Uniaxial Elongational Viscosity of FEP/ a Small Amount of PTFE Blends

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Melt rheology of blends consisting of tetrafluoroethylene/hexafluoropropylene (Teflon® FEP) copolymer and a small amount of polytetrafluoroethylene (Teflon® PTFE) has been studied under shear and uniaxial elongational deformations. The blends were prepared in a twin-screw kneader at 320°C. Compatibility of the components was investigated by DSC measurements, resulting in two separated peaks for the blends, which suggested FEP and PTFE were mixed in immiscible state. Structural observations were performed with optical microscope and SEM. It was clearly observed that PTFE uniaxially elongated like fibril by kneading with FEP, and dispersed relatively uniformly in FEP. Storage modulus $G'$ and complex viscosity $\eta^*$ toward lower frequency region became larger by increasing a loading of PTFE in dynamic shear measurements. The blends showed the strain-hardening property in uniaxial elongational measurements, whose tendency became stronger by increasing a loading of PTFE, though FEP hardly showed strain-hardening property. The results would be explained by the idea that dispersed PTFE fibril deformed during an elongational deformation and then generated a contractile stress, which would be resulted from that long length of dispersed PTFE and a strong adhesive interaction of interfaces between PTFE and FEP.

Key Words: PTFE / FEP / Uniaxial elongational viscosity / Strain-hardening / Melt rheology

1. INTRODUCTION

Tetrafluoroethylene (TFE) / hexafluoropropylene (HFP) copolymer has been known as Teflon® FEP copolymer and has outstanding characteristics in chemical resistance, heat resistance, electrical properties, low flammability, and excellent weatherability. Their typical applications include electric wire cable coating, foaming and tube extrusion, blow molding, and injection molding.1-2) Despite wide applications, very few reports have been published on melt rheological property. Wu3) reported dynamic melt shear rheology and calculated molecular weight distributions, compared with that from the end group analysis. Tuminello5) also calculated the molecular weight distributions with a new method by measuring dynamic shear rheology. Rosenbaum et al.5) studied the influence of pre-thermal history on dynamic shear melt rheology of commercial FEP and dynamic shear rheology of amorphous FEP copolymer. Moreover, Rosenbaum et al.6) published melt fracture behavior and shear rheological property of FEP under high shear rate in capillary rheometer.

The process of electric wire cable coating, foaming, and blow molding, which are very important applications for FEP, includes melt elongational deformation. To our knowledge, however, only one report has been published in the field of uniaxial elongational viscosity of FEP.7) The controlling of elongational viscosity, i.e., strain-hardening or softening property, is essential for improving melt processability. We have studied uniaxial elongational viscosity of FEP (MFR: 6.8g/10 min) to clarify the influence of existing small amount of crystal on uniaxial elongational viscosity near the crystal-melting transition. We have great interest in controlling the rheological properties from both academic and industrial points. It is, however, difficult to make branch or to blend with hydrocarbon polymer due to its chemical structure and their degradation temperature.

Murata et al.8) reported the generation of fibrillated PTFE by kneaded with PP under molten state up to 250°C. They studied the melt tension property which was measured at room temperature by taking up the polymer extruded form capillary die. The melt tension of PP having the fibrillated PTFE was enhanced, as kneading temperature became higher, which was resulted from that fibrillated PTFE became thinner and dispersed more homogeneously in PP matrix by increasing the kneaded temperature. However, no elongational viscosity data appeared. In the present study, we tried to blend FEP and a

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small amount of PTFE, which enable to knead at higher
temperature compared with blend of PP matrix, then
performed the uniaxial elongational viscosity measurements in
an elongational rheometer. The aim of the present study is an
investigation about the influence of a small amount of PTFE
on the uniaxial elongational viscosity of FEP.

2. EXPERIMENTAL

2.1 Sample
The polymer tested here was a commercially available
tetrafluoroethylene (TFE) / hexafluoropropylene (HFP)
random copolymer (Teflon® FEP 100 copolymer, TFE: HFP =
91: 9 (mol%) MFR=6.8 (g/10min, at 372°C under 5 Kg)) and
poly(tetrafluoroethylene)(Teflon® PTFE 7J), which is called a
molding powder, of which the average particle seize was
50 µm. The samples were kindly supplied by Dupont-Mitsui
Fluorochemicals Co., Ltd. The samples were used as received.

2.2 Sample Blend
FEP and PTFE were mixed in various proportions, 100/0,
99/1, 98/2, and 96/4 (weight ratio), under molten state. Firstly,
neat FEP was molten in the batch twin-screw kneader
(Toyoseiki Co., Ltd., Labo Plastomill) with slow rotating (below
5 rpm) at 320°C for 5 minutes. Then, PTFE powder was added
to molten FEP inch by inch. Finally, the mixture was kneaded
intimately (72 rpm) for 10 minutes. The blended samples and
the experiments performed in this study were listed in Table I.

2.3 Thermal Properties
Thermal analysis (non-isothermal) for neat FEP, FEP/PTFE
98/2, 96/4, and neat PTFE was performed by a differential
scanning calorimeter (TA instruments Co., Ltd., DSC 2920).
Measurements were performed with 10±1.0 mg samples in
nitrogen atmosphere from 150°C to 380°C at the heating rate
of 10°C/min and kept at 380°C for 5min, cooled to 150°C at the
cooling rate of 5°C/min, and then reheated to 380°C at 10°C/
min. The reproducible data of the DSC measurements were
obtained.

Table I  The blended samples and the experiments performed in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DSC</th>
<th>Optical Microscope</th>
<th>SEM</th>
<th>Rheological measurements</th>
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2.4 Optical Microscope Observation
Microstructures of samples for neat FEP and FEP/PTFE 98/2
blend were observed with an optical microscope at room
temperature. Sample was hot-pressed to make a thin film by
sandwiching them between polyimide films. Firstly, sample
was molten at 320°C for 5 minutes, then pressed under 8MPa
for 3 minutes, finally rapidly cooled. Thickness of the film was
about 40 µm, which was observed between two sheets of cover
glasses. When observation was performed, film was drenched
with refined water to prevent a reflection of light at interface
between a film and cover glasses. Pictures of microstructure
were taken with a digital camera.

2.5 Scanning Electron Microscopy (SEM) Observation
SEM observation was performed with a SEM (JEOL Co.,
Ltd., JSM-5310). Fracture cross-section of neat FEP and FEP/PTFE
98/2 blend was observed. The sample was fractured
with using an edged tool after immersed for 15 or 30 minutes
in liquid nitrogen. The difference of fracture cross-section
between immerging time for 15 and 30 minutes was not
observed. A membrane of gold was coated in the thickness of
about 200 Å using an ion spattering apparatus to eliminate
charging in electron beam. Pictures of microstructure were
taken with a Polaroid camera.
2.6 Sample Preparation of Rheological Measurements

Neat FEP and blend samples were molded to make the test samples for rheological measurements by hot pressing (Toyoseiki Co., Ltd., Mini Test Press 10). Since the blend samples were molded at 320°C and 340°C, which deformed by themselves ununiformly during melting before measurements, uniaxial elongational measurements were impossible to conduct. Therefore, all the samples were molded as follows. Firstly, the sample was molten at 360°C for 10 minutes, then pressed under 10 MPa for 5 minutes and slow cooling to room temperature. Residual internal stress of the molded sample, which would be caused by PTFE, was removed by molding at 360°C well above melting temperature of PTFE. Figure 1 illustrates the sample preparations. The sample shape for dynamic shear measurements was 25 mm diameter disk in thickness of 1mm, and that for uniaxial elongational measurements was square bar (1.5×7.0×55 mm).

2.7 Rheological Measurements

Dynamic shear measurements over the frequency range from 0.01 to 100 (rad/s) were carried out by means of a 25mm parallel-plate rheometer (Rheometrics Co., Ltd., ARES) at 300°C under nitrogen atmosphere. Gap was set to approximately 0.95mm. Depending on frequency, great care was taken for determining strain to keep the linear viscoelastic region. Data were reproducible within 5%. Uniaxial elongational measurements under constant strain rates (0.1−1.0s⁻¹) were performed using a uniaxial elongational rheometer (Rheometrics Co., Ltd., RME) at 300°C under nitrogen atmosphere. Actual temperature was within the deviation of 0.5°C from a setting temperature. Reproducible data within 10% were obtained and a deformation of sample was uniform. Actual strain rate was estimated by checking a width variation of the sample using a CCD camera.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties

Figure 2 shows melting curves corresponding to FEP/PTFE 98/2 and 96/4 blends, together with that of neat FEP and PTFE. Since there were hardly the differences in the melt behavior from the first to second runs except for PTFE, we showed here only the second heating run. It is just noted that the melting peak of the first run for PTFE was observed at 348°C which was higher than that of the second run for PTFE (331°C). Two separated melting peaks were observed for blend samples. The lower melting peak corresponds with the melting temperature of neat FEP. The higher one corresponds with that of PTFE. Heat of fusion corresponding to PTFE in blend sample gained by increasing a load of PTFE. The only effect that may be detected is a decrease of the melting temperature of FEP in the blend (253°C) with respect to that of neat FEP (262°C). A little bit increase of the melting temperature corresponding to PTFE in blend samples was observed (333°C) compared with that of neat PTFE (332°C).

Figure 3 shows a crystallization behavior of the same sample above. Two separated crystallization peaks were also observed at the same crystallization temperature of neat FEP and PTFE, respectively. A crystallization temperature of the blend samples corresponding with FEP was increased, which would be considered as nucleation effect of PTFE on crystallization of FEP. Temperature for the onset point of crystallization was around 250°C in neat FEP, but around 260°C for blend sample. Our results showed two separated melting and crystallization peaks, which were in agreement with results of Pucciariello and Angioletti⁹ concerning blends of PTFE and FEP including hexafluoropropylene (HFP) comonomer content of 1 mol%. Their blend samples were
prepared through physically and intimately mixing of powders, then taking them to melt at 400°C, holding them at this temperature for 1 min, then cooling them to room temperature. They suggested that absence of cocrystallization in blends between PTFE and FEP may be justified when considering the extremely high melt viscosity of PTFE, which would prevent mixing with other component. The thermal behavior of the present blend samples also showed no cocrystallization. FEP and PTFE were in immiscible state during rheological measurements at 300°C.

3.2 Structural Observation by Optical Microscope
To clear morphology of blend samples, the direct observations of neat FEP and blend sample for FEP/PTFE 98/2 were performed with an optical microscope. The obvious difference between the samples was observed. Figure 4 shows the microstructure of FEP/PTFE 98/2 blend. Though a plain structure was seen in neat FEP sample, fibrous structures less than 1μm in width were seen in the blend sample, which has some branch-like structure and dispersed widely all over the field of view. The aspect ratio of fibrous structure was more than 40. The fibrous structures would be PTFE which formed during kneading with FEP, because the process that PTFE stretched in a kneader was clearly observed during addition of PTFE to molten FEP.

3.3 Structural Observation by Scanning Electron Microscopy (SEM)
Figure 5(a) and (b) show SEM photomicrograph of fracture cross-sections of neat FEP and FEP/PTFE 98/2 blend. In Fig.5(a), the dimple patterns were seen on the fracture surface. This fracture surface was similar to that of PE.10) Figure 5(b) has quite different dimple pattern which was extremely smaller than that of neat FEP and with highly deformed fibrils, which could be caused by a plastic deformation due to presence of PTFE fibril. The long fibrils less than 1μm in diameter were obviously stuck out of the fracture surface, which would be the extended PTFE in term of a diameter and length of the fibrils. From the above observation with optical microscope and SEM, it would be safe to state that PTFE deformed by kneading with FEP and became fine fibrils, which were dispersed relatively uniformly all over the FEP.

Murata et al.8) reported that PTFE became fibrils by kneading with PP up to 250°C, which were about 5μm in diameter. This difference of a diameter for PTFE compared with our present results would be caused by a different kneading temperature (320°C) or a different interfacial property between PTFE and matrix polymer (PP or FEP). The interaction of interfaces between PTFE and FEP would be relatively strong compared with that between PTFE and hydrocarbon polymers.9)

3.4 Oscillatory Shear Measurements
Oscillatory shear experiments of samples for FEP/PTFE 99/1 and 98/2 blends at a linear strain region were performed at 300°C, together with neat FEP. Figure 6(a) and (b) showed that storage modulus $G'$ and loss modulus $G''$, complex viscosity $\eta^*$ as a function of frequency. Figure 6(a) suggested that the height of $G'$ toward lower frequency region became larger by increasing a loading of PTFE, but $G''$ were similar to among samples. Figure 6(b) showed that $\eta^*$ toward lower frequency region increased by increasing a loading of PTFE. It was considered that blend samples had the long relaxation time components, which were induced by the addition of PTFE.
These tendencies have been reported in particle and fiber dispersed polymer composite and immiscible polymer blend systems.  

3.5 Uniaxial Elongational Viscosity Measurements

Figure 7 shows uniaxial elongational viscosity of FEP/PTFE 99/1 and 98/2 blends, together with that of neat FEP at 300°C. A solid line represents a strain rate independent linear viscoelastic envelope predicted from dynamic shear complex viscosity in Fig.6(b). The predicted curves almost fitted with experimental elongational viscosity. Commonly, the elongational viscosity gradually increases with time at small strain region and goes abruptly above a linear viscoelastic envelope, which was called a strain-hardening property. Though neat FEP hardly showed the strain-hardening property in the measurement range, the blend samples showed the strain-hardening property. The tendency of strain-hardening property became larger by increasing a loading of PTFE and strain rate dependence on strain-hardening was relatively small over strain rates performed in this study. In the case of homopolymer melts, degree of strain-hardening is usually decreased, as the strain rate becomes lower.

Murata et al. found an increase of melt strength for PP including a small amount of PTFE up to 3 wt% which hardly changed crystallization temperature even if a load of PTFE was increased. Therefore, they supposed that the increase of melt strength would be resulted from occurring of strain-hardening during extensional deformation of sample. But no experimental data of evidence appeared. In this study, we really performed uniaxial elongational viscosity measurements, it was clarified that strain-hardening property was occurred by the addition of PTFE.

Generally, it has been observed that the strain-hardening property became smaller in molten polymer composites system including hard particles or fibers and in molten immiscible polymer blend system compared with those of matrix polymers. It has been reported that the addition of hard particles inhibited the strain-hardening property and a strain-softening property, which means the elongational viscosity goes below a linear viscoelastic envelope, was observed in fiber filled polymer system.

In molten polymer blend system, Takahashi et al. investigated that the effect of miscibility on elongational viscosity of polymer blends in homogeneous, miscible, and immiscible states by the blends of 1.5wt% of ultra-high-molecular-weight (UHMW) polymer. It was demonstrated that 1.5wt% of UHMW induced strong strain-hardening property in the homogeneous and miscible blends, but was hardly changed in the immiscible blend. The optical microscope observation on the immiscible blend suggested that the UHMW domains were stretched, but that the degree of domain deformation was less than a given elongational strain. Moreover, uniaxial elongational viscosity of acrylonitrile-butadiene-styrene (ABS) polymer melts containing soft and...
hard butadiene particle has been investigated. At a butadiene content of 20wt%, harder butadiene particles made the strain-hardening property weaker. The addition of the soft butadiene particles never enhanced strain-hardening properties of the matrix polymer, though observation by transmission electron microscopy showed that the soft butadiene particles were largely stretched along the elongational direction.

In the present blend samples, it was obvious that PTFE were dispersed as immiscible fibrils domain, and were solid state at the measuring temperature 300°C, which was supported by DSC measurements and structural observations. Therefore, the reason why the strain-hardening property was observed in the present blends system would be interpreted from a fibrillating property of PTFE. The dispersed fibrillating PTFE would be deformed together with FEP matrix in spite of solid state of PTFE during an elongational measurement due to the long fibril of PTFE more than 40 in aspect ratio (see Fig.4) and a strong adhesive interaction on interfaces between PTFE and FEP. Consequently, the extension of dispersed PTFE during an elongational measurement would generate a contractile stress to increase the elongational viscosity of the sample.

4. CONCLUSIONS

Uniaxial elongational and dynamic shear viscosity properties of FEP/PTFE 99/1 and 98/2 blend samples were characterized, together with neat FEP. Compatibility of sample was investigated by using a DSC, which suggested that FEP and PTFE blend were mixed in immiscible state. Structural observations were performed with optical microscope and SEM, which showed PTFE were elongated like a fibril, of which the diameter was less than 1µm and the aspect ratio was more than 40. In dynamic shear measurement, $G'$ and $\eta^*$ toward lower frequency region became larger by increasing a loading of PTFE. Uniaxial elongational viscosity of blend samples showed the strain-hardening properties, whose tendency became stronger by increasing a load of PTFE. The unusual strain-hardening property, in spite of the immiscible polymer blend system, was explained by the idea that the dispersed PTFE would generate a contractile stress during an elongational deformation.

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REFERENCES