

블럭 공중합체를 포함한 폴리스티렌 / 폴리에틸렌 블렌드 II. 유성학적 성질

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Polystyrene/Polyethylene Blends Containing Block Copolymers. II. Rheological Properties

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요약 : 비상용성인 PS/HDPE 및 PS/LDPE 블렌드의 유성학적 성질은 여러가지 서로 연관성이 있는 변수에 좌우된다. 혼합조건, 형태학, 가공조건, 사용 고분자 물질의 특성등이 이에 속한다. PS/HDPE 블렌드에서, 높은 온도(220°와 240°C)와 높은 전단응력을 제외하고, 블렌드 점도는 PS 및 HDPE의 점도보다 낮다. 특히 PS/HDPE=85/15와 15/85의 조성에서 최소 점도의 존재를 보여주고 있는데, 이 두 조성에서의 최소 점도거동은 온도와 전단응력의 영향이 서로 반대되는 현상을 보이고 있다. 블럭 공중합체의 높은 점도는 블렌드 점도를 약간 상승시키지만, 블렌드의 동적 거동에는 거의 영향이 없다. 그러나 PS/HDPE 및 PS/LDPE 블렌드에 블럭 공중합체의 사용은 블렌드의 안정성을 크게 향상시킨다. 그러므로 블렌드 형태학의 재현성이 좋아지고, 형태학의 혼합조건에 대한 의존성이 크게 저하된다.

Abstract : The rheology of incompatible PS/HDPE and PS/LDPE blends is closely related to many interrelated variables. These include blending conditions, morphology, processing conditions, and characteristics of polymers. In PS/HDPE systems, the blend viscosity is generally lower than each individual component except high temperatures(220° and 240°C) and high shear stress. At PS/HDPE=85/15 and 15/85, existence of minimum viscosities is observed but they behave opposite way with temperature and shear stress.

The high viscosity of block copolymer gives slightly high blend viscosity. Almost no influence of block copolymer on dynamic behavior is found. However, incorporation of block copolymer in PS/HDPE and PS/LDPE blends would give much improved stability of heterogeneous blends. Thus, one may have the repeatable blend morphology which is less dependent on blending conditions.

INTRODUCTION

Rheology of incompatible heterogeneous blends is governed by many interrelated variables. These include blend preparation (method of mixing, mixing intensity), morphology (state of dispersion, size of the dispersed phase, size distribution), and processing conditions (temperature, pressure, shear stress). Further, rheology of the blend is also strongly dependent on characteristics of polymers blended (molecular weight and distribution, and chemical structure), composition ratios, and orientation. Nature of interfacial tension, adhesion, and deformability can also play a significant role to the rheology of blends.

Currently, no rigorous theory exists to predict which of the two components in a blend will form the discrete phase dispersed in the other. The state of dispersion depends on the rheological properties of individual polymers, which in turn are influenced by their molecular characteristics.¹⁻⁴

There were some efforts to develop theories on heterogeneous blends to predict rheological or mechanical properties.⁵⁻⁸ Many others carried out experiments to test the theories and to study the rheological properties.^{3,4,9-17} Specifically, some researchers examined the rheology of polystyrene (PS) / polyethylene (PE) blends.^{4,13,14,16,17} However, since morphology of incompatible blends is controlled by many interrelated variables, the rheology of these blends exhibits a big difference even with the same blend systems.

It is known that the block copolymer by itself forms microphase separation, which gives very high elastic and viscous behavior in molten state.¹⁸⁻²¹ Some unique features of block copolymer include very low shear rate for melt fracture and very high sensitivity of temperature on activation energy.¹³

In this study, rheology of PS / PE blends containing block copolymer is described. In the past, the rheology of ternary blend systems containing block copolymer have rarely been studied.

EXPERIMENTS

Materials

Commercial grades of polymers are used in the study : polystyrene(PS), high density polyethylene (HDPE), and low density polyethylene (LDPE). Block copolymers are hydrogenated versions of poly(styrene-*b*-butadiene) (S-E), poly(styrene-*b*-isoprene) (S-EP), and poly(styrene-*b*-butadiene-*b*-styrene) (S-EB-S). First two are diblock copolymers and the last is triblock. More informations on these materials are given elsewhere.²²

Compositions of blends are given in weight ratio unless specified otherwise.

Apparatus

An Instron Capillary Rheometer(Model 3211) is employed to measure viscosity of blends. Blends are prepared by a Brabender Plasticorder with 100rpm rotor speed for 15 minutes at 200°C.

By use of 90° entrance angle of various capillaries, the entrance pressure drop would be reduced significantly. No attempt is made to correct entrance and exit effects.²³ Thus, all viscosities are expressed as "apparent viscosity".

RESULTS AND DISCUSSION

Viscosity of Homopolymers and Block Copolymers

Fig. 1 shows the apparent viscosity of three

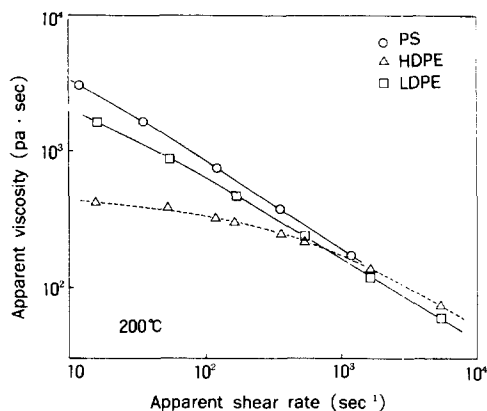


Fig. 1. Apparent viscosity vs. apparent shear rate for three commercial polymers at 200°C.

homopolymers against apparent shear rate at 200°C. Viscosities at other temperatures (180°, 220°, and 240°) exhibit similar behavior. When one plots viscosity against shear stress as shown in Fig. 2, a better rheological understanding may be expected. For example, presence of yield stress can be seen clearly in viscosity-shear stress curve by vertical line. In viscosity-shear rate plot, the yield stress shall show negative 45° line.

Fig. 3 gives viscosity of three block copolymers tested in this study. Comparing with Fig. 2, all three block copolymers exhibit very high viscosity and some tendency of yield stress behavior due probably to microphase separation of block copolymers. In particular, the triblock S-EB-S shows much higher viscosity than other two diblock copolymers, S-E and S-EP. Note that total molecular weight of S-EB-S is 74,000, the lowest among three block copolymers as compared to 120,000 (S-E) and 102,000 (S-EP). Even with this low molecular weight, S-EB-S shows higher viscosity at 240°C than those of two diblocks at 200°C. This implies that the microphase domain structure of S-EB-S triblock is main factor for the very high viscosity.

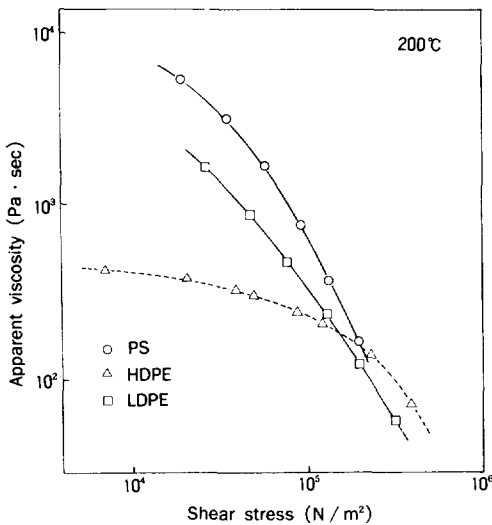


Fig. 2. Apparent viscosity vs. shear stress for three commercial polymers at 200°C.

Viscosity of PS/HDPE and PS/LDPE Blends

Figs. 4 to 7 give viscosity behaviors of PS /

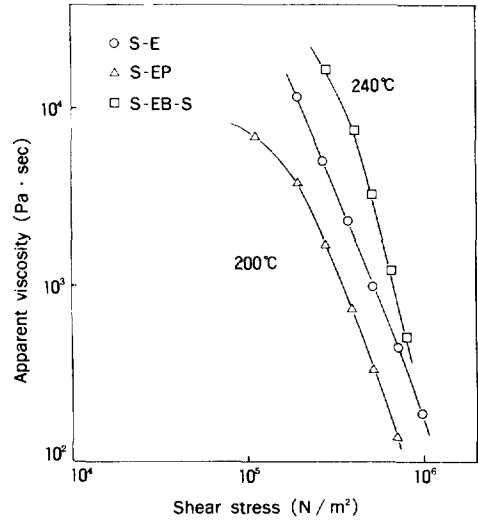


Fig. 3. Apparent viscosity vs. shear stress for three block copolymers. 200°C for S-E and S-EP, and 240°C for S-EB-S.

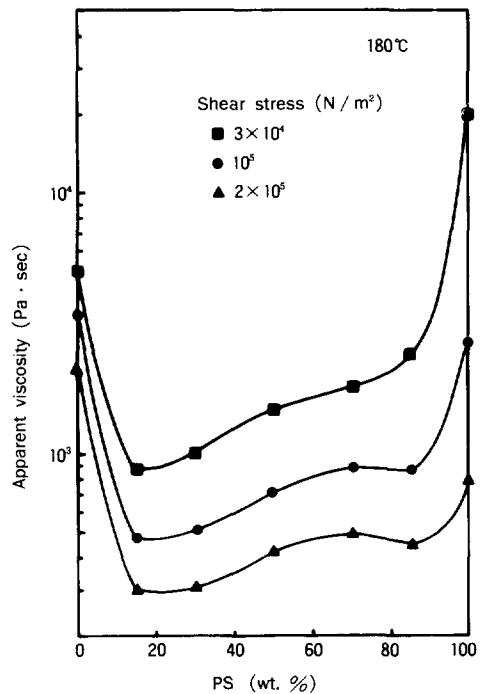


Fig. 4. Apparent viscosity of PS/HDPE blends for three shear stresses at 180°C.

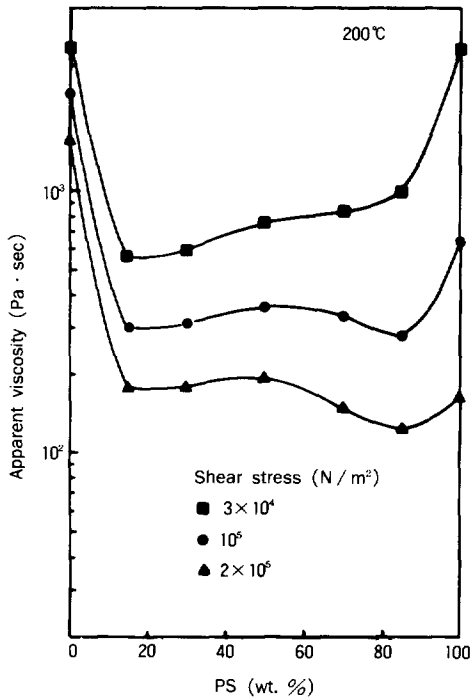


Fig. 5. Apparent viscosity of PS/HDPE blends for three shear stresses at 200°C.

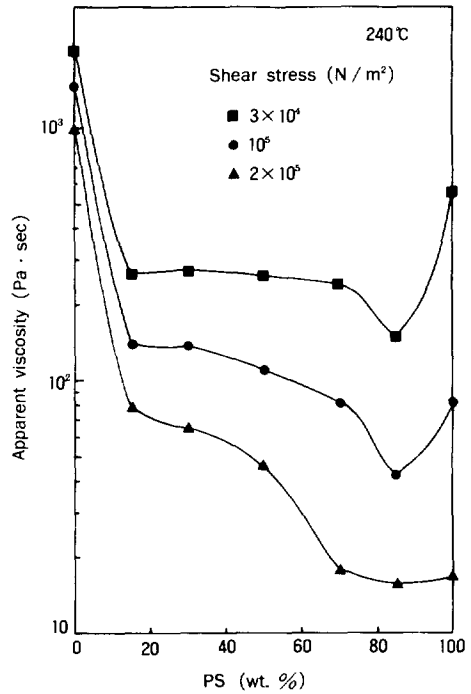


Fig. 7. Apparent viscosity of PS/HDPE blends for three shear stresses at 240°C.

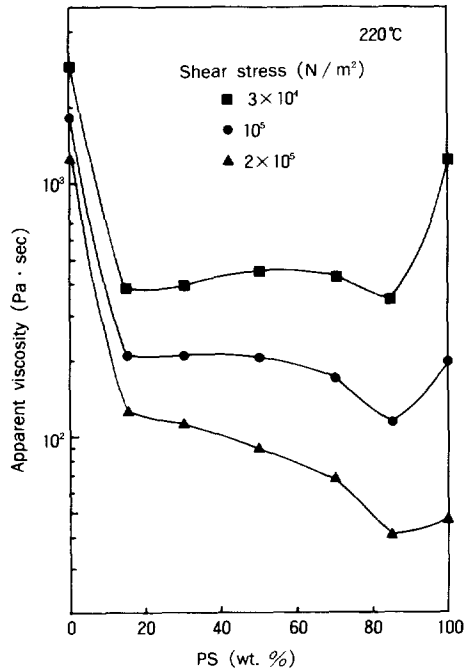


Fig. 6. Apparent viscosity of PS/HDPE blends for three shear stresses at 220°C.

HDPE blends at four temperatures (180, 200, 220, and 240°C) at three shear stresses (3×10^4 , 10^5 , and 2×10^5 N/m²). It is interesting to see that at shear stress 3×10^4 N/m² the blend viscosity is lower than individual polymers at all four temperatures. At 2×10^5 N/m², however, the blend viscosity behaves differently by temperature. In other words, at 180°C, the blend viscosity is lower than both individual polymers but at 200 and 220°C, the blend viscosity is close to PS viscosity. At 240°C, the HDPE-rich blends show viscosity of intermediate range. Further, existence of minimum viscosity at two blend ratios of PS/HDPE=85/15 and 15/85 can be observed. Existence of the minimum viscosity at PS/HDPE=85/15 becomes clearer as temperature and shear stress increase. However, the minimum of PS/HDPE=15/85 shows the opposite way: less clear for higher temperature and shear stress.

This viscosity behavior of PS/HDPE blends

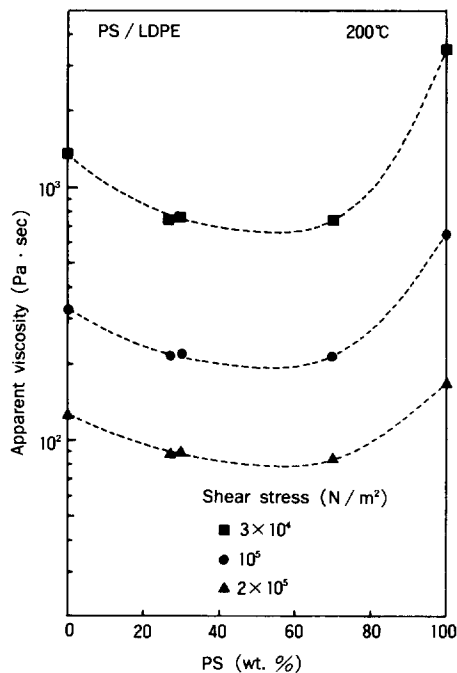


Fig. 8. Apparent viscosity of PS / LDPE blends for three shear stresses at 200°C.

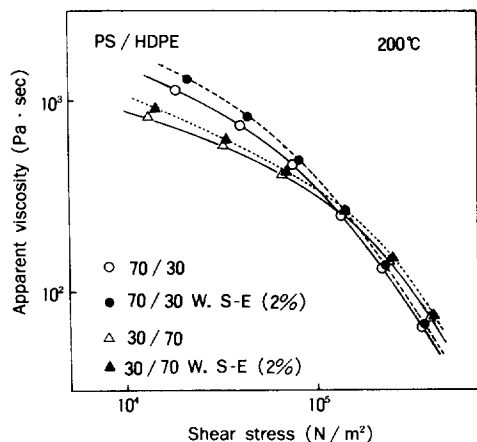


Fig. 9. Effect of diblock copolymer S-E (2 wt. %) on apparent viscosity of two PS / HDPE compositions at 200°C.

is somewhat different from those reported in the literature.^{4,13,23,24} Differences can surely be attributable to many factors involved in the blending operation. These include blending method,

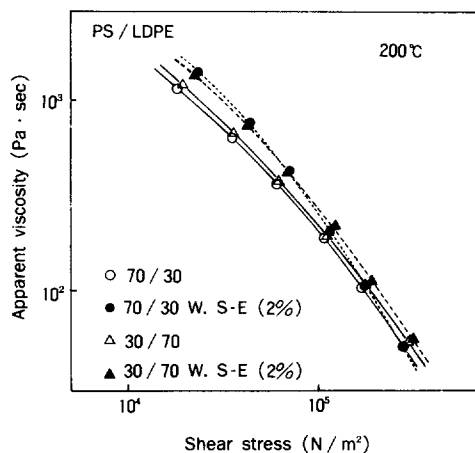


Fig. 10. Effect of diblock copolymer S-E (2 wt. %) on apparent viscosity of two PS / LDPE compositions at 200°C.

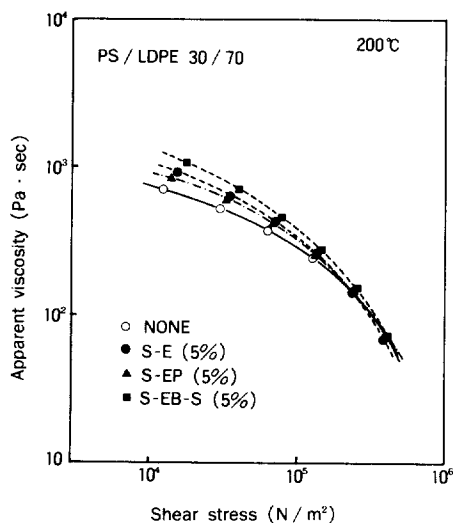


Fig. 11. Effect of three block copolymers (5 wt. %) on apparent viscosity of PS / HDPE 30 / 70 blends at 200°C.

equipment, and polymer characteristics.

Fig. 8 represents viscosity of PS / LDPE blends measured at 200°C. Although lack of data points prevents to make a definite conclusion, PS / LDPE behaves similarly with PS / HDPE blends as compared to Fig. 5.

Effect of Block Copolymers

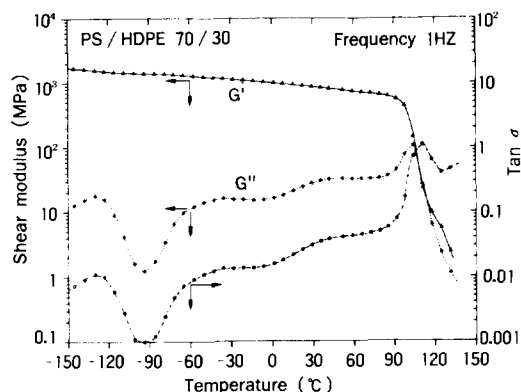


Fig. 12. Storage shear modulus (G'), loss shear modulus (G''), and loss tangent for PS / HDPE 70 / 30 blend.

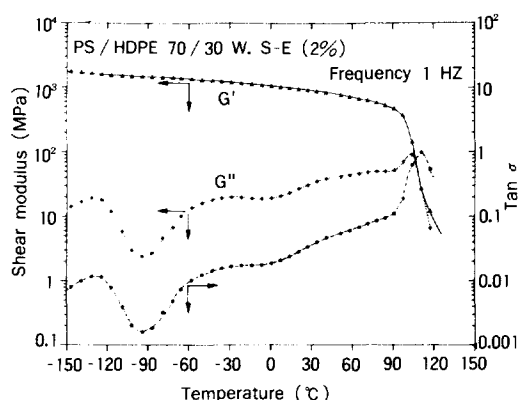


Fig. 13. Storage shear modulus (G'), loss shear modulus (G''), and loss tangent for PS / HDPE 70 / 30 blend containing 2 wt. % S-E.

Figs. 9 and 10 show effect of diblock copolymer S-E on viscosities of two compositions of PS / HDPE and PS / LDPE, respectively. Due to high viscosity of block copolymer, the blend viscosity containing block copolymer is increased slightly. Increase of block copolymer level from 2% to 5% increases viscosity further but not significantly.

Fig. 11 shows comparison of three block copolymers at 5% level with PS / HDPE=30 / 70. It can be seen that high viscosity S-EB-S gives bigger increase than other two diblock copolymers, S-E and S-EP. Effect of block copolymer, however, is diminished at high shear stress range. Other

blend ratios of PS / HDPE and PS / LDPE exhibit similar effect of block copolymers.

Dynamic Behavior of Blends

Figs. 12 and 13 represent dynamic behavior of PS / HDPE=70 / 30 without and with 2% S-E diblock copolymer, respectively. Comparing Fig.12 with Fig.13, storage shear modulus (G'), loss shear modulus (G''), and $\tan\delta(G'' / G')$ of incompatible PS / HDPE blend are not affected by adding small amount of S-E block copolymer. Very similar observations are made with S-EP and S-EB-S block copolymers in other PS / HDPE and PS / LDPE blends.

CONCLUSION

The rheology of PS / HDPE and PS / LDPE blends is governed by many interrelated variables involved in blending. Depending on temperature and shear stress, the blend viscosity of PS / HDPE and PS / LDPE can be minimized. However, one should consider many other factors to judge the rheological behavior of heterogenous blends. It is because slightly different way of mixing can yield grossly different morphology, which in turn changes rheology significantly.

With the relatively low level of block copolymers up to 5%, the viscosity of incompatible PS / HDPE and PS / LDPE blends is not influenced significantly. This low level of block copolymers also gives no change in dynamic behavior. However, the emulsifying and dispersing activity of block copolymer would give much stabilized dispersion state of blends. This improved stability of heterogeneous blends would give better reproducibility with almost same morphology, which makes much less dependency of blend morphology on the blending condition.

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