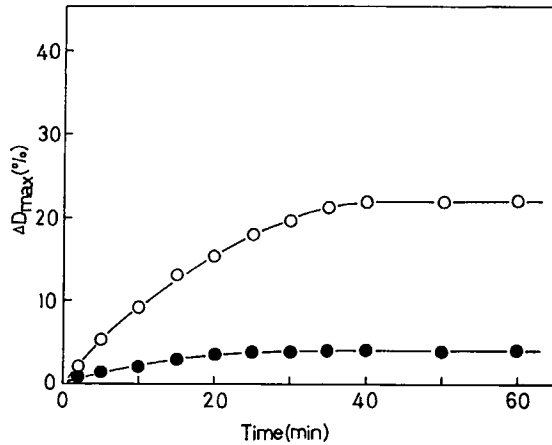
Fig. 5.   Dynamic curves of the diameter variation for the filament during drying at room temperature: PAC (●), CA (○).

References

1. T. Fukui and T. Sekiguchi, *Sen-I Gakkaishi.*, **36,** 313 (1980).

2. P. Lennox-Kerr, *Text. Inst. Ind.,* **19,** 83 (1981).

3. G. Komatsu and S. Bukyo, *Jpn. Res. Assn. Text. End-Uses.,* **23,** 359 (1982).

4. O. Wada and Y. Takatera, *J. Text. Machinery Soc. Japan.,* **36,** 42 (1983).

5. Li Fanting, Xiao Changfa, Yang Mingyuan, Liu Zhaofeng, and Mao Ping-jun, *J. China Text. Eng. Assn.,* **6,** 69 (1985).

6. M. Takahashi, *Chemistry of Hing Polymers* (Japan), **18,** 605 (1961).

7. A. Ziabicki, *Fundamentals of Fiber Formation,* New York, 1976.

8. D. R. Paul, J. W. Barlow, and H. Keskkula, *Polymer Blends,* New York, Vol. 1, 1978.

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