

Strain hardening behavior of linear polymer melts

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Abstract

Linear high-density polyethylene (PE) was controlled to induce strain-hardening behavior by introducing a small amount of second component with an anisotropic structure. In order to form an anisotropic structure in the PE matrix, the polymer was extruded through a twin-screw extruder, and the structure was controlled by varying the extrusion conditions. Depending on conditions, the second component formed a film, thread and droplet structure. If the second component was kept rigid, the morphology evolution could be delayed and the second component could maintain its film or thread structure without further relaxation. In particular, the second component of the thread structure made a physical network and gave rise to remarkable strain hardening behavior under high extension. This study suggests a new method that induces strain hardening behavior by introducing a physically networked second component into the linear polymer melt. This result is anticipated to improve the processibility of linear polymers especially when extensional flow is dominant, and to contribute to our understanding of strain hardening behavior.

Keywords : rheology, polymer blend, strain hardening, thread, anisotropic structure

1. Introduction

The strain hardening behavior is of great importance in the processing of polymer melts involving a significant component of extensional deformation such as fiber spinning, blow molding, and thermoforming processes (Petrie, 1979). As the strain hardening behavior manifests a strong resistance against fast stretching of polymer melt, the polymer processing becomes easier to control if the polymer melt shows strain hardening behavior and the product can be produced in good quality. In the late 1970s and 1980s, many researchers have attempted to induce strain hardening behavior in linear polyethylene in order to extend its applications. There are many studies on the mechanism of strain hardening behavior on polyethylene with both linear and branch structure through phenomenological observations and it is now well understood that the strain hardening behavior is due to its branch structure. However, these studies did not detail the correlation between the branch structure and the strain hardening behavior (Petrie, 1979; Munstedt and Laun, 1981; Minoshima and White, 1986; Linster and Meissner, 1986).

The long chain branching by chemical or physical modification has been introduced through various technologies such as the development of new catalysts, applying a cross-linking agent, electron beam irradiation, etc (Munstedt,

1980; Hingmann and Marczinke, 1994; Kurzbeck *et al.*, 1999; Yan *et al.*, 1999). It was expected that these techniques result in a few ultra high molecular weight (UHMW) chains or long chain branches in the polymer backbone. The existence of a few UHMW chains or long chain branches in a linear polymer was found to lead the pronounced strain hardening behavior. Recently, it was also reported that the dependence of strain hardening behavior on strain rate is also different depending on diverse branching structures (Gabriel and Munstedt, 2003; Wagner *et al.*, 2000). Theoretically, it was explained that under extensional deformation the strain hardening behavior is caused by the restricted stretching of the backbone of the polymer between the branch points connecting to the side branches (Inkson *et al.*, 1999). Based on these previous studies, it is known that the strain hardening behavior can be induced by a minimal amount of the material with a strong resistance against stretching. In addition, as the particle of fiber structure in the suspension increases the extensional viscosity (Mewis and Metzner, 1974), it may well be expected that the strain hardening behavior can be induced in the polymer melt if it is filled with a small amount of the second component with an anisotropic structure.

In this study, an attempt was made to induce strain hardening behavior with a linear polymer by the addition of the second component, which has rarely been tried in immiscible polymer blends (Dumoulin *et al.*, 1984). The second component in the polymer melts acts as a strong backbone

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to resist against extensional flow. In order to induce this particular behavior, special procedures are necessary to embed the second component with a particular microstructure in the matrix. The addition of the second component was performed using a twin-screw extruder.

2. Experimental

2.1. Experimental strategy

Twin-screw extrusion is generally used for blending with an aim of breaking up the dispersed phase and distributing it well into the matrix with the desired size and shape. The extrusion temperatures are normally set at a suitably higher temperature than the melting temperature of the constituent polymers. It is well known that the initial mechanism of the morphology development involves the formation of sheet or ribbon structure of the dispersed phase (Sundararaj and Macosko, 1992; Scott and Macosko, 1995). However, an anisotropic morphology such as sheet or ribbon in the molten state is unstable and quickly changes into thermodynamically stable droplets due to shear force and interfacial tension. Therefore, it is difficult to maintain the anisotropic morphology in the matrix during the mixing process (Champagne *et al.*, 1996). Based on this understanding on the morphology evolution, this study attempts to maintain the anisotropic morphology by controlling the extrusion process. For this purpose, two polymers (PE and PBT) having a large difference in melting temperature were selected (see Table 1). The second component, PBT, could be maintained in an elastic solid state over specific

extrusion conditions, and further deformation into droplets by retraction and relaxation could be retarded or delayed. The extrusion conditions then could be designed to produce polymers embedded with an anisotropic second component by controlling the thermal and deformation history through a second run at different processing conditions. In the first run, minimal energy was supplied to induce deformation of the rigid PBT but also to prevent further morphology development into droplet structures. The deformed blend was then subjected to a second extrusion at different conditions (see Table 2).

2.2. Materials

The PE (Mw; 151 K) used in this study was supplied by Honam Petrochemical Corp. The PBT (Mw; 53 K) was purchased from Sigma-Aldrich Co. The melting temperature and complex viscosity of the homopolymers are listed in Table 1. Fig. 1 shows the complex viscosity of PBT at four temperatures. The phase transition of PBT is evident from the rheological behavior. PBT shows a solid-like behavior until 225°C, and there is a considerable reduction in the modulus below 227°C, after which it shows a liquid-like behavior. Prior to extrusion, it was dried under vacuum at 80°C for at least 12 hours in order to remove moisture. This study did not use any chemicals to modify the interface between the polymers.

2.3. Extrusion

1 wt% or 5 wt% of PBT was embedded in the PE matrix using a counter-rotating conical twin screw extruder (L/D = 16, D = 4/3 inch, Haake). The extruder barrel is divided into 3 zones that are heated individually. They consist of solid conveying, melting, and metering zones. The processing conditions are listed in Table 2. The polymers were fed into an extruder after dry mixing. The measured melt temperature under condition 1 (170/190/220/210°C) was 210°C at the die (set temp. = 210°C). As the screw rotor speed was maintained at a low level of 25 rpm and the matrix viscosity was not high, there is no significant effect of viscous dissipation. All the extrudates were solidified in air without drawing.

2.4. Measurement of rheological properties

A Rheometrics Mechanical Spectrometer (RMS800, Rheometric Scientific) with a parallel plate fixture of 25mm diameter was used to perform the small amplitude oscillatory shear measurements. The complex viscosity (η^* [Pa·s]), storage modulus (G' [Pa]), and loss modulus (G'' [Pa]) were measured as a function of the frequency (ω). A Meissner-type extensional rheometer (RME, Rheometric Scientific) was used to observe the extensional behavior of the materials. All the measurements were performed under a nitrogen environment in order to reduce any degradation occurring at high temperatures.

Table 1. Viscosity ratio and melting temperature

	Viscosity [kPas] (1[rad/sec], 225°C)	Viscosity [kPas] (1[rad/sec], 230°C)	Melting temperature (°C)
PBT	2,300	0.9	227
PE	4.6	4.5	126
Viscosity ratio	500	0.2	

Table 2. Processing conditions

Condition	First Run	Second Run	Rotor speed (rpm)
	Temperature ^{a)}	Temperature ^{a)}	
A	170/210/210/210	×	25
B	170/220/220/220	×	25
C	170/230/230/230	×	25
1	170/190/220/210	×	25
2	170/190/220/210	130/150/160/150	25
3	170/190/220/210	150/170/190/180	25
4	170/190/220/210	170/190/220/210	25

^{a)}Temperature profile at feeding, transition, metering and die zone, sequentially.

2.5. Morphology Observation

The blend morphology was examined using both scanning electron microscopy (SEM; JSM 840A, JEOL) and optical microscopy (OM; BX51, Olympus) coupled with a hot stage (Linkam CSS-450). OM was used to probe the morphology of the second component at high temperature with relatively low magnification. At 180°C, the PBT phase could easily be discriminated from the PE matrix because PBT is still in the solid state at this temperature. Through SEM, the two phases were also easily distinguished without extracting the dispersed phase because of the polar functional groups of PBT.

3. Results and discussion

In order to determine the optimum processing condition that maintains the anisotropic morphology, a preliminary test was first carried out by changing the extrusion temperature from 210°C (170/210/210/210°C, condition A) to 230°C (170/230/230/230°C, condition C). The morphology varied significantly in this temperature range because PBT shows a dramatic change of rheological properties near the melting temperature (227°C), as shown in Fig. 1. Above 227°C (condition C), the viscosity ratio ($\lambda_{PBT}/\lambda_{PE}$) became less than one (see Table 1). Therefore at this condition, the morphology developed into droplets with an average diameter of 2.2 μm in a short time. On the other hand, at 220°C (170/220/220/220°C, condition B), which is slightly below the melting temperature of PBT, the rigid PBT softened enough to be deformed by mechanical abrasion. The deformed PBT phase was dragged apart into irregularly shaped fragments of micron scale. However, it did not develop into a droplet structure because PBT was not suf-

ficiently viscous to be influenced by either the flow or interfacial tension at this condition ($\lambda_{PBT}/\lambda_{PE} \approx 500$). When PBT/PE was extruded at 210°C (condition A), the PBT pellets passed through the extruder without melting. PBT was too rigid to deform by mechanical force. From this preliminary investigation it was decided that the processing temperature should be 220°C in order to induce and maintain the deformed state of PBT at the rotor speed of 25 rpm.

In order to fix the anisotropic morphology, experiments were conducted at conditions 1–4 listed in Table 2. In the first run (condition 1), the temperature of the metering zone was set at 220°C (170/190/220/210°C) to delay the morphology development. Drag was a dominating factor for the morphology development in this condition because the temperature was lower than the melting temperature of PBT and a high pressure was applied in the metering zone. When the extrudate was processed twice, the extrusion temperature was set lower (conditions 2 and 3) to obtain a slower morphology evolution rate. In condition 4, the extrusion condition of the second run was kept the same as in the first.

Fig. 2 presents the micrographs of the extrudate under the condition 1. In this condition, the PBT pellet was dragged and stretched out into a film as shown in Fig. 2. The film structure that can be conventionally observed at an early stage of morphology development maintained its structure up to solidification because PBT was stiff at this condition. In this paper, the film structure was defined as a structure of approximately 10 μm in thickness and greater than 100 μm in width. It is meaningful that the anisotropic structure can be maintained during extrusion and be obtained as a final product by controlling the processing conditions. For conditions 2, 3 and 4, the extrudate produced under condition 1 was subjected to another extrusion in order to observe the subsequent stages of morphology development as more shear is applied.

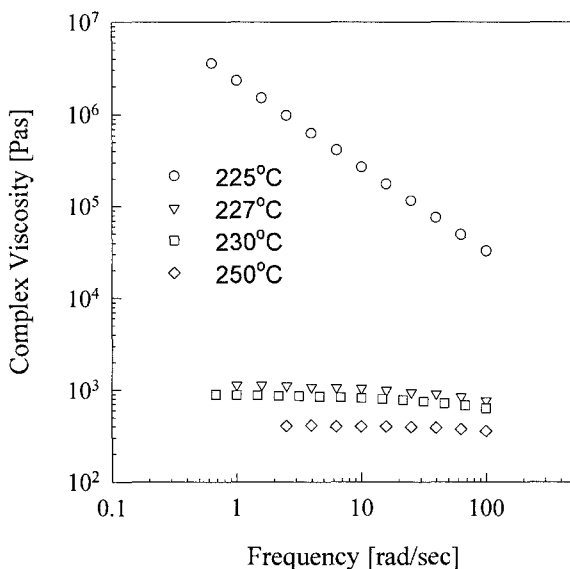


Fig. 1. Complex viscosity of PBT at four temperatures from 225 to 250°C.

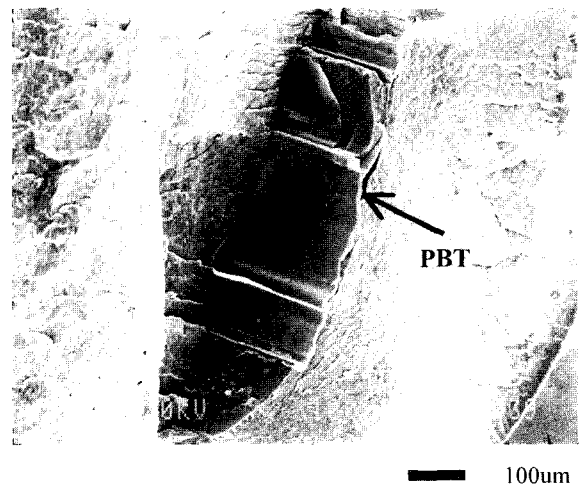


Fig. 2. SEM photograph of 1 wt% PBT/PE under condition 1.

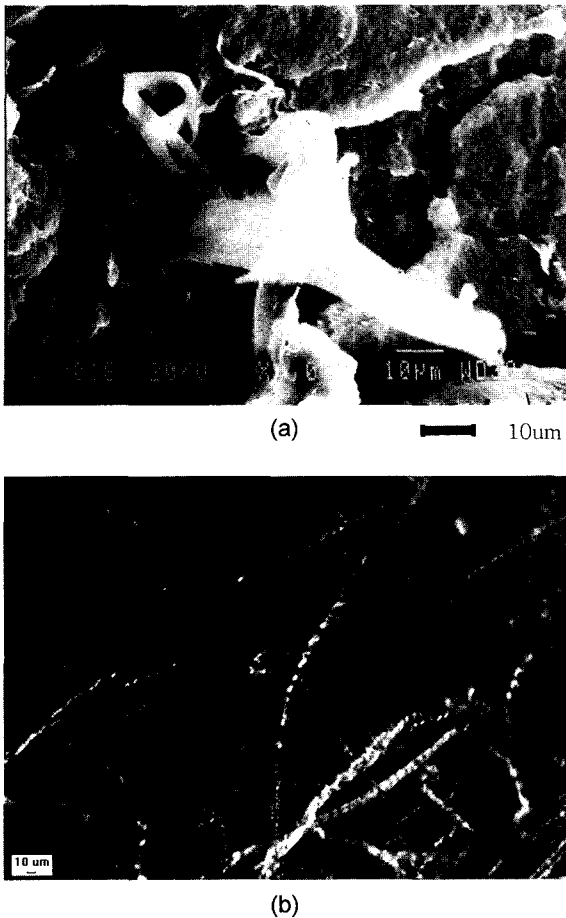


Fig. 3. SEM (a) and OM photographs (b) of 1 wt% PBT/PE under condition 2.

In condition 2, the morphology evolution from the film structure was mainly caused by drag because the temperature for the second run was set at much lower than 220°C. During the second run, many holes in the film were formed by drag and they broke up into a bundle of threads by a mechanical force. Fig. 3(a) shows the trace that the film structure turns into a bundle of threads. In addition, it disintegrated into many threads as shown in Fig. 3(b). In condition 3, the morphology was the same as in condition 2 because PBT was still rigid, even though the temperature was slightly increased to 190°C. When the extrudate under condition 1 was extruded again at the same condition (condition 4), the film structure formed during the first run broke up into many small spherical droplets. From these observations, it is possible to maintain anisotropy such as film or thread structure embedded in the final product if the second component is rigid enough to avoid the relaxation process. From the above strategy, the second component of the film, thread or droplet structure can be embedded in a linear polymer depending on the thermal and deformation history.

Fig. 4 shows the transient extensional viscosity of PE and

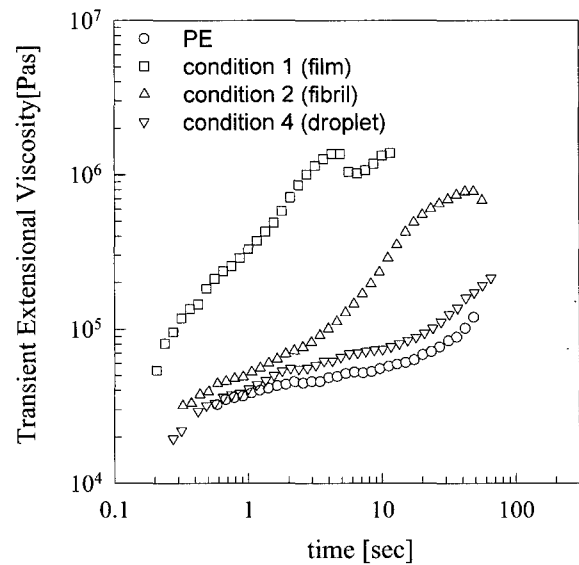


Fig. 4. Transient extensional viscosity of PE and PE with 1 wt% PBT of diverse structure at 150°C. The strain rate is 0.05[1/sec].

the PE with an anisotropic second component. It was measured at a rate of 0.05[1/sec] and at temperature 150°C. Under these conditions, the anisotropic PBT phase remains as a solid. In the case of PE embedded with PBT film, the viscosity increases linearly with extension as a result of the solid-like contribution of PBT. However, the PE embedded with PBT film fails much earlier than the PE embedded with other structures. The film structure does not seem to be effective because the stress concentrated at PBT with relatively large length scale gives heterogeneous extensional deformation. In the case of thread structure, the size is reduced into micrometer scale while still maintains anisotropy. The PE with a thread structure still shows a significant strain hardening behavior. Since PBT threads entangle and make many physical networks, they induce significant resistance against extension, leading to the enhancement of the extensional properties without losing ductility. Another point of interest is that the amount of the second component is quite small; only 1 wt%. The thread structure, though distinct in SEM photographs, does not cause a defect in the sense that the blend does not lose its transparency. As the composition is increased above 1 wt%, the turbidity of PE increases as is usually observed for immiscible polymer blends. It should be noted that this embedding method can induce a strain hardening behavior with only a small amount of second component.

Fig. 5 shows the complex viscosity of the PE embedded with PBT having both droplet and film structures at 150°C. This graph also compares the PE with 1 wt% and 5 wt% PBT. There is no increase in the complex viscosity compared to PE homopolymer when 1 wt% PBT is added for either film or droplet structure. Different from the uniaxial

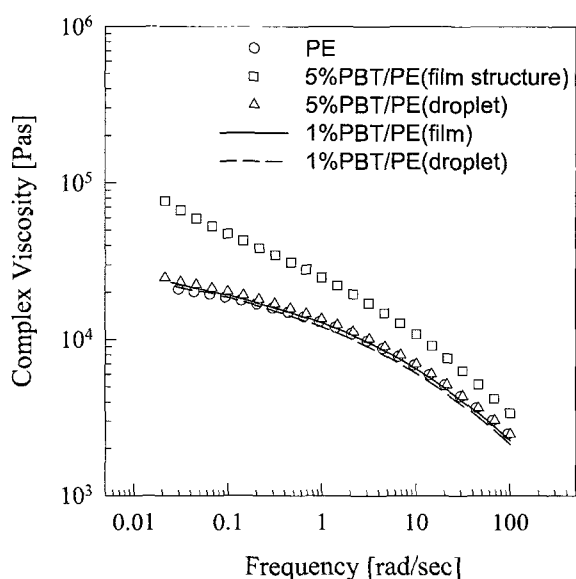


Fig. 5. Complex viscosity of PE with 1 and 5 wt% PBT of both film and droplet structure at 150°C.

extensional flow, the flow behavior with different morphology is not clearly distinguished under shear flow with as small as 1 wt% of PBT. However, as the composition is increased to 5 wt%, a large difference between film and droplet structure is reflected in the complex viscosity. When a small fraction (ϕ) of non-interactive spherical particles are dispersed in a Newtonian matrix (η_m), the viscosity is simply represented by $\eta_s = \eta_m \left(1 + \frac{5}{2}\phi\right)$, according to which the viscosity of each blend can be increased by only 1.25% and 6.5%, respectively over the matrix viscosity in 1 wt% and 5 wt% PBT/PE blends with a droplet structure ($\phi_{\text{vol. of 1 wt\%PBT}} = 0.005$ and $\phi_{\text{vol. of 5 wt\%PBT}} = 0.026$). As the anisotropy of the dispersed phase increases, it becomes more energy dissipative under flow than the dispersion of the droplets. However, the blend composition of 1 wt% may not be characterized under the shear flow.

It is suggested that the strain hardening behavior can be induced significantly by adding a small amount of the second component if the second component maintains elastic solid state and has an anisotropic structure, even though there is no interaction between the two components. This strategy has been applied to polystyrene/PBT system in order to prove its applicability to other systems. Polystyrene (PS) is a good polymer to prove the strategy suggested in this study because the strain hardening behavior of PS is rarely observed just by the increase of the molecular weight or by the broadening of molecular weight distribution. It is known that the strain hardening behavior in PS can only be induced by the modification of molecular structure (Munstedt, 1980). The morphology observed in PS/PBT system is qualitatively the same as that with the PE/PBT system (see Fig. 6). PS embedded with PBT fibrils also shows a significant strain hardening behavior as can be seen in Fig. 7. This confirms again that this physical

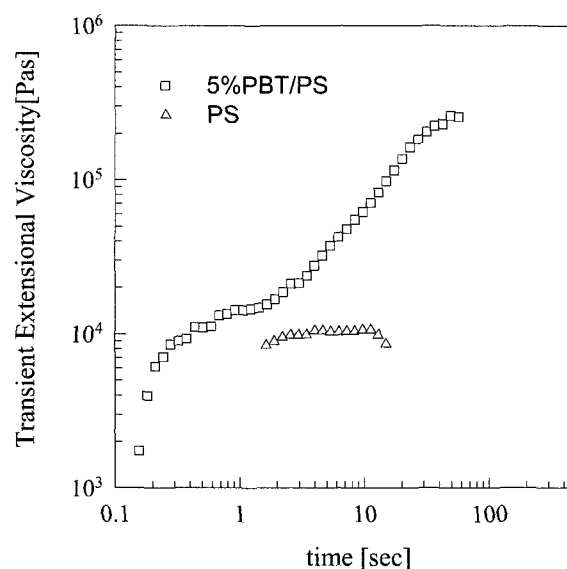


Fig. 7. Transient extensional viscosity of PS with 5 wt% PBT fibrils at 210°C.

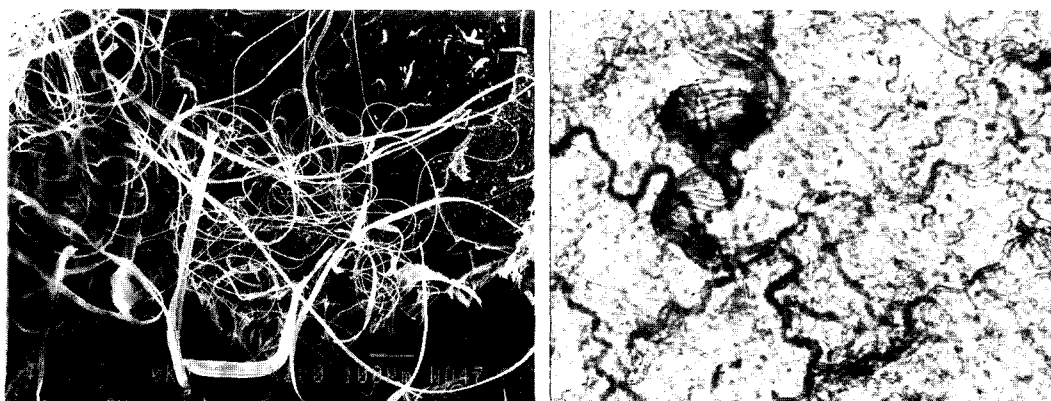


Fig. 6. SEM photograph of 5 wt% PBT/PS under condition 2. The sample was taken by etching PS phase in cyclohexane.

treatment can induce strain hardening behavior in linear polymer melts.

4. Conclusions

This study suggests a new method that induces strain hardening behavior of linear polymer melts by simply blending with a small amount of the second component. In order to achieve this, the structure of the second component needs to be controlled such that the second component exhibiting a highly anisotropic thread structure is maintained. By controlling the processing conditions, the morphology evolution can be retarded when the linear polymer is mixed with a small amount of the second component whose melting temperature is higher than that of the matrix. When the linear polymer is mixed with the second component slightly below the melting temperature of the second component, the rigid second component forms film or thread structure as a result of the competition between hydrodynamic drag and thermal energy. The second component does not develop into droplet structure unless a significant amount of additional heat or shear is applied. Therefore, anisotropic structures such as films or threads in the final product can be maintained by keeping the dispersed phase sufficiently rigid enough to avoid or delay relaxation process. In the case of thread structure, the geometrical characteristics enhance resistance against stretching when compared with the droplet structure and result in a significant strain hardening behavior despite the lack of any interaction between the two components.

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