

## 블럭 공중합체를 포함한 폴리스티렌 / 폴리에틸렌 블렌드 I. 기계적 성질

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## Polystyrene/Polyethylene Blends Containing Block Copolymers I. Mechanical Properties

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요 약 : PS / PE 블렌드에서 세 블럭 공중합체의 영향을 기계적 성질로써 연구하였다. 시험한 블럭 공중합체는 두 가지 diblock S-E와 S-EP이고, 하나의 triblock S-EB-S이다. 인장강도와 연신률이 측정된 기계적 성질인데, PS / HDPE, PS / LDPE 블렌드에서 블럭 공중합체의 함량에 따라 측정하였다. 시험한 세 공중합체 중에서 diblock S-E와 triblock S-EB-S는 PS / HDPE 및 PS / LDPE 블렌드의 인장강도를 크게 향상시켰다. 그러나 두 블럭 공중합체 공히 2%에서 최고의 인장강도를 주고 있다. 파단시 연신률도 두 블럭 공중합체에 의해 향상되고 있는데, 공중합체의 함량에 따라 계속 증가하였다. S-E와 S-EB-S 공중합체에 의한 인장강도와 연신률의 향상은 PS / LDPE 블렌드보다 PS / HDPE에서 더 크게 나타났다. 전반적으로 S-E가 S-EB-S보다 더 좋은 향상을 보였다. 그러나 diblock S-EP는 PS / PE 블렌드의 인장강도와 연신률을 증가시키지 못했다. 이 이유는 비 결정성 EP 블럭이 결정성 PE상과 상용성이 없어, 두 상간에 새로운 계면이 형성되기 때문이라 생각된다.

**Abstract:** Three block copolymers are studied in PS / PE blends in terms of mechanical properties. Block copolymers tested are two diblock S-E and S-EP, and a triblock S-EB-S. Tensile strength and elongation are mechanical properties measured with block copolymer level in both PS / HDPE and PS / LDPE blends. Of three block copolymers examined, diblock S-E and triblock S-EB-S improve tensile strength of PS / HDPE and PS / LDPE blends significantly, exhibiting a maximum tensile strength at 2 wt. % level. Elongation at break is also enhanced by S-E and S-EB-S but it is increased with block copolymer level. Improvement in tensile strength and elongation by S-E and S-EB-S is much more noticeable in PS / HDPE blends than in PS / LDPE. In general, S-E outperforms S-EB-S.

The diblock S-EP, however, gives little effect on the tensile strength and elongation of PS/PE blends. It is speculated that non-crystalline EP block is responsible for this. Since the non-crystalline EP block is not compatible with crystalline PE phase, there may be a new interface formed between EP block and PE phase.

## INTRODUCTION

Polystyrene(PS) and polyethylene(PE) are two commodity polymers representing a typical incompatible system in blending. It is a well-known fact that the incompatible blends exhibit very poor mechanical properties due mainly to the lack of adhesion at the interface. There have been many attempts to improve mechanical properties of these incompatible blends. One of methods is incorporation of compatibilizer such as block or graft copolymers. In the past, PS/PE blends containing block or graft copolymers have been studied by many researchers.<sup>1-15</sup>

As compatibilizer for PS/PE blends, some researchers employed block copolymer<sup>2-7,13</sup> and others used graft copolymers.<sup>1,7-12</sup> Still some others examined chlorinated polyethylene as compatibilizer.<sup>9,10,14,15</sup> These studies revealed that there were some improvements in mechanical properties including tensile strength, tensile modulus, elongation, and impact strength. However, a relatively high level of compatibilizer was needed, typically 5-50 % level.

Of three types of compatibilizers mentioned, the block copolymer would give the best compatibilizing role by its peculiar chemical structure of di-or triblock features. For the effective compatibilizing activity, however, the blocks should be compatible with each constituent of blends. Further, molecular weight of each block would have a significant role for efficiency of compatibilization.

The activity of block copolymer in polymeric blend systems includes interfacial activity,<sup>16-18</sup> surface activity,<sup>19-22</sup> compatibilizing activity,<sup>23-25</sup> and dispersing activity.<sup>26-28</sup> These unique functions of block copolymer suggest that the better and finer dispersion would be expected in blends

containing block copolymer. In other words, the block copolymer not only provides the chemical bond at the interface of incompatible blends but minimize and stabilize the phase domain. Therefore, one may expect much improved mechanical properties by incorporation of block copolymer.

In this study, three block copolymers were studied in PS/PE blends. To examine the compatibilizing activity of block copolymer, mechanical properties were measured with block copolymer content.

## EXPERIMENTS

### Materials

Table 1 shows the characteristics of polymers used in two blend systems, PS/HDPE and PS/LDPE.

Three block copolymers studied are given in Table 2. Of three block copolymers, one is synthesized

Table 1. Characteristics of Polymers

	Density (g / cm <sup>3</sup> )	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Source
PS	1.05	166,000	260,000	2.1	Dow's Styron 666D
HDPE	0.96	19,000	59,000	3.1	DuPont's Alathon7050
LDPE	0.92	13,500	-	-	Eastman's 6018

Table 2. Description of Block Copolymers

Code <sup>(1)</sup>	Molecular Weight	Density	Source
S-E	60,000S / 60,000E	0.985	MMI <sup>(2)</sup>
S-EP	37,000S / 65,000EP	0.950	Shell's Kraton G-1701 MX
S-EB-S	10,000S / 54,000EB / 10,000S	0.955	Shell's Kraton G-1650

(1) S-E : Hydrogenated Poly(styrene-b-butadiene)

S-EP : Hydrogenated Poly(styrene-b-isoprene)

S-EB-S : Hydrogenated Poly(styrene-b-butadiene-b-styrene)

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in the laboratory by living anionic technique (S-E) and two are commercial products. The blend ratio in this study is given by weight.

In S-EB-S triblock copolymer, random distribution of 1,4-type and 1,2-type polymerization of butadiene would yield non-crystalline ethylene / butylene(EB) mid-block by hydrogenation. Approximate E and B contents are known to be 60 wt. % and 40 wt. %, respectively.

#### Apparatus

A Brabender Plasticorder was used to prepare various compositions of PS / HDPE and PS / LDPE blends. The blending conditions are : 200°C of temperature, 15 minutes mixing time, and 90-100rpm rotor speed. The rotors were rotating at same speed countercurrently.

An Instron Universal Testing Machine (Model TM-SM) was employed to measure mechanical properties. For tensile test, dumbbell type specimen was made by compression molding. Approximate dimensions were 0.49cm in width and 2.0cm of testing length with varying thickness. Dimensions of each sample were measured accurately before each testing. Results are average of at least 5 samples.

## RESULTS AND DISCUSSION

### PS/HDPE Blends

Figs. 1 and 2 show tensile strength and elongation at break with blending ratios of PS / HDPE, respectively. As expected, both properties exhibit a typical behavior of incompatible blends, a minimum value at a certain composition ratio.

For tensile strength, the minimum is observed around PS / HDPE=70 / 30 ratio. Further, yield behavior is seen only with blends of PS content less than 30%. Elongation at break is also drastically decreased by adding small amount of PS. In other words, as seen in Fig. 2, PS / HDPE=15 / 85 blend shows about 1 / 100 elongation at break compared to HDPE. This can also be seen in stress-strain curve as shown in Fig. 3. From Fig. 3, only HDPE and PS / HDPE=15 / 85 give yield behavior while others exhibit very

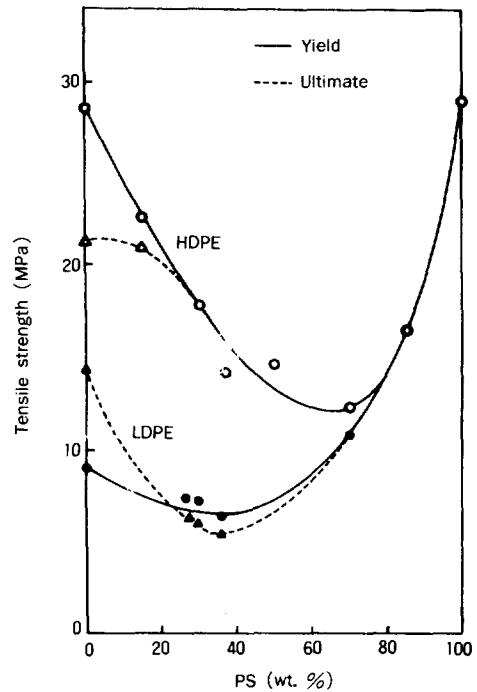


Fig. 1. Tensile strength of PS / LDPE and PS / HDPE blends.

brittle behavior.

Effect of block copolymers on tensile strength is shown in Fig. 4. For two PS / HDPE blend ratios, 70 / 30 and 30 / 70, one may observe the following interesting facts.

1) At PS / HDPE=70 / 30 where the minimum tensile strength is seen, two block copolymers, S-E and S-EB-S, improve the tensile strength significantly. Of two, the diblock copolymer S-E is better than the triblock S-EB-S. The diblock S-EP, however, does not improve the tensile strength at all.

2) At PS / HDPE=30 / 70, similar observations can be made although degree of improvement by S-E and S-EB-S is somewhat inferior to the 70 / 30 case.

3) For S-E and S-EB-S, tensile strength is rapidly increased as the block copolymer content increases up to 2%. But, at 5%, however, the tensile strength is lower than at 2%.

Effect of block copolymer on elongation at break

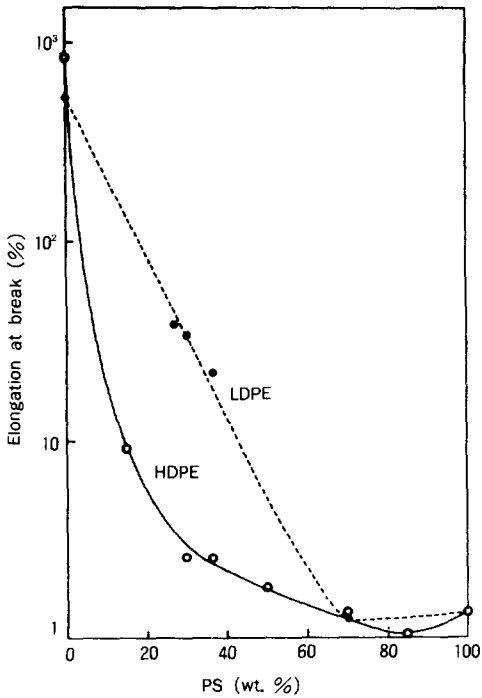


Fig. 2. Elongation at break of PS/LDPE and PS/HDPE blends.

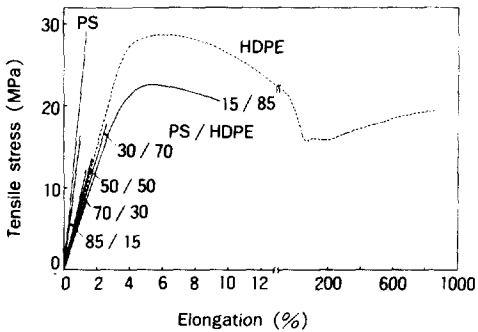


Fig. 3. Tensile stress vs. elongation for various PS/HDPE blends.

is shown in Fig. 5. For S-E and S-EB-S, elongation at break is monotonously increased with block copolymer content while S-EP does give little effect. As with the tensile strength, S-E outperforms S-EB-S in PS/HDPE=30/70. But in 70/30 blends there is little difference between S-E and S-EB-S.

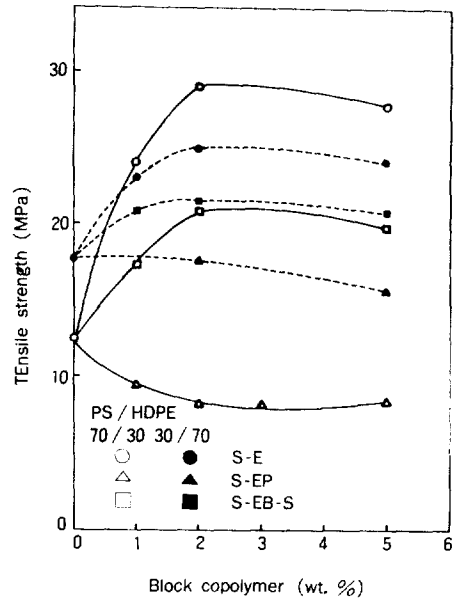


Fig. 4. Tensile strength vs. block copolymer level for PS/HDPE 70/30 and 30/70 blends with three block copolymers.

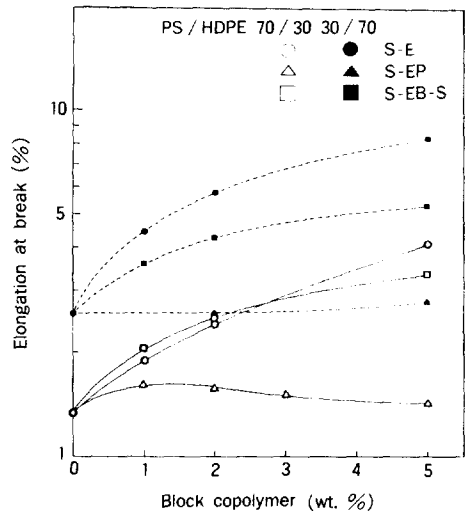


Fig. 5. Elongation at break vs. block copolymer level for PS/HDPE 70/30 and 30/70 blends with three block copolymers.

Different results for three block copolymers in blends may be explained as follows. The diblock copolymer S-E which shows best results

may be the best compatibilizer for PS/HDPE. That is, S and E blocks may be completely compatible with PS and PE phases, respectively. The crystalline E block can be participated in crystallization process of PE phase. Therefore, the junction of two blocks (chemical bond) is located at the interface of two phases. This is the most probable way (lowest energy state of the system) of block copolymer configuration.<sup>16-18, 26-28</sup> On the other hand, non-crystalline EP block (complete alternating sequence of ethylene(E) and propylene (P) from hydrogenation of isoprene) in S-EP diblock copolymer would result in new interface between PE phase and EP segment. The S block, however, is miscible with PS phase.

The S-EB-S triblock copolymer contains non-crystalline (or very low crystalline) EB mid-block. Nevertheless, the enhanced mechanical properties by S-EB-S may be attributable to loop-like formation around an interface and bridge-like entanglements between two interfaces. Further, there is still some possibility of cocrystallization of EB block into PE phase, especially in the bridge-like entanglement case.

Observation of the maximum tensile strength at 2% S-E and S-EB-S is not fully understood yet. However, considering the critical micelle concentration concept in low molecular weight surfactant, a relatively low level of block copolymer as polymeric surfactant would be sufficient to cover the interface of separated phase.

#### PS/LDPE Blends

Tensile strength and elongation at break for PS/LDPE blends are also shown in Figs. 1 and 2. From these figures, one can observe similar results with PS/HDPE. However, the minimum tensile strength appears to be at PS/LDPE=30/70. Fig. 6 gives stress-strain curve for PS/LDPE blends. When PS content is high (e. g. PS/LDPE=70/30), the blend becomes very brittle while high LDPE content gives yielding behavior.

Figs. 7 and 8 show tensile strength and elongation at break with block copolymer level at two composition ratios, respectively. As seen with PS/HDPE blends, two block copolymers, S-E

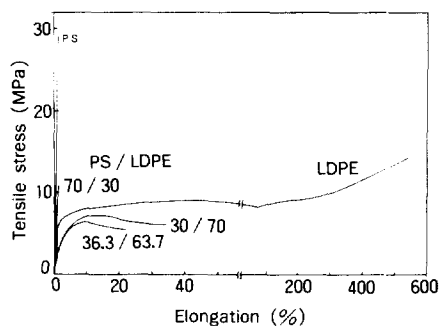


Fig. 6. Tensile stress vs. elongation for various PS/LDPE blends.

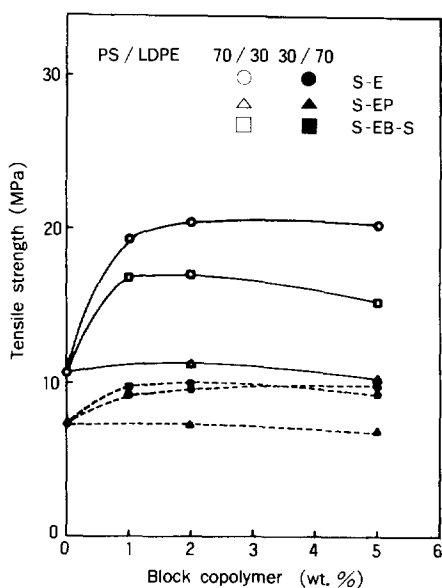


Fig. 7. Tensile strength vs. block copolymer level for PS/LDPE 70/30 and 30/70 blends with three block copolymers.

and S-EB-S, improve the tensile strength while S-EP does little effect. The improvement in tensile strength is higher with PS/LDPE=70/30. With PS/LDPE=30/70, S-E and S-EB-S show almost identical improvement in tensile strength. Again, a maximum tensile strength is seen at 2% for S-E and S-EB-S. Elongation at break is also improved by S-E and S-EB-S as seen in Fig. 7. However, with PS/LDPE=70/30, S-EB-S gives better elongation than S-E.

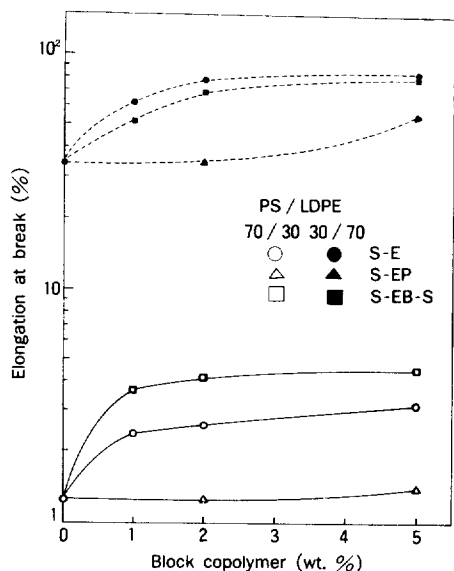


Fig. 8. Elongation at break vs. block copolymer level for PS/LDPE 70//30 and 30//70 blends with three block copolymers.

Lower efficiency of S-E and S-EB-S in PS / LDPE than in PS / HDPE may be due to lower crystallinity of LDPE than HDPE. The low crystallinity of LDPE stems from high degree of many irregular branchings, which in turn may result in loose packing (crystallization) or weaker entanglements of E or EB blocks in PE phase.

## CONCLUSION

In PS / HDPE and PS / LDPE blends, a diblock S-E and a triblock S-EB-S improve tensile strength and elongation significantly. Since the block copolymer consists of blocks that are compatible with each component of the blend, S-E and S-EB-S can be used as compatibilizer for PS / PE systems. The compatibilizing activity of S-E and S-EB-S suggests that a maximum tensile strength may be observed at a relatively low level of block copolymer as a polymeric surfactant, 2 wt. % in PS / PE blends. Elongation at break, however, is increased with block copolymer level.

The diblock copolymer S-EP, however, is not proper choice for PS / PE blends. The reason might

be in the noncrystalline EP block which gives incompatibility with PE phase. In other words, amorphous EP block would create a new interface between PE phase and EP block although S block is compatible with PS phase.

For the best compatibilizing activity, one should include the following for design of block copolymer: block size (molecular weight and distribution), number of blocks, compatibility with blend component (including crystallinity and branching), processability (viscoelastic behavior), and main property to be improved.

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## REFERENCES

1. W. M. Barentsen and D. Heikens, *Polymer*, **14**, 579(1973).
2. R. Fayt, R. Jerome, and Ph. Teyssie, *Makromol. Chem.*, **187**, 837(1986).
3. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys.*, **19**, 1269(1981).
4. R. Fayt, R. Hadjiandreou, and Ph. Teyssie, *J. Polym. Sci., Polym. Chem.*, **23**, 337(1985).
5. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Lett.*, **19**, 79(1981).
6. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys.*, **20**, 2209(1982).
7. D. Heikens, N. Hoen, W. Barentsen, P. Piet, and M. Laden, *J. Polym. Sci., Polym. Symp.*, **62**, 309(1978).
8. C. L. Locke and D. R. Paul, *J. Appl. Polym. Sci.*, **17**, 2791(1973).
9. A. Ghaffar, C. Sadrnoghagheh, and G. Scott, *Europ. Polym. J.*, **17**, 941(1981).
10. M. Hajian, C. Sadrnoghagheh, and G. Scott, *Europ. Polym. J.*, **20**, 135(1984).
11. W. M. Barentsen, D. Heikens, and P. Piet, *Polymer*, **15**, 119(1974).
12. D. Heikens and W. Barentsen, *Polymer*, **18**, 69(1977).
13. C. R. Lindsay, D. R. Paul, and J. W. Barlow,

- J. Appl. Polym. Sci.*, **26**, 1(1981).
14. D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.*, **13**, 202(1973).
  15. C. E. Locke and D. R. Paul, *Polym. Eng. Sci.*, **13**, 308(1973).
  16. J. Noolandi and K. M. Hong, *Macromol.*, **15**, 482(1982).
  17. R. Cantor, *Macromol.*, **14**, 1186(1981).
  18. G. Riess, J. Nervo, and D. Rogez, *Polym. Eng. Sci.*, **17**, 634(1977).
  19. H. B. Gia, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys.*, **18**, 2391(1980).
  20. M. J. Owen and T. C. Kendrick, *Macromol.*, **3**, 458(1970).
  21. G. L. Gaines, Jr. and G. W. Bender, *Macromol.*, **5**, 82(1972).
  22. J. J. O'Mally, H. R. Thomas, and G. M. Lee, *Macromol.*, **12**, 996(1979).
  23. A. R. Ramos and R. E. Cohen, *Polym. Eng. Sci.*, **17**, 639(1977).
  24. G. Riess, J. Kohler, C. Tournut, and A. Banderet, *Rubb. Chem. Tech.*, **42**, 447(1969).
  25. Y. Ikada, F. Horii, and I. Sakurada, *J. Polym. Sci., Polym. Chem.*, **11**, 27(1973).
  26. D. J. Meier, *J. Phys. Chem.*, **71**, 1861(1967).
  27. D. J. Meier, in "Polymer Blends and Mixtures", D. J. Walsh, J. S. Higgins, and A. Maconnachie, Ed., NATO ASI Series E, Applied Sciences No. 89, Martinus Nijhoff Publ., Dordrecht, Netherland, 1985, p173.
  28. D. H. Napper, "Polymeric Stabilization of Colloidal Dispersions", Academic Press, New York, 1983..