

열방성 액정 고분자와 폴리페닐렌 설파이드와의 블렌드에 관한 물성

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(1994년 9월 6일 접수)

Properties of Blends of a Thermotropic Liquid Crystalline Polymer with Polyphenylene Sulfide

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(Received September 6, 1994)

요 약

열방성 액정 고분자인 벡트라와 폴리페닐렌 설파이드와의 블렌드를 주사 전자 현미경, 시차 주사 열분석기, 그리고 모세관 레오미터를 이용하여 전 조성 범위에 대하여 연구하였다. 블렌드의 결정화와 용융에 관한 연구결과로부터 두 고분자 사이에는 상호작용이 없음을 알 수 있다. 이는 두 개의 상이 완전히 분리되기 때문이다. 폴리페닐렌 설파이드를 많이 포함하고 있는 블렌드의 점도는 상당히 감소되었으며 이는 높은 전단속도에서 열방성 액정 고분자가 섬유구조를 갖기 때문이다. 열방성 액정 고분자의 섬유구조는 열방성 액정 고분자와 등방성상과의 점도비와 전단속도에 의해 영향을 받음을 알 수 있다.

Abstract—Blends of Vectra A900, a thermotropic liquid crystalline polymer (LCP), and polyphenylene sulfide (PPS) were studied over the entire composition range using scanning electron microscope, differential scanning calorimeter, and capillary rheometer. Melting and crystallization data suggest that there is no interaction between the polymers since complete phase separation is observed between the two phases. Significant depression of the viscosity is observed in the PPS-rich blends and this is mainly due to the fibrous structure of the LCP at the high shear rate. The appearance of the fibrils of LCP is shown to dependent on the viscosity ratio of LCP to isotropic phase and the shear rates.

Keywords: Liquid crystalline polymer, polyphenylene sulfide, blend, rheology, morphology, thermal property, X-ray diffraction

1. Introduction

Blends of thermotropic liquid crystalline poly-

mers (LCPs) with flexible-chain melts offer the potential of improved properties and unique properties [1] such as fibrous structure of the LCP [2,3] and viscosity reduction of the blend [4-6]

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when the small amount of LCP is added to the matrix. Several researchers have studied blends of thermotropic LCPs and flexible polymers [7, 8] including polyphenylene sulfide (PPS) [9-12].

We report here on the relation between morphology and rheology of blends of Vectra A900, a random copolyester containing 73 mol% 4-hydroxybenzoic acid (HBA) and 27 mol% 6-hydroxy-2-naphthoic acid (HNA), with PPS over the entire compositional range. Also the blends of Vectra with poly(ethylene terephthalate) (PET) are compared with the results of Vectra and PPS blends. The blends have been characterized using thermal analysis and scanning electron microscope, while rheological measurements were made using capillary rheometer. The viscosity of the PPS-rich phases is decreased significantly compare to that of the pure PPS at high shear rates. The decrease in viscosity is mainly due to the fibrous structure of dispersed Vectra phase in the blends. The appearance of the fibrils of LCP was shown to dependent on the viscosity ratio of LCP to isotropic phase and the shear rates. Complete phase separation is observed between Vectra and PPS phases, and there is no change in PPS melting and crystallization temperatures with annealing times in all the blend compositions. This is somewhat comparative results with the blends of Vectra and PET [6].

2. Experimental

2.1. Polymers

Vectra A900, manufactured by Hoechst-Celanese, is a random liquid crystalline copolyester containing 73 mol% 4-hydroxybenzoic acid (HBA) and 27 mol% 6-hydroxy-2-naphthoic acid (HNA). The sample of polyphenylene sulfide (PPS) was supplied by Tohpren Co. (Japan). The Hoechst-Celanese poly(ethylene terephthalate) (PET) used in this work has an intrinsic viscosity of 0.65 dL/g. The glass transition temperature (T_g) and melting points (T_m) reported in Table 1 were measured by differential scanning calorimetry (DSC), using procedures reported elsewhere [6].

Table 1. Characteristics of polymer samples used in this work

| | T_m , °C | T_g , °C | ΔC_p (J g ⁻¹ K ⁻¹) |
|-------------|------------|------------|---|
| Vectra A900 | 280.4 | 92.9 | 0.031 |
| PPS | 280.0 | 98.3 | 0.081 |
| PET | 253.1 | 82.0 | 0.137 |

2.2. Blend Preparation

Blends with weight fraction of Vectra from 0.1 to 0.9 in increments of 0.1 were prepared by screw-extrusion and mixer. The polymer samples were dried under vacuum (< 1 mmHg) at 120°C for 24 h before use. Blends with PPS were prepared using a Brabender Plasti-Corder PL 2000 twin-screw extruder and mixer. The temperature of the extruder was set at 310°C in the barrel zones, and the screw speed was set at 30 rpm. For both the extruder and mixer blending, nitrogen was purged into the hopper to minimize the chemical modifications of the polymers at high temperature. Blends with PET were prepared using a 19.1-mm-diameter laboratory-scale single-screw extruder, described elsewhere [6].

2.3. Scanning Electron Microscopy (SEM)

The morphology of cross-sections of the extrudate prepared by cryogenic fracturing was examined by SEM in a Model Cambridge 250-MK3 microscope at 15 kV accelerating voltage after gold sputter coating (500 Å).

2.4. Differential Scanning Calorimetry

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, Model DSC-7, with a thermal analysis data station. Temperature calibration was performed using indium. Blend samples of 10 to 20 mg were initially heated in a nitrogen atmosphere from 40 to 310°C at a heating rate of 20 K/min, followed by 310 K/min cooling. The samples were then reheated from 40 to 310°C at a heating rate of 20 K/min, held at 310°C for 10 to 30 min, and then cooled immediately to 40°C. They were then reheated at 20 K/min

to 310°C. The melting point reported here is the maximum peak temperature.

2.5. X-ray Diffraction

Wide-angle X-ray diffraction (WAXD) patterns were obtained with a Siemens, Model D500 diffractometer using copper target at 40 kV and 30 mA. The recorded diffraction patterns ranged from 10.0 to 35.0 (2 θ).

2.6. Rheology

Rheological measurements were carried out on an Instron capillary rheometer Model 3211. Samples were loaded in pellet form at 310°C. Approximately 10 min was required following loading for the system to reach thermal equilibrium. Capillary of diameter 0.762 mm (L/D=33.3) was employed to cover a shear rate of 30 to 4 $\times 10^3$ s⁻¹. The Rabinowitch correction was applied to all data and only the true shear rate is shown.

3. Results and Discussion

3.1. Scanning Electron Microscopy

The morphology of the Vectra/PPS blends was studied using scanning electron microscope (SEM). Fig. 1 shows micrographs of cryogenically-fractured cross-sections of extrudate of the blends with 0.9, 0.7, 0.5, 0.3, and 0.1 weight fractions Vectra (Fig. 1(a), (b), (c), (d) and (e), respectively). Similar morphology was observed for the Vectra/PPS blends prepared by mixer. Vectra appears to be a continuous phase up to 0.7 weight fraction Vectra.

At 0.1 weight fraction Vectra, the LCP exists as spherical inclusions of 6.5 μ m in average size in a continuous PPS phase. The inclusion size of the Vectra or PPS is not changed significantly in all the blend compositions with different annealing times (10 and 30 min) in DSC. There is no indication of adhesion between the Vectra fibrils and the PPS for the investigated compositional range. The poor adhesion between the Vectra and PPS was also observed by Ramanathan and co-workers [9].

3.2. Thermal Behavior

The experimental nematic transition temperature (T_m) of Vectra was found to be 280.4°C (cf. Table 1) as previously reported elsewhere [6]. The T_m of PPS was found to be 280.0°C which is close to the T_m of Vectra. Therefore the T_m s of the Vectra and PPS were not able to determine separately. Since the heat of fusion of PPS (34.7 J/g) was very large compared to that of Vectra (1.2 J/g), the T_m of the blends was considered as the mostly melting of the PPS. All blend compositions showed a single glass transition in the DSC which was the value between 93 and 98°C associated with the Vectra and PPS phase, respectively. The T_g s could not be detected separately since the two T_g s were so close. The T_g of pure PPS processed in the mixer at 310°C for 10 min was shown to 98.7°C, which is close to the T_g of the unprocessed PPS. Therefore it is said that the possibility of melt curing of PPS would be very low.

The effect of annealing on the PPS melting and crystallization temperature (T_c) for all the composition is shown in Fig. 2. The blend samples used in this study were prepared by screw extruder and mixer. No significant depression of T_m (PPS) and T_m (Vectra) is observed for all the blend compositions with different annealing time in DSC. In the blend of Vectra and PPS, Seppala and co-workers [11] reported the melting point of PPS in the range 283 to 285°C which is close to the T_m of pure PPS.

The T_m (PPS) of Vectra/PPS blend in the present study is somewhat comparative with the result of thermal behavior of Vectra/PET blend which has been reported earlier [6] and shown in Fig. 3. For the Vectra/PPS blend, there is no interaction between chains in the nematic and isotropic phases since complete phase separation is observed from the micrographs (see Fig. 1). Therefore it is possible that the crystalline part of the PPS is not affected by Vectra and the T_m of the PPS is not changed appreciably even though there is some gas evolution from Vectra at high temperature. For the Vectra/PET blend [6], the

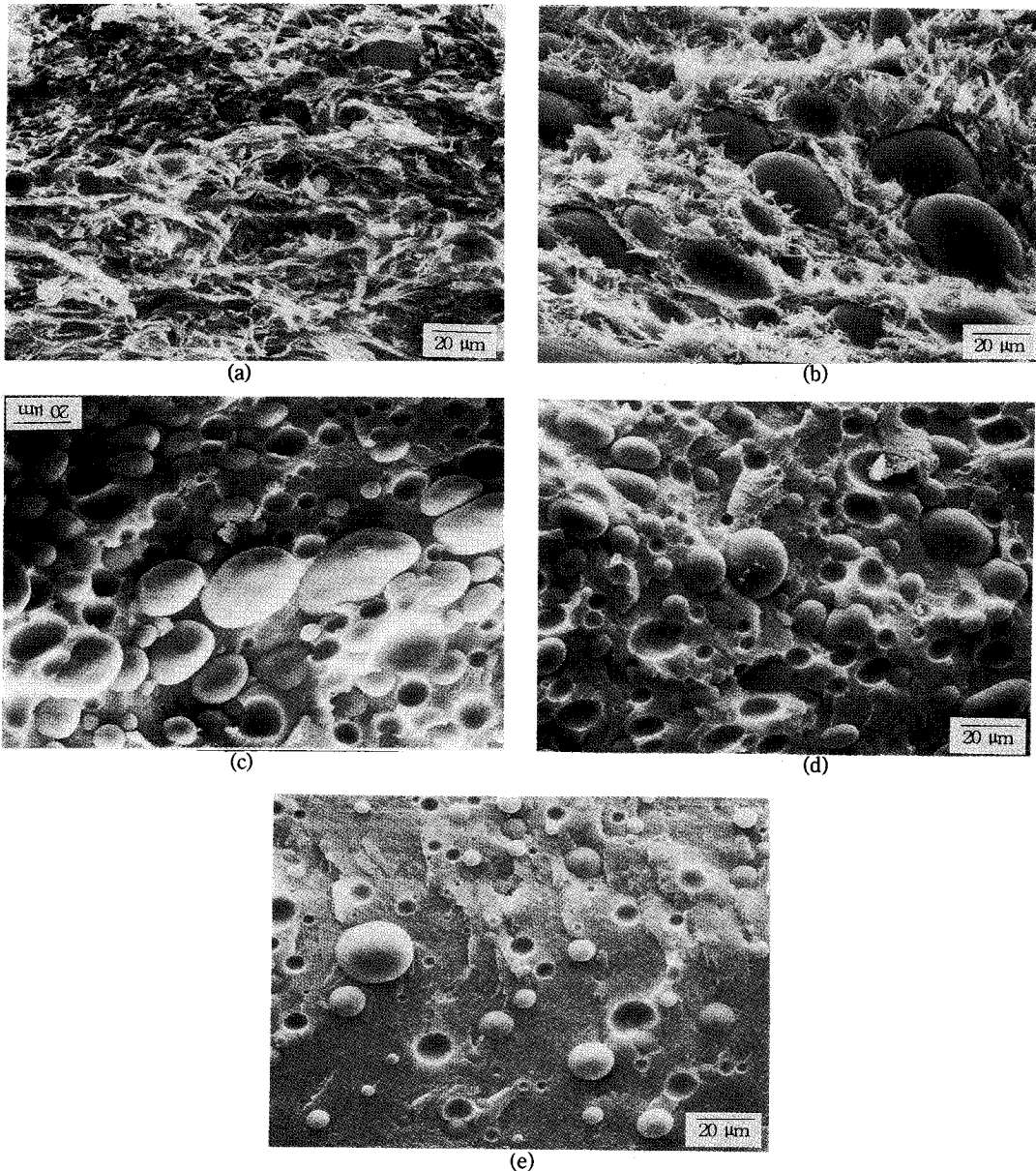


Fig. 1. Scanning electron micrographs of cryogenically-fractured cross-sectional surfaces of Vectra/PPS blends: (a) 9/1; (b) 7/3; (c) 5/5; (d) 3/7; (e) 1/9.

depressions of $T_m(\text{PET})$ and $T_c(\text{PET})$ were observed for Vectra-rich compositions. The melting point depression in the PET was considered to be the result of dissolved low molecular weight species associated with the gas evolution from Vectra at high temperature, and this resulted in changes of crystal perfection of the PET [13, 14].

There are at least two processes that can cause Vectra and PET to mix microscopically in the annealed blends. Some interdiffusion might occur despite the unfavorable thermodynamics, since Vectra is not perfectly rigid. Transesterification, a chemical reaction between polyesters, is also a possibility [15].

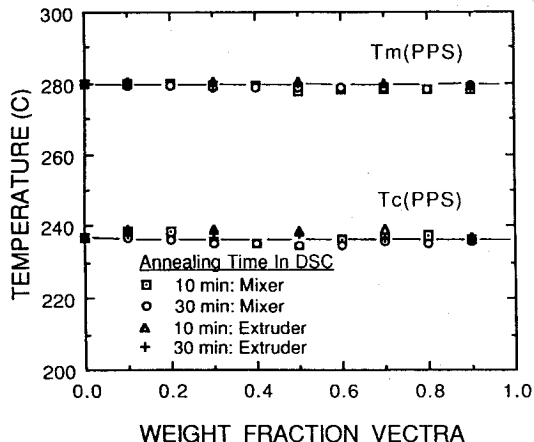


Fig. 2. Effect of annealing time in the DSC at 310°C on the melting peak and crystallization temperature of PPS. Samples were prepared by screw extruder and mixer.

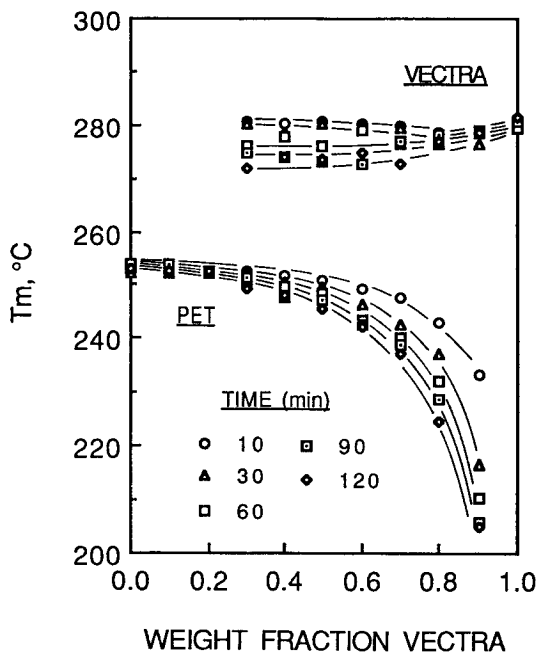


Fig. 3. Effect of blend composition and annealing time at 310°C on the melting points of PET and Vectra for Vectra/PET blends [6].

In Fig. 4 is shown the effect of annealing on the WAXD pattern for compression molded sample of 0.9 weight fraction of Vectra in blend at 310°C for 10 min. For Vectra which is shown in

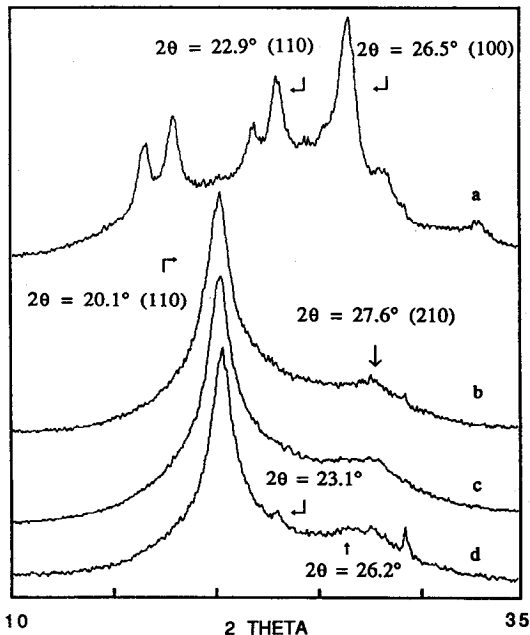


Fig. 4. Effect of annealing on the WAXD profile of 9/1 Vectra/PET blends: (a) PET; (b) Vectra; (c) compression molded of the blend at 310°C for 10 min; (d) annealed of the sample (c) at 200°C for 1 hr in DSC.

Fig. 4(b) we can see the two distinct reflections at $d = 4.42 \text{ \AA}$ ($2\theta = 20.1^\circ$) and at $d = 3.23 \text{ \AA}$ ($2\theta = 27.6^\circ$) which can be assigned to the (110) and (211)/(210) directions, respectively, as reported by Kaito *et al.* [16]. For PET which is shown in Fig. 4 (a) an improved crystalline orders are observed which is appeared to similar PET WAXD pattern by Roland [17]. Some reflections at $d = 4.93 \text{ \AA}$ ($2\theta = 18.1^\circ$), $d = 3.87 \text{ \AA}$ ($2\theta = 22.9^\circ$), and $d = 3.36 \text{ \AA}$ ($2\theta = 26.5^\circ$) can be assigned to the (010), (110), and (100) directions, respectively. For the 0.9 weight fraction of Vectra in blend which is shown in Fig. 4(c) no indication of PET peak is observed. After annealing the sample of Fig. 4(c) at 200°C for 1 h in DSC two additional reflections at $2\theta = 23.1^\circ$ and $2\theta = 26.2^\circ$ are observed in Fig. 4(d), which are believed from PET, although the peak intensities are low. These two additional peaks are mainly due to the annealing sample in DSC as a consequence of changes of crystalline structure of the PET.

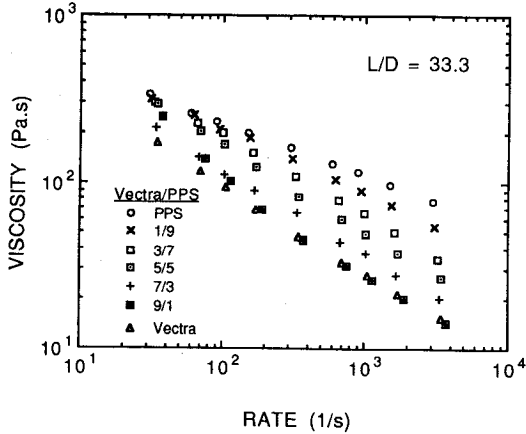
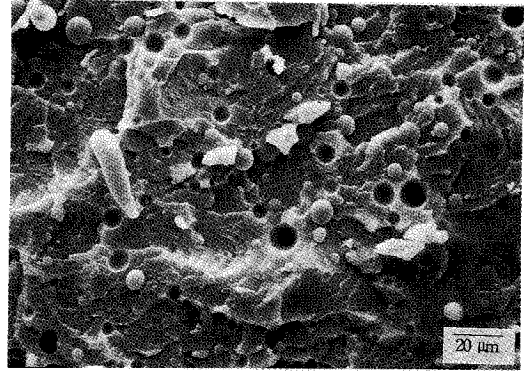


Fig. 5. Capillary viscosity data for Vectra/PPS blends: $L/D=33.3$, 310°C .

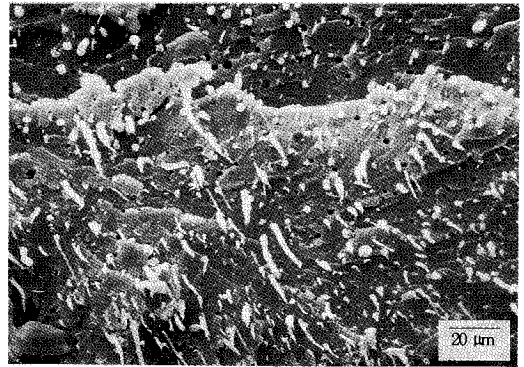
3.3. Rheology

Fig. 5 shows the capillary measurements of the viscosity of Vectra/PPS blends when the L/D is 33.3. Data for all the blend compositions show shear thinning behavior over approximately three decades of shear rate. For the Vectra, the value of viscosity is in good agreement with that of reported by Kalika and co-workers [18] and Nuel and Denn [19]. For the blends a significant drop in viscosity is observed at 0.1 and 0.3 weight fractions Vectra in the shear rate above 10^3 s^{-1} . At the shear rate about $3 \times 10^3 \text{ s}^{-1}$ the viscosity of the 0.1 and 0.3 weight fractions Vectra is about 70 and 45 percent of that of the pure PPS, respectively.

The decrease in viscosity is mainly due to the fibrous structure of the Vectra which is shown in Fig. 6(b). Fig. 6(a) and 6(b) show the micrographs of the 1/9 Vectra/PPS blend extruded from the capillary rheometer when L/D is 33.3 and the shear rate is 32 s^{-1} and $3,200 \text{ s}^{-1}$, respectively. When the shear rate is low, the fibrous structure is not observed [Fig. 6(a)]. The diameter of these fibrils shown in Fig. 6(b) is observed to be 1 to $3 \mu\text{m}$. This fibrous structure of the LCP may act as a reinforcement for the matrix such that for 0.2 and 0.3 weight fractions Vectra in Vectra/PPS blends (Heino and Seppala, [10]), mechanical properties such as tensile strength and elastic modulus were increased 2.0- and 2.6-fold, respectively.



(a)



(b)

Fig. 6. Scanning electron micrographs of cryogenically-fractured cross-sectional surfaces of 1/9 Vectra/PPS blends extruder from capillary rheometer: (a) $\dot{\gamma}=32 \text{ s}^{-1}$; (b) $\dot{\gamma}=3,200 \text{ s}^{-1}$, $L/D=33.3$.

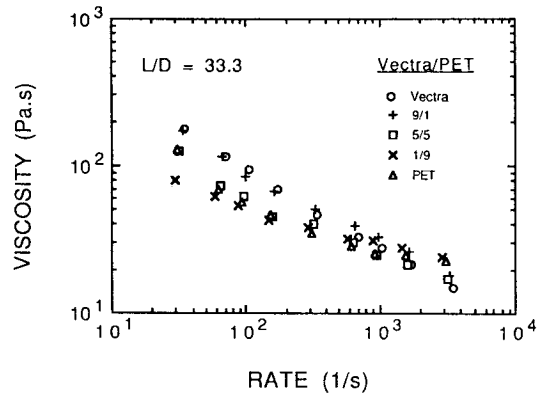


Fig. 7. Capillary viscosity data for Vectra/PET blends: $L/D=33.3$, 310°C .

The low shear rate rheology and the effect of capillary L/D ratio on the morphology is under in-

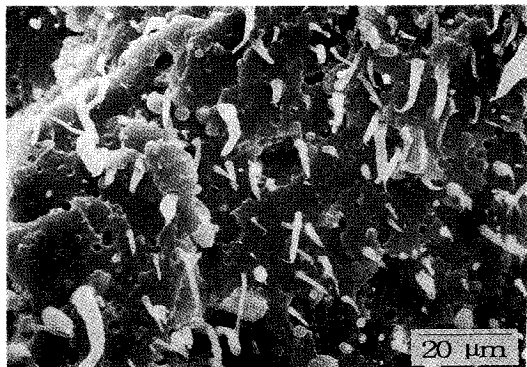


Fig. 8. Scanning electron micrograph of cryogenically-fractured cross-sectional surfaces of 1/9 Vectra/PET blends extruded from capillary rheometer: $\dot{\gamma}=3,200 \text{ s}^{-1}$, $L/D=33.3$.

vestigation in our laboratory [20].

In Fig. 7 shows the viscosity of Vectra/PET blends when the L/D is 33.3. For the Vectra/PET blends, the decrease in viscosity is not observed appreciably at the high shear rates. Fig. 8 shows the micrograph of the 1/9 Vectra/PET blend extruded from the capillary rheometer when L/D is 33.3 and the shear rate is $3,200 \text{ s}^{-1}$. The viscosity behavior shown in Fig. 7 is due to the less fibrous structure shown in Fig. 8. This may be due to the viscosity ratio of Vectra to PET, which is about 0.68 for Vectra/PET blend and 0.19 for Vectra/PPS blend at $3 \times 10^3 \text{ s}^{-1}$.

For the blend of 0.3 weight fraction LCP in p-hydroxybenzoic acid/poly(ethylene terephthalate) (HBA/PET) and polycarbonate, Blizard and Baird [3] observed L/D dependent morphology; the fibrous structure of the LCP was no longer present for the L/D ratios greater than 21.4 at the shear rates 45.7 s^{-1} and 457 s^{-1} . For the blends of HBA/HNA copolyester with polycarbonate, poly(butylene terephthalate), and nylon-6, Beery and co-workers [21] observed the morphology-rheology relationships using capillary rheometer with $L/D=33$, and reported that fibrous structure took place when the viscosity of the matrix polymer (isotropic) is higher than that of the suspended LCP one.

In the present study, the viscosity ratio of Vectra to PPS is always less than one in the shear

rate ranges studied, however, fibrous structure is not always observed at low shear rate (32 s^{-1}). Comparing the above results with the present study, it should be considered the processing variables such as shear rate, viscosity ratio of LCP to isotropic phase, and L/D ratios of the capillary die in order to obtain fibrous structure of the LCP in the blend with flexible polymers.

4. Conclusions

Melting and crystallization data suggest that there is no interaction between chains in the nematic and isotropic phases since complete phase separation is observed between the two phases. Therefore the crystalline part of the PPS is not affected by Vectra and the T_m of the PPS is not changed appreciably even though there is some gas evolution from Vectra at high temperature.

In the Vectra/PPS blends, a significant depression of viscosity is obtained in the PPS-rich blends at the high shear rate. The decrease in viscosity is mainly due to the fibrous structure of the LCP. The decrease in viscosity of PPS-rich blends is consistent with the known "flow-modifier" property of thermotropic LCPs. For the Vectra/PET blends, the viscosity of the blends is not changed appreciably compare to the unblended polymers. The decrease in viscosity and the appearance of the fibrils of LCP in the blends are dependent on the viscosity ratio of LCP to isotropic phase and the shear rates.

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation under Contract No. 93-0300-02-01-3.

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