

일축신장흐름에서의 PS/HDPE Blend의 모폴로지 변화에 관한 연구

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Study on the Morphology Evolution of PS/HDPE Blend During Uniaxial Elongational Flow.

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Abstract

Our study have aimed to identify the deformation and breakup mechanism of minor phase in polymer blends under uniaxial elongational flow. Experimentally, we measured the transient elongational viscosity of PS/HDPE blends using the uniaxial elongational rheometer at two temperatures. And we observed the evolution of blend morphology with elongation time. Morphological change was observed by quenching the specimen after deformation.

If the viscosity variation of PS was compared with that of HDPE at each temperature, PS showed larger temperature dependence than HDPE.

At 155°C, the dispersed phase of larger size were easily affected by affine deformation. The initial spherical shape changed to flat ellipsoid at first, then flat ellipsoid to bulbous shape, and bulbous to thin thread and its satellites. But dispersed phase of smaller size showed the change from sphere to ellipsoid. At 175 °C, the dispersed phase were mostly deformed from spherical shape to ellipsoid. As a result, the morphological change of dispersed phase in elongational deformation is affected by chain flexibility and viscosity ratio. We need to further study to make sure the mechanism of elongation of viscoelastic polymer blends.

Introduction

Polymer blends is a mixture of at least two polymers. Producing of blend with valid property very difficult. it could be mentioned that most of polymer blends is heterogeneous because of thermodynamically immiscibility of each component. miscibility is determined according to value of the free energy of mixing.

$$\Delta G_m = \Delta H - T\Delta S \quad (1)$$

To investigate the morphology and deformation of dispersed phase, generally, there have been used viscosity ratio and capillary number as a important parameter. Delaby et al.[1], Mighri et al. [2], Milliken et al.[3] were focused on the deformation of isolated droplets in flow is controlled by the well-known capillary number defined by the ratio between the viscous force, which attempts to break the drop and interfacial force, which seeks to keep it spherical. And Delaby et al.[1], H. B. Chin et al.[4], studied on the effect of viscosity ratio on morphological evolution of Newtonian and non-Newtonian droplet in Newtonian suspending medium during deformation. As the recent results of Mighri et al.[5], they measured the deformation of droplet in converging and diverging flow. They proposed that elasticity of droplet played a more important role about deformation of droplet than that of matrix, and deformation of drops is increased with elasticity of matrix, while decreased with elasticity of

drop. Martin et al.[6] proposed that during creep flow of HDPE/PS blend at low shear stress, a large increase in the diameter of the dispersed HDPE particles was observed, but the droplets kept their spherical shape even at relatively high deformations. At higher shear stress, the initial emulsion-like structure was transformed into a fibrillar one. They also described that the coalescence is occurred at high initial shear stress.

Experimental

In this study, we were used polystyrene(PS) and high density polyethylene(HDPE) and GPC data of polymers was listed in table. Blend contained 90wt% HDPE and 10wt% PS. PS/HDPE blend was made using a Haake single screw extruder, which had a screw of a 3/4 inch diameter and the capillary die of 3.5mm diameter was connected. the rotation speed of extruder was adopted 25rpm not to cause significant structure modification and temperature profile of extruder was set at 170, 190, 210, 200°C respectively. temperature of molten materials in melt zone of extruder increased over 200°C. from figure, viscosity of PS is much lower than that of HDPE at that temperature.

To measure dynamic and steady properties of polymer melts, we carried out using a Rheometrics Mechanical Spectrometer(Model RMS 800) with parallel plate fixture of 25mm diameter under nitrogen atmosphere. And to measure transient elongational viscosity, we used the uniaxial elongational rheometer of home-made Meissner type that was performed in constant strain rate mode. Blend were subjected to a transient uniaxial elongational flow of constant strain rate 0.05[1/sec], 0.1[1/sec] at 155, 175 °C, their transient elongational viscosity are represented in figure 1b. During uniaxial elongation flow, the strain rate is kept constant and equation (2a) is velocity field of sample. As can be seen at equation (2b), the Hencky strain increased linearly with time and was related to the stretch ratio. The length would increase exponentially with time, whereas the area decreased exponentially with time.

$$v_1 = \dot{\epsilon}x_1, \quad v_2 = -\dot{\epsilon}x_2, \quad v_3 = 0 \quad (2a)$$

$$\lambda = \frac{L}{L_0}, \quad \lambda = e^{\dot{\epsilon}t} \quad (2b)$$

$$\eta_e = \frac{\tau_{11} - \tau_{33}}{\dot{\epsilon}} \quad (2c)$$

where, $\dot{\epsilon}$ is strain rate, L_0 is initial length of sample.

The transient elongational viscosity of PS at 155°C was not included in figure because its viscosity is too high to measure in the rheometer. and also, at 175 °C, and also, it is not available in our rheometer due to very lower level of viscosity. so we could not measure the elongational viscosity of PS.

We analyze the deformation of dispersed phase using microscope. A scanning electron microscope(SEM) was prevalently used to observe the shape of dispersed phase in the principle of reflection of electronical beam. Size distribution of dispersed phase broad and may be unstable due to no usage of compatibilizer, however, we neglected that.

Results and discussion

Both the storage modulus and complex viscosity of components and blend do not exhibit particular viscoelastic behavior. We performed the transient tests in the linear viscoelastic region. We conformed the stress relaxation modulus $G(t, \gamma)$ of the PS measured at 155 °C and 165 °C. For long time, $G(t, \gamma)$ at 155 °C gradually decrease, while $G(t, \gamma)$ at 165 °C rapidly

decrease with time. And if compare with HDPE, it is noted that PS hardly relaxed after applying small deformation. But at 175 °C, PS will show more rapidly relaxed than HDPE as temperature increase. These are related to difference of chain flexibility between HDPE and PS. From figure 1a, if viscosity variation of PS is compared with that of HDPE at two temperature, PS shows larger temperature dependence behavior than HDPE.

The order of the elongational viscosity of blend is more increased than that of HDPE by addition of 10% PS. We believe that, for small deformation, the Trouton ratio is not much different from 3, so the elongational viscosity ratio of the dispersed phase and matrix should be approximately the same as the shear viscosity ratio. Moreover, if blend does not show strain hardening behavior, the elongational viscosity ratio (λ) was not profoundly different with the shear viscosity ratio for large deformation. We could know that at 155 °C, dispersed phase of blend have higher elongational viscosity than matrix ($\lambda > 1$), inversely, at 175°C dispersed phase of blend have lower elongational viscosity than matrix ($\lambda < 1$). These are reflected on the deformation of dispersed phase.

From figure 2, at 155 °C, the morphology change of the dispersed phase exhibit two modes of time dependent deformation. these initial spherical shape change to flat ellipsoid at first, then flat ellipsoid to bulbous shape, and bulbous to thin thread and its satellites. But dispersed phase of comparatively smaller size seems to be changed from sphere to ellipsoid. At 175°C, the dispersed phase of blend are generally deformed from spherical shape to ellipsoid.

Conclusion

From the phenomenological point of view, we have investigated the morphological evolution of the dispersed phase with elongation time. The study was carried out to examine how the deformability of dispersed phase is affected by the increase of temperature. Morphology is affected mainly by initial size of disperse phase, viscoelastic property of each phase and the deformation rate. Based on our results, deformation of the dispersed phase would be mainly influenced by transferred stress level. Stress transfer from matrix to the dispersed phase was dependent upon the value of elongational viscosity. At 155 °C, the dispersed phase had higher elongational viscosity than matrix ($\lambda > 1$), inversely, at 175 °C, the dispersed phase had lower elongational viscosity ($\lambda < 1$). It could be noted that at lower temperature, stress was less transferred to the dispersed phase due to the larger level of elongational viscosity. And also, the stress relaxation modulus affected to the deformation of dispersed phase.

In addition, the morphology evolution of blend was quite similar to that of Newtonian fluids in uniaxial elongational flow. Elongational viscosity ratio showed the same tendency with viscosity ratio in deformation of minor phase. We have investigated another morphology evolution of viscoelastic blend, which it was different from the end pinching morphology that is frequently observed in the typical polymer blends.

Reference

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Table 1. GPC data of HDPE and PS

	HDPE (matrix)	PS(dispersed phase)
M_n	10.84K	114.6K
M_w	212.7K	287.9K
M_z	1,109K	735.7K
PI	19.62	2.51

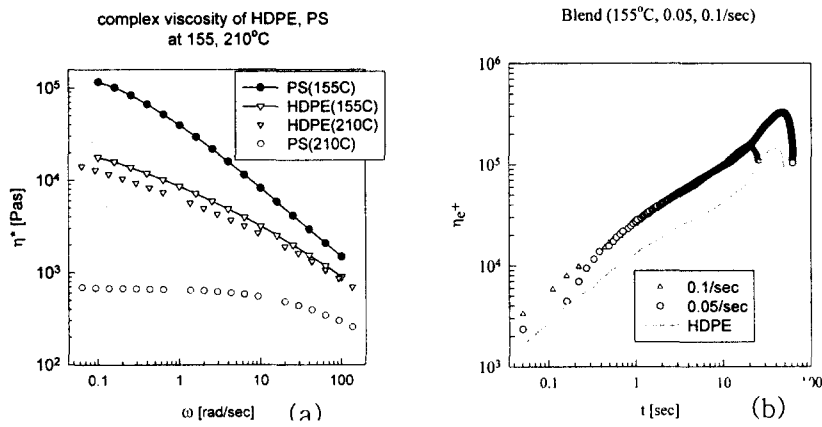


figure 1. measurement of complex viscosity(a) and transient elongational viscosity(b).

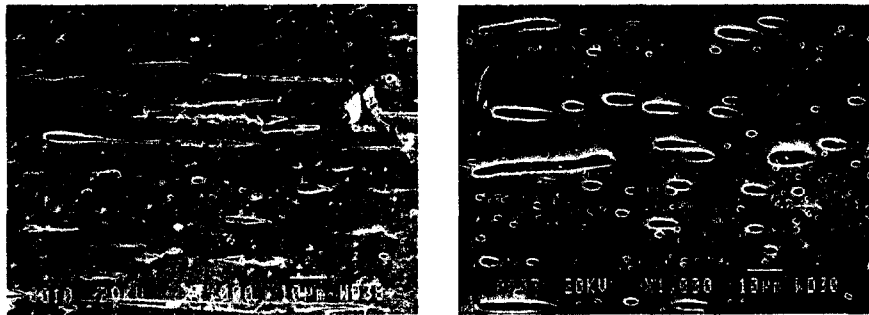


figure 2. Microphotographs of PS/HDPE blend at 155 °C (left) and 175°C(right) at the experimental condition of strain rate = 0.05/sec and elongation time = 30sec.