Properties of Blends of Syndiotactic-Rich and Atactic Poly(vinyl Alcohols)

SHUJI MATSUZAWA, KAZUO YAMAURA, MASANOBU NAGURA, and TOYOHIKO FUKUTA, *Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan*

Synopsis

The crystallinity, solubility, degree of swelling, and hygroscopicity of the blends of syndiotactic-rich (st-PVA) and atactic poly(vinyl alcohols) (at-PVA) were studied. The crystallinity of the blends increased with increasing annealing temperature and that of the blends annealed at 200°C was larger than that of at-PVA. In the 200°C annealed blends containing st-PVA about 50%, the insoluble fraction in boiling water was larger than the fraction of st-PVA in each blend. The soluble fraction for the blend containing 75% st-PVA was 1.7%. The moisture regain of the blends was less than that of at-PVA.

INTRODUCTION

Syndiotactic-rich poly(vinyl alcohol)(st-PVA) is insoluble in water at temperatures below 100°C and soluble at those above 100°C,[1-3] whereas commercial poly(vinyl alcohol)(at-PVA) which is atactic, is soluble at temperatures below 100°C. Since syndiotactic sequences of different lengths are present in at-PVA molecules,[4] the solubility of the at-PVA and st-PVA blend is considered to be lowered if longer syndiotactic sequences in at-PVA can interact with syndiotactic sequences in st-PVA. This paper presents results of the study of the crystallinity, solubility, degree of swelling, and hygroscopicity of the blends.

EXPERIMENTAL

A syndiotactic-rich poly(vinyl alcohol) derived from vinyl trifluoroacetate was used as st-PVA, of which the degree of polymerization and the syndiotactic diad content were 1670 and 56%, respectively. A commercial poly(vinyl alcohol) of the degree of polymerization of 1700 was used as at-PVA. The syndiotactic diad content of the PVA was 49%. The degree of polymerization (*DP*) of st-PVA was determined from the intrinsic viscosity ([η]) obtained from dilute benzene solution of acetylated st-PVA using the equation [η] = $8.91 \times 10^{-3} \ DP^{0.62}$(dL/g, 30°C).[5] The syndiotactic diad content was determined from the ratio of optical density at 916 cm^{-1} to that at 849 cm^{-1}(D_{916}/D_{849}) estimated from the infrared spectrum of the PVA films using the equation s-(diad)% = 72.4 × (D_{916}/D_{849})$^{0.43}$.[6]

Different ratios of st-PVA and at-PVA (total amount 0.5 g) were dissolved in water (10 mL) at 120°C in sealed tubes to make solutions which were cast on glass plates and dried at room temperature (ca. 25°C). The films had a thickness of about 0.09 mm. Films of different blends were annealed at 50°C

CCC 0021-8995/88/061661-05$04.00

for 10 min in a vacuum drying oven at 100°C for 3 min or at 200°C for 3 min in a silicone bath. The dissolution temperature of the films was determined as follows. The films (1 × 2 cm) were put with water in test tubes that were sealed and placed in an ethylene glycol bath of 30°C. The temperature of the bath was raised at the rate of 1°C/min and the temperature at which the films dissolved was determined. When the films were insoluble in water at 100°C, the ampoules were stored for 1 h. After cooling, the swollen films were weighed and then dried to determine the degree of swelling and solubility. The degree of swelling is expressed as (the weight of swollen film/dried film) − 1 and the solubility as 1 − (the ratio of the weight of the dried film after treatment to that before treatment).

The hygroscopicity of the films (1 × 2 cm) was determined at 100% humidity. The crystallinity of the films was determined from the density of the films using[7]

$$\frac{1}{d} = \frac{\alpha}{1.345} + \frac{(1 - \alpha)}{1.269}$$

where d is the density of the blends, α is the crystallinity, 1.345 is the density of crystal region and 1.269 is the density of the amorphous region. The crystallinity was also determined by X-ray diffraction using a Rigaku Geigerflex 2028 diffractometer with Cu$k\alpha$ radiation. The crystallinity X was estimated by,

$$X = \int_5^{45} Ic(\theta) \, d\theta / \int_5^{45} I(\theta) \, d\theta$$

where $Ic(\theta)$ and $I(\theta)$ are the intensities for crystalline contribution and the total sample at the scattering angle θ, respectively. In the use of this equation, scattering from air was corrected as is shown in Figure 1. Scattering from crystalline regions was assumed to be that above amorphous scattering. Correction due to incoherent scattering was ommited; therefore, the crystallinity obtained is underestimated.

RESULTS AND DISCUSSION

Table I shows the crystallinity determined by the density and X-ray methods. Although the crystallinity by the density method is greater than that by the X-ray method for each sample, the increase in density is considered to be due to that in crystallinity. The X-ray diffraction curves along equators are shown in Figure 1 in which the curves for air and the assumed amorphous parts are shown. No difference is observed among diffraction patterns for the blends, at-PVA, and st-PVA. This shows that the crystal structure of each blend is identical. The crystallinity of the blends increases with increasing annealing temperature.

Table II shows the behavior of the blends in water. The blends containing st-PVA above 50% had, after annealing at 100°C, an insoluble fraction which increased with increasing content of st-PVA.

Figure 2 shows the relation between solubility and crystallinity. In blends with almost the same crystallinity the solubility decreased with increasing content of st-PVA. A similar relation was observed between the degree of
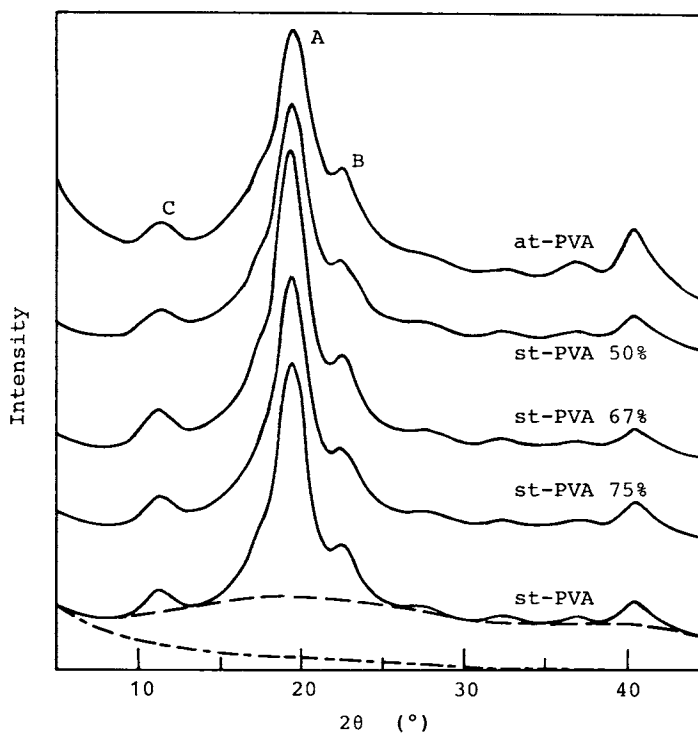
Fig. 1. X-ray diffraction curves of blend, st-PVA, and at-PVA along equators. (-----) assumed scattering from amorphous parts; (---) scattering from air. (A) scattering from 101 plane; (B) from 200 plane; (C) from 100 plane.

TABLE I
Crystallinity of Blends of st-PVA and at-PVA

Content of st-PVA (%)	Annealing temperature (°C)	Crystallinity	
		Density method	X-ray method
0	50	0.265	—
	100	0.295	—
	200	0.453	0.24
50	50	0.212	—
	100	0.273	—
	200	0.553	0.30
67	50	0.233	—
	100	0.289	—
	200	0.560	0.33
75	50	0.210	—
	100	0.320	—
	200	0.524	0.31
100	50	0.267	—
	100	0.285	—
	200	0.545	0.33

MATSUZAWA ET AL.

TABLE II
Solubility and Degree of Swelling of Blends

Content of st-PVA	Annealing temperature	Dissolution temperature	Solubility at 100°C	Degree of swelling at 30°C
(%)	(°C)	(°C)	(%)	
	50	63	100	—
0	100	65	100	—
	200	94	100	—
	50	95	100	—
50	100	95	100	—
	200	> 100	41.2	4.42
	50	98	100	—
67	100	98	100	—
	200	> 100	16.2	1.68
	50	> 100	a	a
75	100	> 100	a	a
	200	> 100	1.7	1.44
	50	> 100	a	—
100	100	> 100	a	—
	200	> 100	0.64	0.74

[a] Films became gelatinous and the determination of the solubility and the degree of swelling was very difficult.
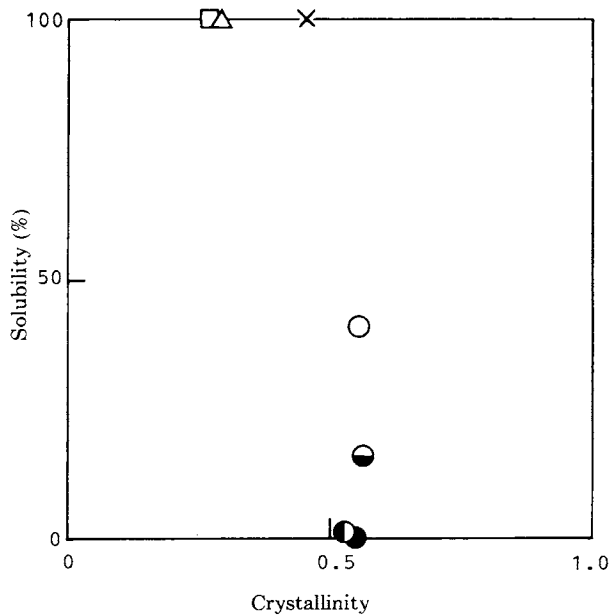

Fig. 2. Solubility as a function of crystallinity at 100°C. (×) st-PVA content 0; (○) 50; (◕) 67; (◑) 75; (●) 100% (annealed at 200°C);, (□) st-PVA content 50; (△) 67(annealed at 100°C).

TABLE III
Hygroscopicity of Blend Films (Moisture Regain after 48 h)

Content of st-PVA (%)	Moisture regain	
	Annealed at 100°C	Annealed at 200°C
0	53.9	18.3
50	29.0	16.5
67	22.8	12.8
75	30.3	14.2
100	33.1	9.3

swelling and crystallinity. It is considered that at-PVA molecules which crystallize in a manner similar to st-PVA increase with increasing content of st-PVA.

Table III shows the hygroscopicity of the blends. The moisture regain of the blends is lower than that of at-PVA. In the samples annealed at 200°C, that of st-PVA is lower than that of others, whereas in those annealed at 100°C no difference was found between the blend and st-PVA. This might suggest that the surface structure of the blends and st-PVA was identical; however, further investigation is necessary.

References

1. H. C. Haas, E. S. Emerson, and N. W. Schuler, *J. Polm. Sci.*, **22**, 291 (1956).
2. I. Sakurada, T. Itoh, and K. Noma, *Koubunshi Kagaku*, **16**, 115 (1959).
3. K. Fujii, T. Mochizuki, S. Imoto, J. Ukida, and M. Matsumoto, *J. Polym. Sci.*, **A2**, 2327 (1964).
4. K. Yamaura, Y. Hōe, S. Matsuzawa, and Y. Go, *Kolloid-Z. u. Z. Polymere*, **243**, 7 (1971).
5. A. Nakajima, *Kobunshi Kagaku*, **11**, 142 (1954).
6. S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *Kobunshi Kagaku*, **23**, 605 (1966).
7. I. Sakurada, Y. Nukushina, and Y. Sone, *Kobunshi Kagaku*, **12**, 506 (1955).