에틸렌 - 비닐알콜 공중합체와 나일론 블렌드의 유변학 및 형태학

김창기 · 김병규 · 정한모* · 허정도**

부산대학교 고분자공학과

*울산대학교 화학과

**포항공과대학 화학공학과

(1989년 6월 15일 접수)

Rheology and Morphology of Ethylene-Vinyl Alcohol Copolymers/Nylons Blends

Chang Kee Kim, Byung Kyu Kim, Han Mo Jeong* and Jung Do Huh**

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea
**Department of Chemistry, Ulsan University, Ulsan 680-749, Korea*
***Department of Chemical Engineering, Pohang Institute of Science & Technology,
Pohang 790-600, Korea*
(Received June 15, 1989)

요 약

비닐 알코올의 함량이 62(EVOH-62) 및 71(EVOH-71) mole% 인 에틸렌 비닐알코올 공중합체와 나일론(나일론 -6, 나일론 -6/12 및 나일론 -12)과의 블렌드를 이축 압출기에서 제조하였으며, 이들 블렌드의 형태학 및 유변학적 성질을 SEM, TEM 및 RDS로 측정하였다.

EVOH-62/나일론 -6 및 EVOH-71/나일론 -6 블렌드는 나일론의 조성이 많은 영역에서는 균일상을, EVOH 조성이 많은 영역에서는 미세한 상분리(약 0.2μ)를 나타내었다. 한편, EVOH-71/나일론 -6/12 및 EVOH-71/나일론 -12 블렌드는 상분리가 뚜렷하였으며, EVOH 조성이 많은 영역에서는 피브릴화가 나타났다.

낮은 진동주파수 영역에서 점도 대 조성곡선은 전반적으로 양의 편차를 보였으나, Cole-Cole plot 은 나일론 -6 과의 블렌드가, 나일론 -6/12 나 나일론 -12 와의 블렌드에 비해 유변학적인 측면에서보다 상용성이 우수함을 보였다.

Abstract—Melt blends of ethylene vinyl alcohol copolymers, containing 62 (EVOH-62) and 71 (EVOH-71) mole% vinyl alcohols, with nylons (nylon-6, nylon-6/12, and nylon-12) have been prepared in a twin screw compounding machine. The morphological textures of the blends were determined from SEM and TEM, and rheological properties were measured using RDS.

Morphological observations indicated that the EVOH-62/nylon-6 and EVOH-71/nylon-6 blends showed homogeneous phase morphologies in nylon-6 rich region, and fine phase separations (c.a. 0.2 μ) in EVOH rich region. On the contrary, clean phase separations in large domains were observed from EVOH-71/nylon-6/12 and EVOH-71/nylon-12 blends. Fibrillation was also obtained from EVOH rich blends.

Blend viscosities at low frequencies gave positive deviation from the simple additive rule, regardless of blend systems tested. However, futher analysis using the Cole-Cole plots indicated better rheological miscibility for blends with nylon-6 than those with nylon-6/12 and nylon-12.

Key words: ethylene-vinyl alcohol copolymer/nylon blends/rheology/morphology/miscibility

INTRODUCTION

Because of its superior gas barrier property, excellent transparancy, high oil resistance, and good processability, ethylene vinyl alcohol copolymer (EVOH) has emerging value in packaging films, and especially those for use with food and other products that require protection from oxygen (1, 2).

EVOH with more than 85 mole% vinyl alcohol tends to be difficult to extrude while that with less than 45 mole% vinyl alcohol reduces oxygen barrier performance. In fact, most commercially available EVOH contain 55-75 mole% vinyl alcohol in its structure (1, 2).

Since EVOH containing 55-75 mole% vinyl alcohol has certain level of compatibility with nylon-6, the industrial application of EVOH/nylon-6 blends appeared in several patents (2, 3). However, detailed study on their phase behavior is sparse (4).

When the chemical structure of a components in polymer blend is systematically varied, miscibility optimum often exists over a certain range of composition (5-7). For example, when the poly (ϵ -caprolactone) is blended with poly (styrene-co-acrylonitrile) (SAN), best miscibility is obtained with SAN containing 20 wt% AN (8). In tetramethyl bisphenol-A polycarbonate/aliphatic polyester blends, completely miscible blend is obtained with aliphatic polyester whose ratio of aliphatic carbons to ester groups, i.e., CH_2/COO in the repeat unit is seven (9). These phase behavior is properly explained in terms of sufficiently repulsive intramolecular interaction relative to the intermolecular interaction in binary interaction model (5, 6, 7, 10).

It is therfore natural to expect that the miscibility of EVOH/ny'on blends varies with the ratio of aliphatic carbor᠎ to amide groups ($CH_2/-CO-NH-$) of nylon. Therefore this paper considers the blends of EVOH, containing 62 (EVOH-62) and 71 (EVOH-71) mole% vinyl alcohol, with nylon-6, and blends of EVOH-71 with three types of nylon characterized by its $CH_2/-CO-NH-$ ratio, viz., 5 (nylon-6), 8 (nylon-6/12) and 11 (nylon-12). The phase behavior of the blends has been examined from morphological and rheological points of view. Attempts were also made to interprete the rheological behavior from morphologies.

EXPERIMENTAL

Sample preparations

Commercial grades of the polymers, listed in Table 1, as received were used for blending. Blends were prepared by first mixing the dried chips thoroughly, follwed by melt mixing in a twin screw compounding machine (Baker Perkins) at 225-230°C (EVOH/nylon-6, EVOH/nylon-6/1) or 215-220°C (EVOH/nylon-12). The blended samples were subsequently quenched in water, pelletized (Berlyn, PEL-2) into chips, and dried in vacuum for 3 days at 80°C. These dried chips were used for morphological observation from transmission electron microscopy (TEM).

Samples for scanning electron microscopy (SEM) were prepared from injection molding (Tohsiba, IS-60B) of the compounded chips at 230-235°C (nylon-6, nylon-6/12), or 210-220°C (nylon-12) with the mold temperature of 80°C.

Morphology

Morphologies of the blends were observed from SEM (Jeol, JSM-35CF) and TEM (Jeol, JEM-100CX). SEM micrographs were taken from cryogenically (in liquid nitrogen) fractured surfaces of injection moulded plaque, sputtered with gold before viewing.

For the observation from TEM, the nylon rich phase of the chips was stained with OsO_4 in aqueous solution of formaldehyde for 3 days (11), and thin sections of the samples were obtained using an ultramicrotome.

Rheological properties

Rheological properties of the samples were determined from a Rheometric Dynamic Spectrometer

Table 1. List of Polymers used.

Sample Name	Manufacturer	Trade Name
nylon-6	Tongyang Nylon	Toplamid 1021 BR
nylon-6/12	Du Pont	Zytel
nylon-12	Dicel Huels	Daiamid
EVOH-62	Nippon Synthetic Chemical	Soanol-E
EVOH-71	Nippon Synthetic Chemical	Soanol-Z

RRESULTS AND DISCUSSION

Morphology

SEM micrographs for EVOH/nylon blends are shown in Fig. 1. Blends of nylon-6 with EVOH do not show clear phase separation throughout the blend compositions tested. On the contrary, blends of nylon-6/12 and nylon-12 with EVOH show spherical EVOH particles (order of 1 μ in diameter) dispersed in nylon phase in nylon rich composition (80 wt% nylon), and fibrillation of nylon in EVOH-rich composition (80 wt% EVOH). It is also noted that the phase separation is clearer in EVOH/nylon-12 than in EVOH/nylon-6/12.

Phase morphology observed from SEM is essentially in line with a theoretical prediction based on the following equation (5),

$$\Delta \bar{H}_{mix} = \phi_1 \phi_2 \{(\delta_1 - \delta_2)^2 + 2k_{12}\delta_1\delta_2\} \qquad (1)$$

where $\Delta \bar{H}_{mix}$ = enthalpy of mixing per uit volume ϕ_1 and ϕ_2 = volume fraction of components 1 and 2, respectively, δ_1 and δ_2 = solubility parameter of components 1 and 2, respectively, k_{12} = parameter describing the departure from the geometric mean value with smaller difference in solubility parameters between the components, $\Delta \bar{H}_{mix}$ will in general become smaller, and better miscibility results. The solubility parameters calculated from the group contribution method (12) were 13.7, 14.2, 13.7, 12.2, and 11.4 (cal/cm³)¹/² for EVOH-62, EVOH-71, nylon-6, nylon-6/12, and nylon-12, respectively. For blends with significant intermolecular interactions, contribution of the second term in eq. (1) is notable, in general. However, with the above values and neglecting the second term in eq. (1), the $\Delta \bar{H}_{mix}$ is obtained in the increasing order of EVOH-62/nylon-6 < EVOH-71/nylon-6 < EVOH-71/nylon-6/12 < EV-

OH-71/nylon-12, an order consistent with the phase behavior from SEM.

The phenomenon of fibrillation, observed in EVOH rich composition of EVOH-71/nylon-6/12 and EVOH-71/nylon-12 blends, has also been reported for several other systems (13-15), and is a phenomenon often observed in immiscible blends where phase separations occur.

During the compounding process, it was observed that the melts of EVOH-71/nylon-6/12 and EVOH-71/nylon-12 blends swelled up to over 5 times the extruder die diameter. The die swell was more pronounced with nylon-12 than with nylon-6/12, and in EVOH rich phase. In fibrill forming system, die swell is mainly due to the relaxation of the phenomenon of fibrillation upon exiting from the die (14).

Fig. 2 shows the TEM micrographs of the EVOH/nylon blends. As mentioned earlier, the nylon phase of the blend was selectively stained with O_sO_4. In EVOH rich composition of the EVOH-71/nylon-6 blends, phase separations with the spherical nylon particles, order of 0.2 μ in diameter, finely dispersed in EVOH matrix are seen. Such fine phase separation in the EVOH rich composition (>35 wt% EVOH) of EVOH/nylon-6 blends was reported by others (2, 4) and the present results confirm this.

Rheological properties

Melt viscosities of the blends, measured at 230°C from RDS, are shown in Figs. 3-6. Blends of EVOH-62 and EVOH-71 with nylon-6 show limiting viscosities at low frequency range. On the contrary, the blends of EVOH-71 with nylon-6/12 and nylon-12 generally gives viscosity yield at low frequency range. In polymer blends, the yield behavior has often been observed from immiscible systems, or particle filled systems where the interactions between the particles are very strong (16-20). The particle-in-matrix structure of the blends (Figs. 1 and 2) plus strong interactions between the nylon particles and nylon/EVOH interfaces should be responsible for the existence of yield.

Low frequency viscosities (ω = 0.1 rad/sec) as a function of composition are given in Fig. 7. Viscosities of the blends are higher than those of the components. Regardless of the blend systems,

(a)
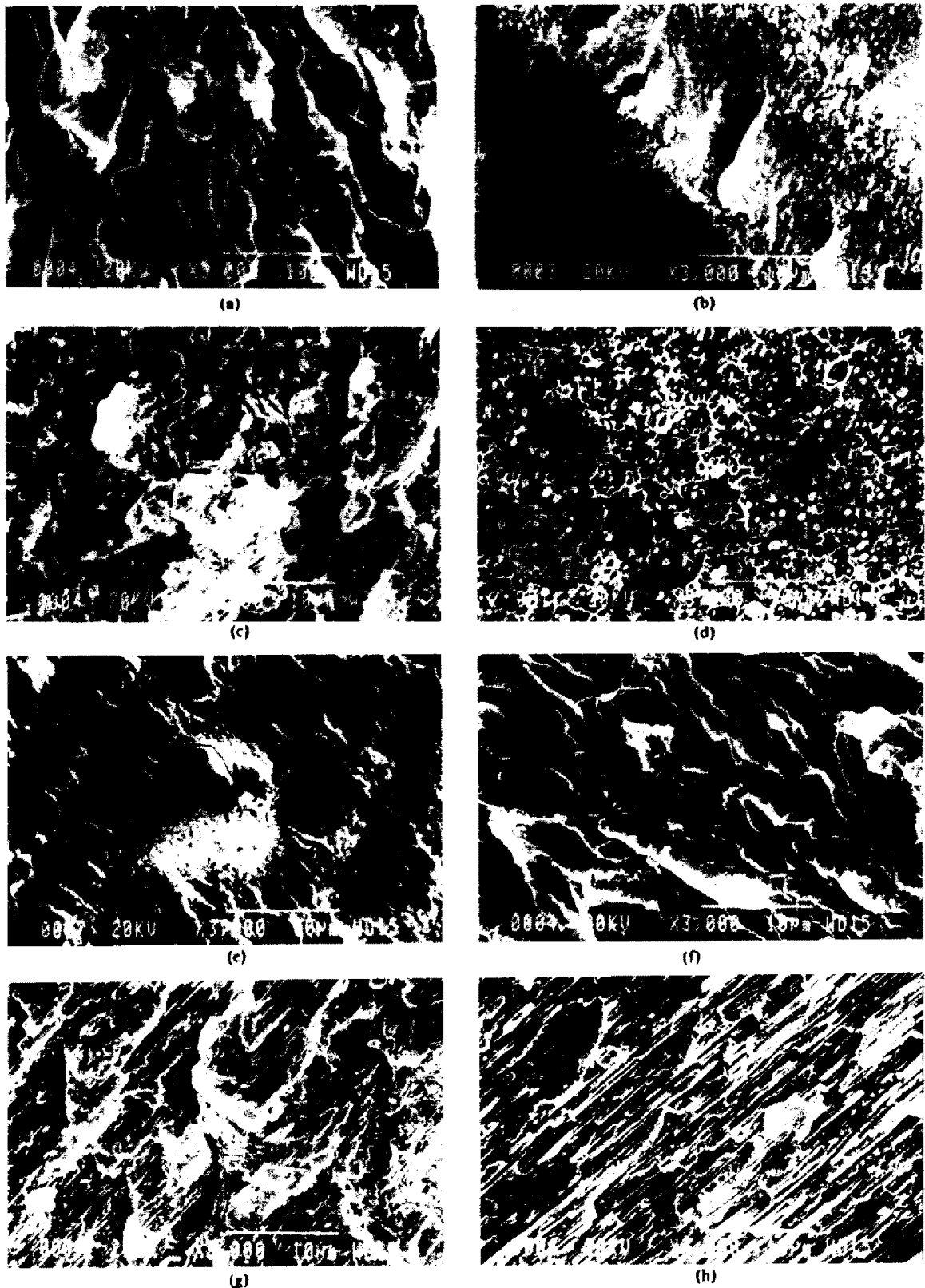
(b)

(c)

(d)

(e)

(f)

(g)

(h)

Fig. 1. SEM microphotographs of fractured surfaces for EVOH/nylon blends:
(a) EVOH-62/nylon-6 (30/70), (b) EVOH-71/nylon-6 (30/70), (c) EVOH-71/nylon-6/12 (20/80), (d) EVOH-71/nylon-12 (20/80), (e) EVOH-62/nylon-6/nylon-6 (70/30), (f) EVOH-71/nylon-6 (70/30), (g) EVOH-71/nylon-6/12 (80/20), (h) EVOH-71/nylon-12 (80/20).
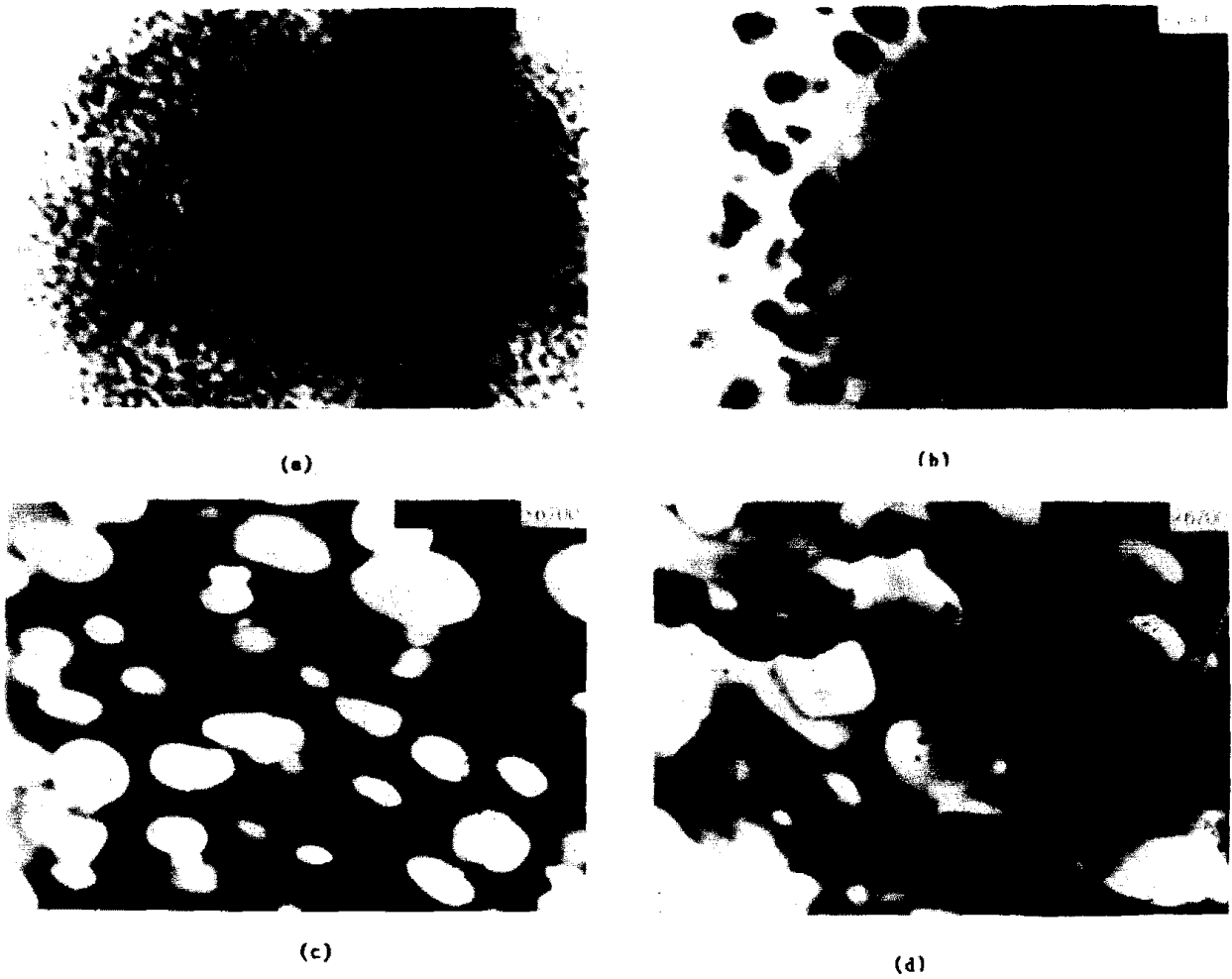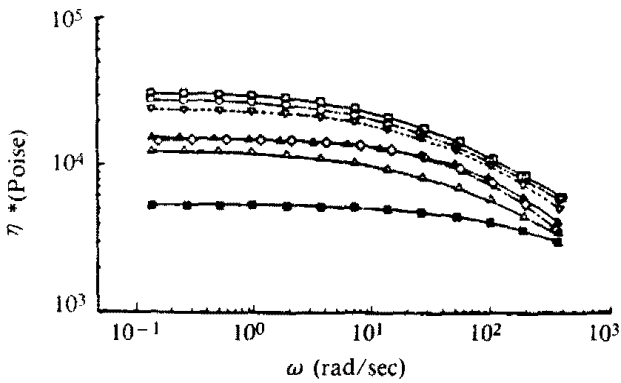
(a)

(b)

(c)

(d)

Fig. 2. TEM microphotographs of EVOH/nylon blends:
(a) EVOH-71/nylon-6 (30/70), (b) EVOH-71/nylon-6 (70/30), (c) EVOH-71/nylon-6/12 (40/60), (d) EVOH-71/nylon-12 (40/60).

Fig. 3. Complex viscosity vs. frequency for EVOH-62/nylon-6 blends at 230°C:
0/100 (■), 10/90 (△), 30/70 (○), 50/50 (□), 70/30 (▽), 90/10 (◇), 100/0 (▼).
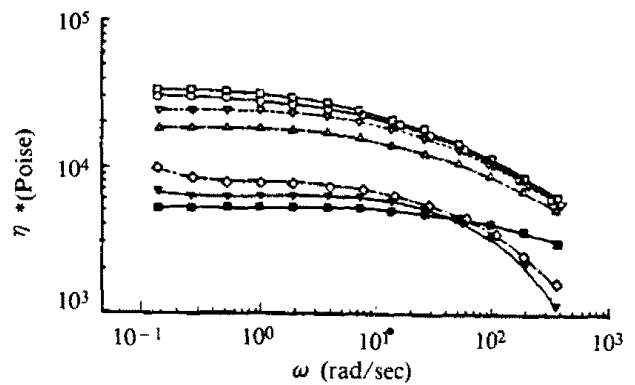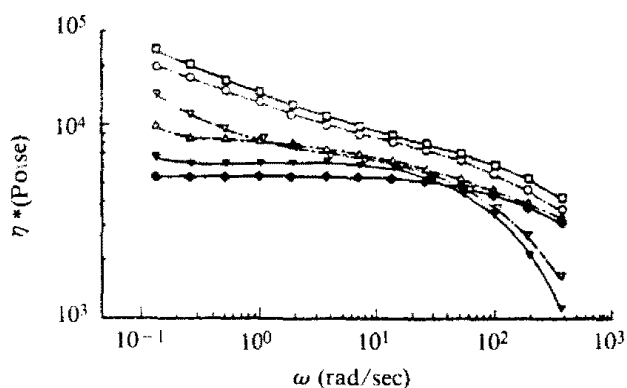
Fig. 4. Complex viscosity vs. frequency for EVOH-71/nylon-6 blends at 230°C:
0/100 (■), 10/90 (△), 30/70 (○), 50/50 (□), 70/30 (▽), 90/10 (◇), 100/0 (▼).

Fig. 5. Complex viscosity vs. frequency for EVOH-71/nylon-6/12 blends at 230°C: 0/100 (◆), 20/80 (△), 40/60 (○), 60/40 (□), 80/20 (▽), 100/0 (▼).
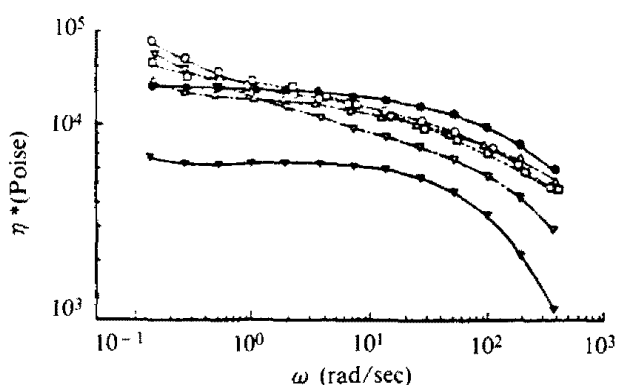

Fig. 6. Complex viscosity vs. frequency for EVOH-71/nylon-12 blends at 230°C: 0/100 (●), 20/80 (△), 40/60 (○), 60/40 (□), 80/20 (▽), 100/0 (▼).
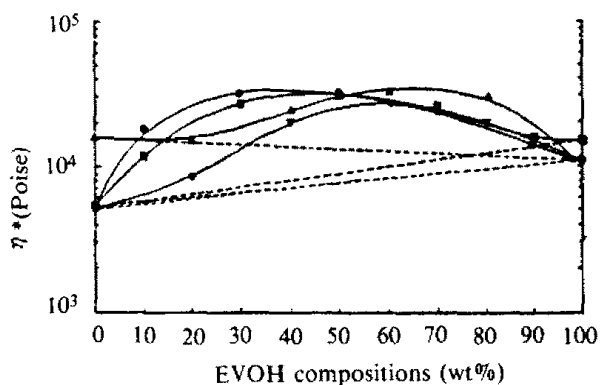

Fig. 7. Viscosity vs. blend composition for EVOH/nylon blends: EVOH-62/nylon-6 (■), EVOH-71/nylon-6 (●), EVOH-71/nylon-6/12 (▼), EVOH-71/nylon-12 (▲)

positive deviations are obtained with regard to low frequency viscosity. Following the literature (16), positive deviation in viscosity generally occurs when there are strong interactions between phases at low rate of shear, or when the blend has an interlocked morphology. The positive deviation in viscosity is greater in nylon-rich composition for the EVOH-71/nylon-6 and EVOH-71/nylon-6 blends, and in the EVOH-rich region for EVOH-71/nylon-6/12 and EVOH-71/nylon-12 blends than the other side of composition, respectively. The viscosity-composititon curves for the blends with nylon-6, better dispersion was observed in nylon-rich composition of the blends (Fig. 2). With better dispersion, the inerfacial area sould increase. When the increased interfacial area is coupled with the greater nylon/EVOH interactions over those of nylon/nylon (4), the resistance to flow should increase, resulting in higher viscosity.

The maximum viscosity deviations observed in EVOH-rich composition for the blends with nylon-6/12 and nylon-12 are direct response of the existance of viscosity yield (Figs. 5 and 6). The viscosity yield found in EVOH/nylon blends, on the other hand, should be possibly related to the phenomenon of the fibrillation, observed in EVOH-rich composition of the blends (Fig. 1).

Cole-Cole plots using dynamic data are useful ways of rheological characterization (21). In these plots, the effect of temperature is virtually neglected, and temperature independent master curves are obtained. Cole-Cole plot can be prepared either in a ordinary coordinate or in full-log scale. When plotted in a ordinary coordinate, the plot gnerally gives long linear region. For the present blends, G' vs. G" curves are given in Figs. (8-11). The advantage of these plots over the conventional plots against frequency are well documented in reference (17, 22, 23). Notably, the breadth of G' curves for the blends is an indication of rheological miscibility, viz., with narrow breadth better miscibility is indicated. From the figures, it is noted that the breadth of G' curves is in the increasing order of the EVOH-62/nylon-6, EVOH-71/nylon-6, EVOH-71/nylon-6/12, and EVOH-71/nylon-12, an order consistent with the phase behavior observed from SEM and TEM.

When the Cole-Cole plot is prepared in logarithmic scales, data for homopolymers and compatible blends lie on a semicircle, whereas the incom-
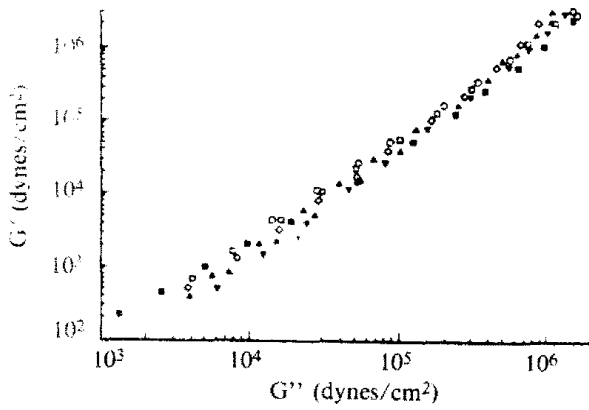
Fig. 8. Storage modulus vs. loss modulus for EVOH-62/nylon-6 blends:
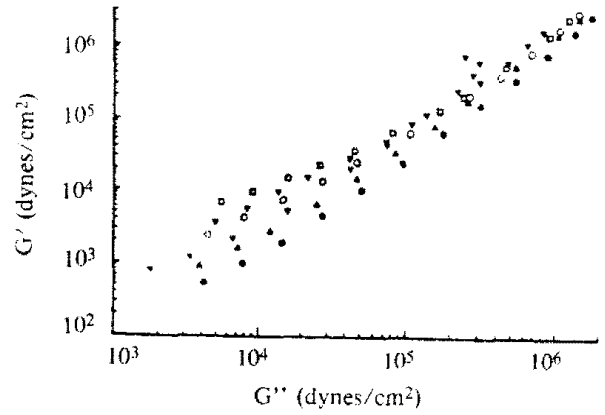0/100 (■), 10/90 (△), 30/70 (○), 50/50 (□), 70/30 (▽), 90/10 (◇), 100/0 (▲).

Fig. 11. Storage modulus vs. loss modulus for EVOH-71/nylon-6/12 blends:
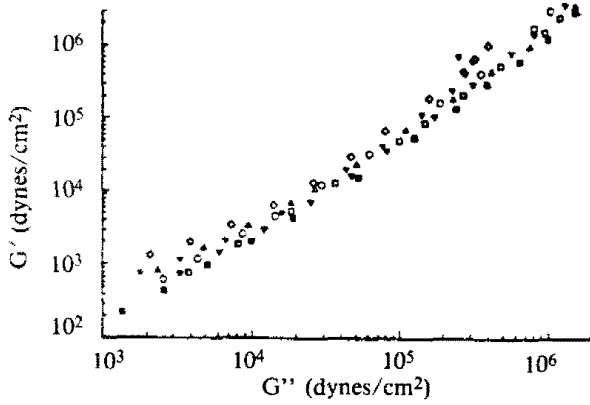0/100 (●), 20/80 (△), 40/60 (○), 60/40 (□), 80/20 (▽), 100/0 (▼).

Fig. 9. Storage modulus vs. loss modulus for EVOH-71/nylon-6 blends:
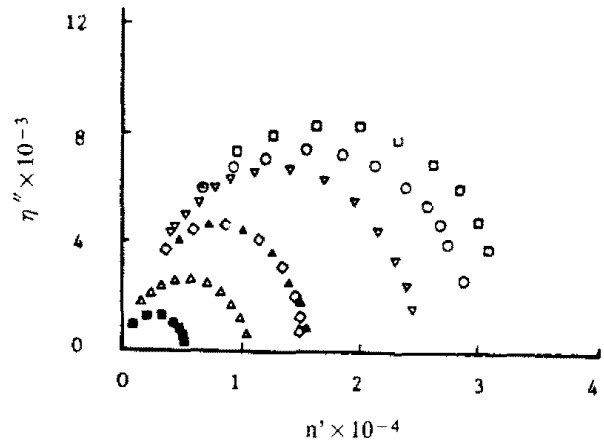0/100 (■), 10/90 (△), 30/70 (○), 50/50 (□), 70/30 (▽), 90/10 (◇), 100/0 (▼).

Fig. 12. Cole-Cole plot for EVOH-62/nylon-6 blends:
0/100 (■), 10/90 (△), 30/70 (○), 50/50 (□), 70/30 (▽), 90/10 (◇), 100/0 (▲).
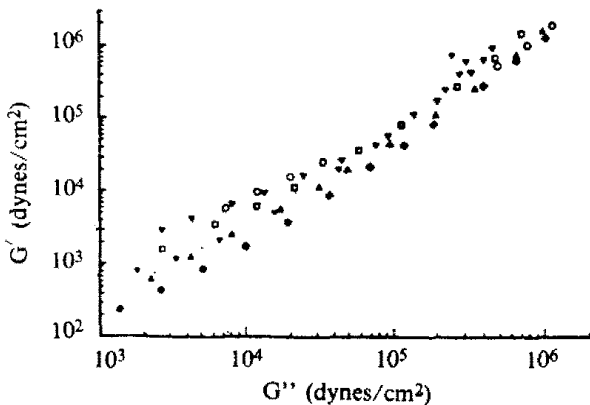

Fig. 10. Storage modulus vs. loss modulus for EVOH-71/nylon-6/12 blends:
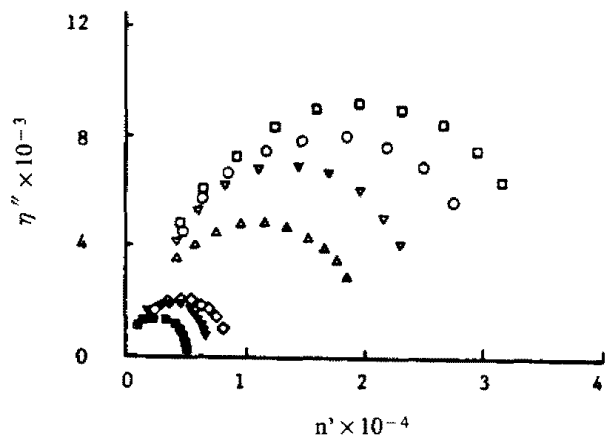0/100 (◆), 20/80 (△), 40/60 (○), 60/40 (□), 80/20 (▽), 100/0 (▼).

Fig. 13. Cole-Cole plot for EVOH-71/nylon-6 blends:
0/100 (■), 10/90 (△), 30/70 (○), 50/50 (□), 70/30 (▽), 90/10 (◇), 100/0 (▼).

patible blends give drift from the semicircle (24). For modern views and interpretation of the Cole-Cole plot, the reader is referred to refs. (25) and (26). In this experiment, data for blends with nylon-6 fall nicely on a semicircle (Figs. 12 and 13), and the blends with nylon-6/12 and nylon-12 show incompatible drift (Figs. 14 and 15).
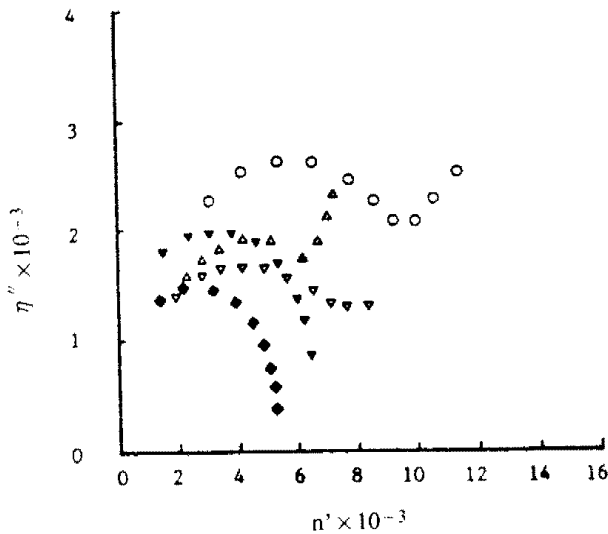

Fig. 14. Cole-Cole plot for EVOH-71/nylon-6/12 blends: 0/100 (◆), 20/80 (△), 40/60 (○), 60/40 (□), 80/20 (▽), 100/0 (▼).
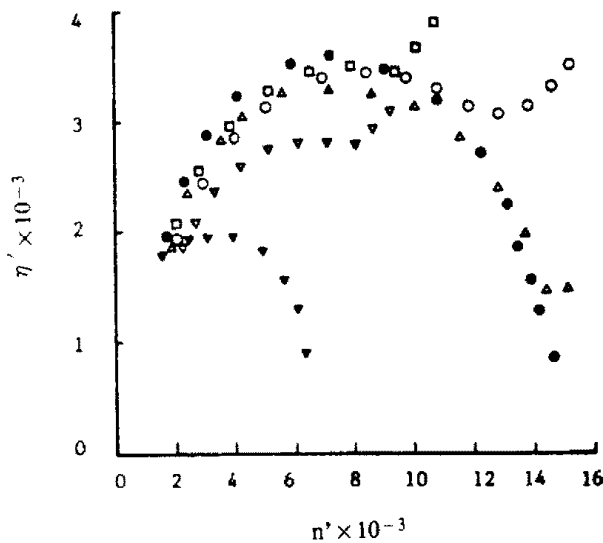

Fig. 15. Cole-Cole plot for EVOH-71/nylon-12 blends: 0/100 (●), 20/80 (△), 40/60 (○), 60/40 (□), 80/20 (▽), 100/0 (▼).

CONCLUSIONS

The blends of ethylene vinyl alcohol copolymers with nylons of different structures have been prepared, and analyzed in terms of morphology and rheology. Morphological observations indicated that the EVOH-62/nylon-6 and EVOH-71/nylon-6 blends showed homogeneous phase morphologies in nylon-6 rich region, and fine phase separations (c.a. 0.2μ) in EVOH rich region. On the contrary, clean phase separations in large domains were observed from EVOH-71/nylon-6/12 and EVOH-71/nylon-12 blends. Fibrillation was also obtained from EVOH rich blends.

With regard to linear viscoelastic properties, blend viscosities at low frequency ranges showed positive deviation from the simple additive rule, regardless of the blend systems tested. Positive deviation was greater in nylon-rich composition for blends with nylon-6, and in EVOH-rich composition for blends with nylon-6/12 and nylon-12 than the other side of composition, respectively. Futher rheological analysis using the Cole-Cole plots indicated better miscibility for the blends with nylon-6 than the other combinations. The phase behavior observed from rheology measurement was qualitatively in good agreement with the morphology for the particular blends considered in this paper.

REFERENCES

1. T. Iwanami and Y. Hirai, *Tappi Journal*, **66**(10), 85 (1983).
2. U.S. Patent, 4, 427, 825 (1984).
3. U.S. Patent, 4, 347, 332 (1982).
4. G.M. Venkatesh, R.D. Gilbert and R.E. Fornes, *Polymer*, **26**, 45 (1985).
5. D.R. Paul and J.W. Barlow, *Polymer*, **25**, 487 (1984).
6. J.W. Barlow and D.R. Paul, *Polymer, Eng. Sci.*, **27**, 1482 (1987).
7. T. Shiomi, F.E. Karasz and W.J. MacKnight, *Macromolecules*, **19**, 2274 (1986).
8. J. Kressler and H.W. Kammer, *Polymer. Bull.*, **19**, 283 (1988).
9. A.C. Fernandes, J.W. Barlow and D.R. Paul, *Polymer*, **27**, 1799 (1986).
10. A.C. Fernandes, J.W. Barlow and D.R. Paul, *J. Appl. Polym. Sci.*, **32**, 5357 (1986).

11. G. Weber, D. Kuntze and W. Stix, *Coll, Polym. Sci.,* **260**, 956 (1982).

12. D.W. Van Krevelen, "Properties of Polymers", ch.7, Elsevier, Amsterdam-Oxford-New York (1976).

13. J. Lyngaae-Jorgensen, F.E. Andersen and N. Alle, in D. Klempner and K.C. Frisch, eds., "Polymer Alloy III", p.105, Plenum, New York (1983).

14. G.V. Vinogradov, B.V. Yarlykov, M.V. Tsebrenko, A.V. Yudin and T.I. Ablazova, *Polymer,* **16**, 609 (1975).

15. C.D. Han and T.C. Yu, *Polym. Eng. Sci.,* **12**, 81 (1972).

16. C.D. Han, "Multiphase Flow in Polymer Processing", p.190, Academic, New York (1981).

17. C.D. Han and H.H. Yang, *J. Appl. Polym. Sci.,* **33**, 1221 (1987).

18. B.R. Liang, J.L. White, J.E. Spruiell and B.C. Goswami, *J. Appl. Polym. Sci.,* **28**, 2011 (1983).

19. H.K. Chuang and C.D. Han, *J. Appl. Polym. Sci.,* **29**, 2205 (1984).

20. K.J. Wang and L.J. Lee, *J. Appl. Polym. Sci.,* **33**, 431 (1987).

21. C. Wisnie, G. Marin and P.H. Monge, *Eur. Polm. J.,* **21**, 479 (1985).

22. C.D. Han and K.W. Lem, *Polym. Eng. Rev.,* **2**(2), 135 (1982).

23. C.D. Han and H.H. Yang, *J. Appl. Polym. Sci.,* **33**, 1199 (1987).

24. C. Wisnie, G. Marin and P.H. Monge, *Eur. Polym. J.,* **21**, 479 (1985).

25. C.D. Han and M.S. Jhon, *J. Appl. Polym. Sci.,* **32**, 3809 (1986).

26. A. Ajji and R.E. Prud, homme, *J. Polym. Sci., Polym. Physics.,* **26**, 2279 (1988).