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블럭 공중합체를 포함한 폴리스티렌/폴리에틸렌 블렌드 Ⅲ. 형태학

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Polystyrene/Polyethylene Blends Containing Block Copolymers Ⅲ. Morphology

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요 약 : PS/HDPE 및 PS/LDPE 블렌드의 형태학을 세 블럭 공중합체의 함량에 따라 조사하였다. PS/HDPE에서는 PS가 분산상이고, 이들의 입자크기는 블럭 공중합체의 함량에 따라 크게 감소한다. 특히 PS/HDPE=30/70 블렌드에서 diblock S-E가 제일 좋은 효과를 나타내어, 5 wt. %에서 미크론보다 작은 입자크기가 된다. Triblock S-EB-S는 S-E보다 약간 낮은 효율을 보이고, diblock S-EP가 세블럭 공중합체 중에서 제일 낮은 효율을 보이고 있다. PS/LDPE 블렌드에서의 형태학은 조성비에 크게 좌우되고 있다. PS/LDPE=70/30는 PS와 LDPE가 서로 연속상으로 되어있는데, 블럭공중합체를 포함할때 더 뚜렷하다. 그러나 PS/LDPE=30/70는 PS가 분산상이고, 입자크기는 블럭 공중합체의 영향을 거의 받지 않는다.

Abstract : The phase morphology of PS/HDPE and PS/LDPE blends is examined by three block copolymer levels. In PS/HDPE systems, the particle size of PS as the dispersed phase is significantly reduced by increasing level of block copolymers. In particular, PS/HDPE=30/70 with diblock S-E exhibits the drastic particle size reduction to submicron sizes at 5 wt. % level. The triblock S-EB-S is somewhat inferior to S-E while the diblock S-EP shows the least efficiency of three block copolymers tested. In PS/LDPE blends, the phase morphology seems to strongly dependent on the composition ratio. With PS/LDPE=70/30, the co-continuous phase is observed, in particular with block copolymers. The PS/LDPE=30/70 blend shows PS as the dispersed phase whose particle size changes little by block copolymers.

INTRODUCTION

It is already seen in two previous papers[1,2] that the properly designed block copolymer can be very effective compatibilizer with the controlled rheology in PS / PE blends. This compatibilizing activity of block copolymer in the blend makes a drastiic reduction of interfacal tension,[3] and a finer homogeneous particle size of dispersed phase.[4]

Since the phase morphology of incompatible blend is largely dependent on blending conditions, composition ratio, viscosity ratio, and interfacial tension, a wide variation of particle sizes reported in the literature for PS / PE blends is not abnormal.[4~8] Further, the dispersed phase of the incompatible blend is rather unstable so that the particles tend to coalesce thermodynamically for lower energy state.

Effect of viscosity ratio is critically examined by Taylor.[9,10] Recently, many researchers[11~17] reexamined Taylor's results to conclude as follows:

1) When the viscosity ratio (dispersed / medium) is too small, there is no break-up of dispersed phase but long elongation.

2) When the ratio is too large, very limited deformation of dispersed phase occurs.

3) When the viscosity ratio is in the range of 0.005-4, in particular 0.3-0.6, the particle of dispersed phase can easily be broken into small sizes.

4) The lower interfacial tension yields easier break-up of dispersed particle.

In view of rheological behavior of PS / PE blends,[2] the viscosity ratio of PS / HDPE and PS / LDPE blends will be in the range of 0.3-2.5 at the blending conditions(200℃). Therefore, according to Taylor,[9,10] particles of these PS / HDPE and PS / LDPE blends will easily be broken into small particle sizes depending on the blending conditions. Incorporation of block copolymer in PS / PE, however, would reduce particle size of the dispersed phase further as well as stabilize them.

In this study, effect of three block copolymers on the morphology of PS / HDPE and PS / LDPE blends is examined.

EXPERIMENTS

Materials : Polymers used in the study are commercial grades of polystyrene(PS), high density polyethylene(HDPE), and low density polyethylene (LDPE). Block copolymers tested are the 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.[1]

Microscopy : A scanning electron microphotograph (SEM) (Hitachi Model S-510) is used to examine the phase morphology. The sample for SEM is prepared by ethching PS phase in toluene for 3 minutes at 20℃.

RESULTS AND DISCUSSION

PS/HDPE Blends

Fig. 1 shows the morphology of PS / LDPE=70 / 30 with diblock copolymer S-E level, indicating that PS is the dispersed phase even with this PS-rich blend. From Fig. 1(a), it is seen that size of dispersed phase(PS) is very big and irregular. With 1 wt. % S-E, the size becomes in the order of 20μm(Fig.1(b)). Further increase of S-E level reduces the PS particle size drastically in the order of 2-5μm range as seen in Fig. 1(c) and (d). However, the triblock copolymer S-EB-S is not so effective as S-E as shown in Fig. 2.

Figs. 3 and 4 demonstrate the phase morphology of PS / HDPE=30 / 70 blend with S-E and S-EB-S, respectively. This HDPE-rich blend shows that PS is the dispersed phase and the block copolymer is very effective to reduce the particle size of PS. With 5 wt. % S-E, the particle size becomes submicron sizes as seen in Fig. 3(d). Again, the triblock S-EB-S is less effective than S-E as shown in Fig. 4.

Comparison of three block copolymers, S-E,

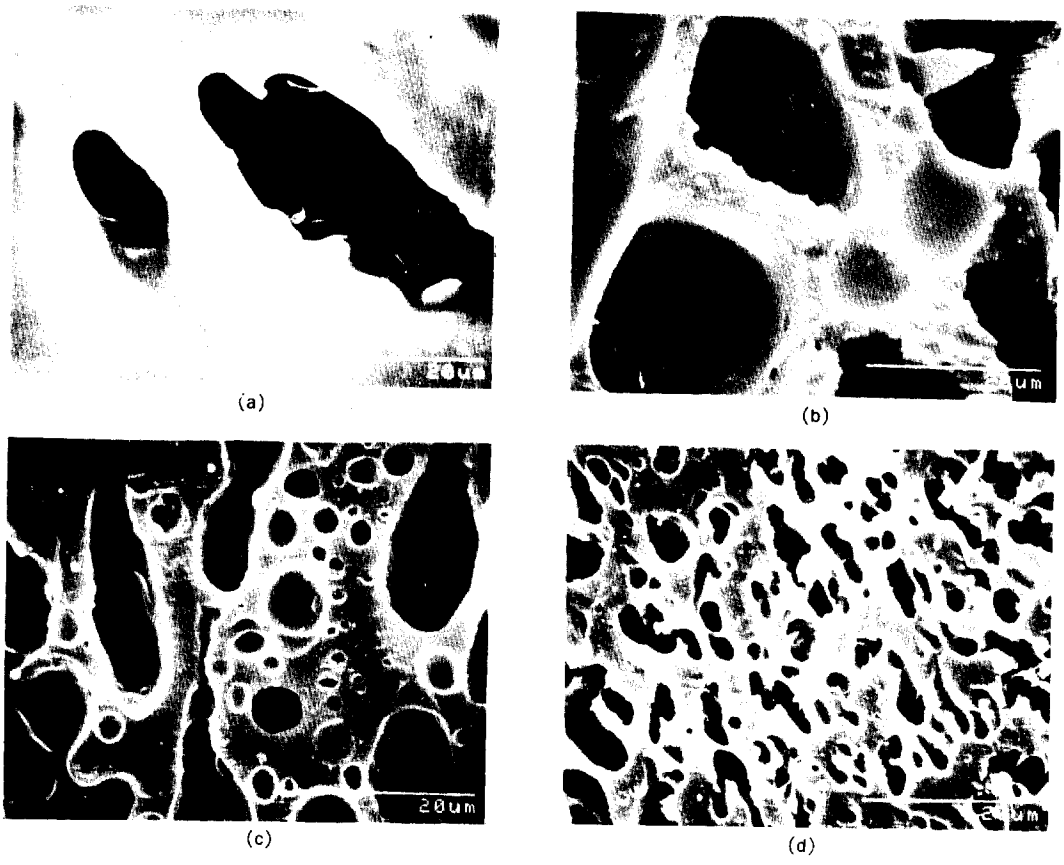


Fig. 1. Microphotographs of PS / HDPE=70 / 30 blends with diblock S-E levels (×2,000): (a) 0 wt.%, (b) 1%, (c) 2%, (d) 5%.

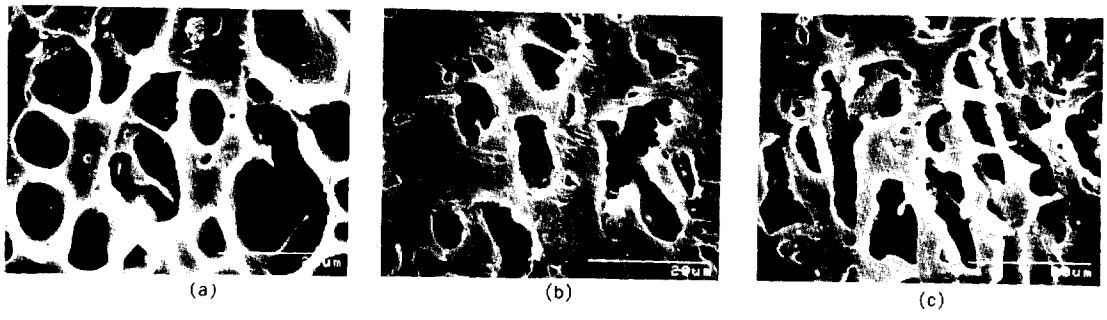


Fig. 2. Microphotographs of PS / HDPE=70 / 30 blends with triblock S-EB-S levels (×2,000): (a) 1 wt.%, (b) 2%, (c) 5%.

S-EP, and S-EB-S, is given in Figs. 5 an 6. With PS / HDPE=70 / 30(Fig. 5), S-E exhibits the finest particle size, then followed by S-EB-S. The diblock S-EP is clearly inferior to S-E and S-EB-S as seen in Fig. 5(b). Effect of three block copolymers is not obvious with PS / HDPE=

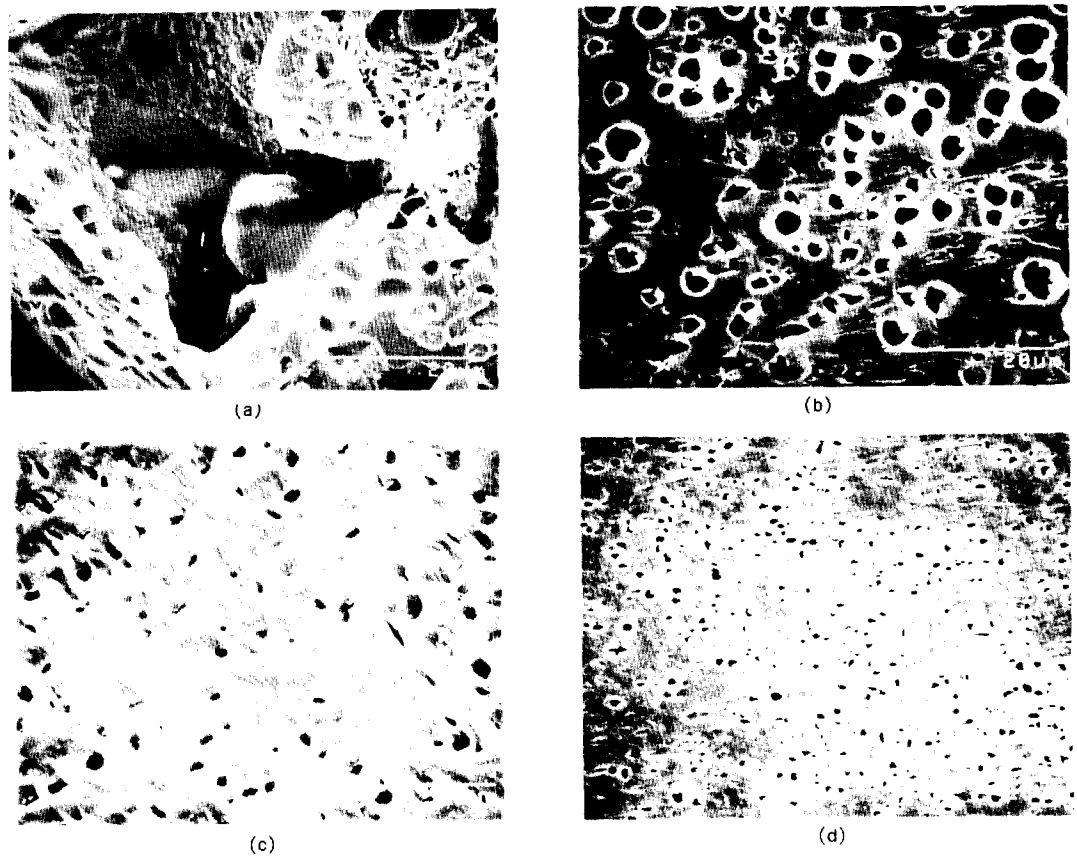


Fig. 3. Microphotographs of PS / HDPE=30 / 70 blends with diblock S-E levels (×2,000): (a) 0 wt. %, (b) 1%, (c) 2%, (d) 5%.

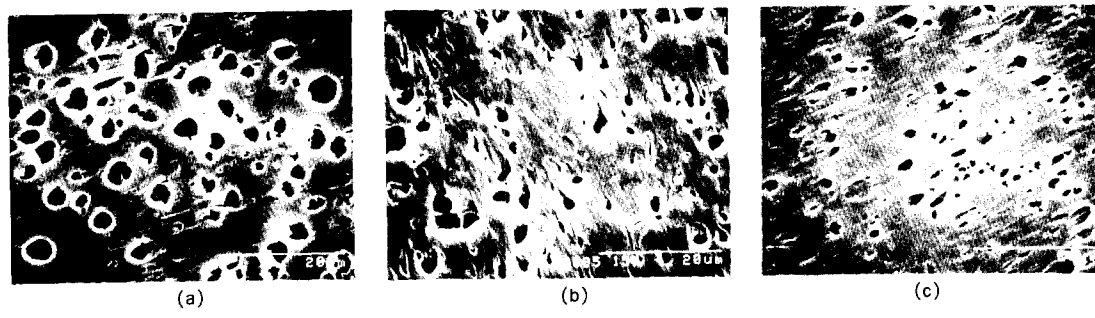
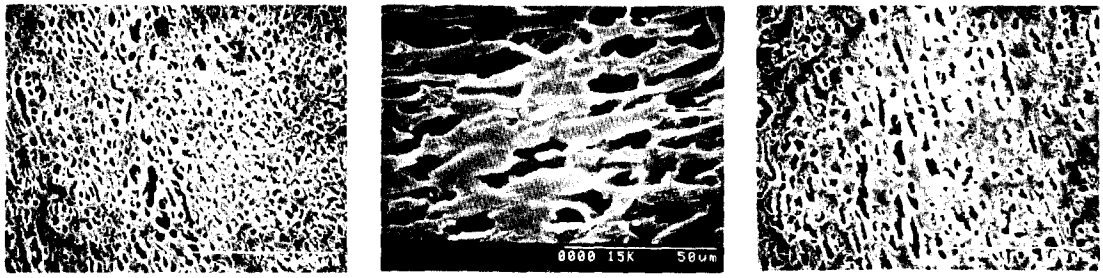


Fig. 4. Microphotographs of PS / HDPE=30 / 70 blends with triblock S-EB-S levels (×2,000): (a) 1 wt. %, (b) 2%, (c) 5%.

30 / 70 as shown in Fig. 6.

Morphology of PS / HDPE blends is consistent with the mechanical and rheological properties reported for the same system.[1,2] In other words, the diblock S-E gave best mechanical properties followed by the triblock S-EB-S, the order of



(a) (b) (c)

Fig. 5. Microphotographs of PS / HDPE=70 / 30 blends with three block copolymers at 5 wt. %. (a) S-E(×500), (b) S-EP(×1,000) (c) S-EB-S (×500).

(a) (b) (c)

Fig. 6. Microphotographs of PS / HDPE=30 / 70 blends with three block copolymers at 2 wt. % (×2,000), (a) S-E, (b) S-EP, (c) S-EB-S.

efficiency to reduce the particle size observed. Of three block copolymers, the diblock S-EP shows the least efficiency for particle size reduction matching wth virtually no improvement of mechanical properties.[1]

PS/LDPE Blends

The particle size reducing tendency of dispersed phase is seen in Fig. 7 for PS / LDPE=70 / 30. However, a noticeable difference between PS / LDPE and PS / HDPE is that in this PS-rich PS / LDPE=70 / 30 blend PS phase can be continuous medium as shown in Fig. 7(b) and (c). When 5% S-E is used, Fig. 7(d) exhibits that PS appears to be the dispersed phase again. With S-EB-S, however, the continuous medium PS phase at 1 wt. % level(Fig. 8(a)) changes to co-continuous texture with LDPE phase for 2 and 5% S-EB-S levels (Fig. 8(b) and (c)).

This kind of phase change is not observed with the LDPE-rich PS / LDPE=30 / 70 system. Figs. 9 and 10 demonstrate this, exhibiting PS is the dispersed phase. Further, two block copolymers, S-E and S-EB-S, give a limited particle size reduction. In fact, contrary to PS / HDPE case, the triblock S-EB-S seems to be slightly more effective than S-E in PS / LDPE=30 / 70. This is again consistent with the mechanical properties observed[1].

Fig. 11 shows effect of three block copolymers in morphology of PS / LDPE=30 / 70. It is seen that three block copolymers exhibit little effect on particle size of dispersed PS phase in this PS / LDPE=30 / 70. However, the phase morphology of PS / LDPE blends is found to be largely dependent on composition ratio as shown in Fig. 12.

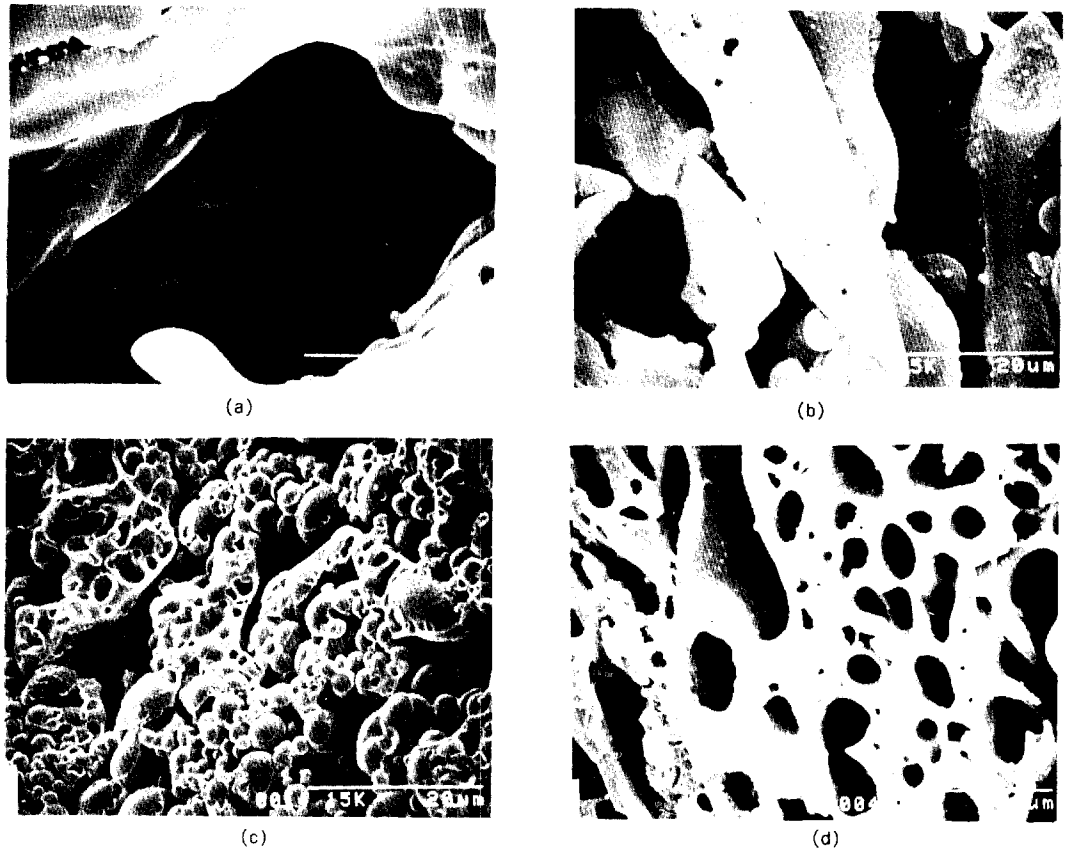


Fig. 7. Microphotographs of PS / LDPE=70 / 30 blends with diblock S-E levels (×2,000): (a) 0 wt. %, (b) 1%, (c) 2%, (d) 5%.

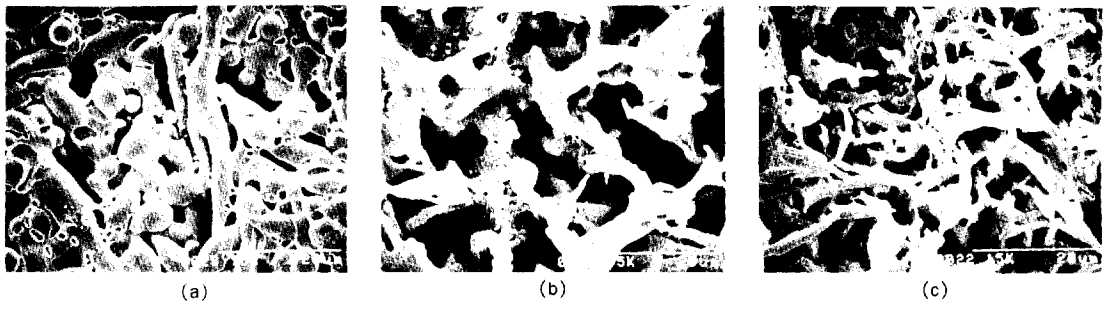
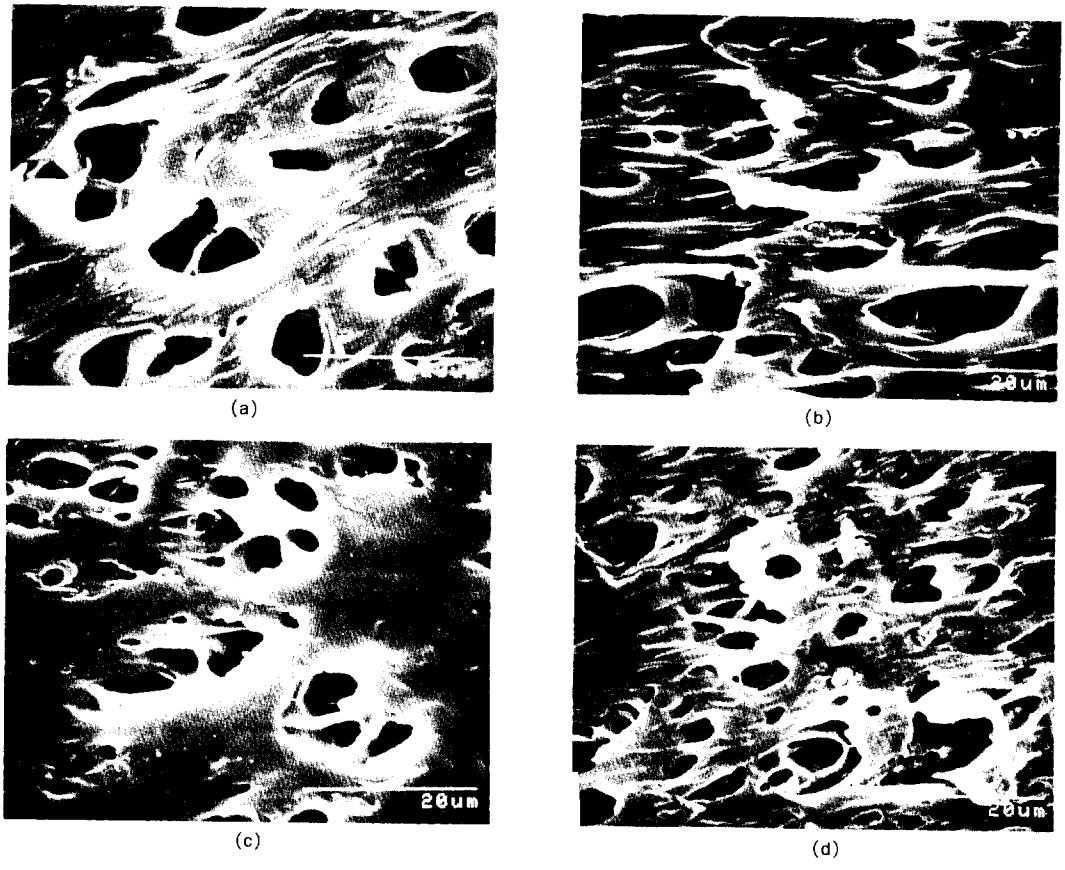


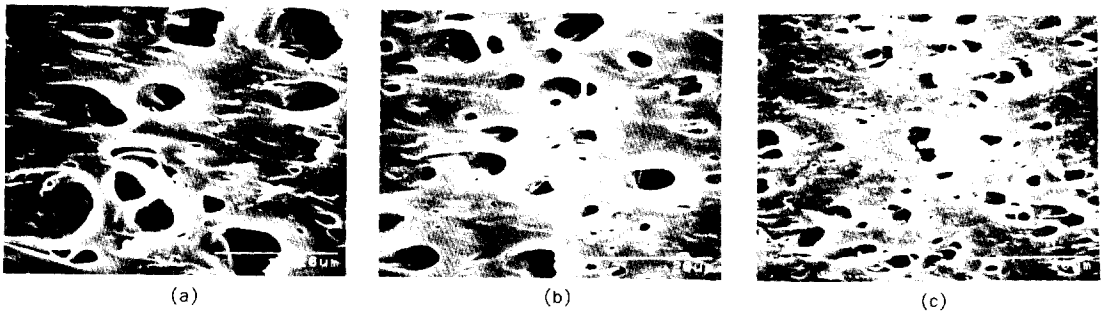
Fig. 8. Microphotographs of PS / LDPE=70 / 30 blends with triblock S-EB-S levels (×2,000): (a) 1 wt. %, (b) 2%, (c) 5%.

Limited improvement by S-E and S-EB-S in mechanical properties of PS / LDPE blends[1] is easily explained by the limited particle size reduction observed.



(a) (b) (c) (d)

Fig. 9. Microphotographs of PS / LDPE=30 / 70 blends with diblock S-E levels (×2,000): (a) 0 wt. %, (b) 1%, (c) 2%, (d) 5%.



(a) (b) (c)

Fig. 10. Microphotographs of PS / LDPE=30 / 70 blends with triblock S-EB-S levels (×2,000): (a) 1 wt. %, (b) 2%, (c) 5%.

CONCLUSION

In PS / HDPE blends, the diblock copolymer S-E reduces the particle size of dispersed phase (PS) very effectively for both 70 / 30 and 30 / 70 composition ratios. The triblock copolymer

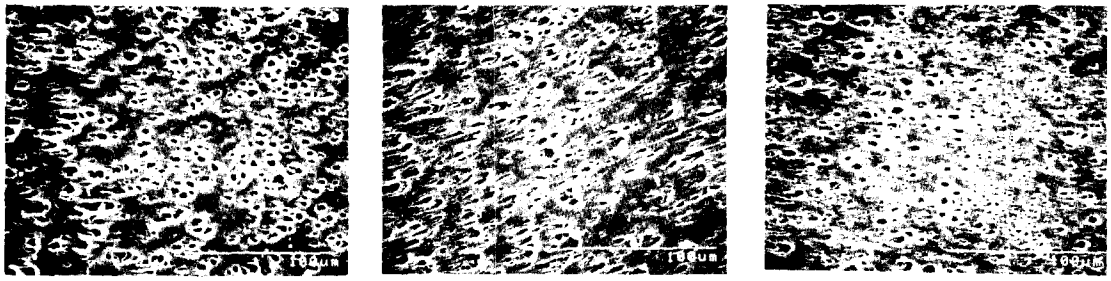


Fig. 11. Microphotographs of PS / LDPE=30 / 70 blends with three block copolymers at 2 wt. %(×500): (a) S-E, (b) S-EP, (c) S-EB-S.

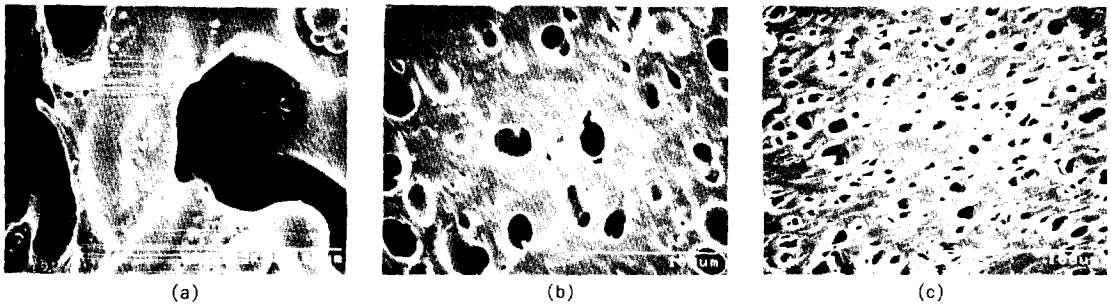


Fig. 12. Microphotographs of three PS / LDPE blend ratios: (a) PS / LDPE=70 / 30(×300), (b) 36.3 / 63.7(×500), (c) 30 / 70(×500).

S-EB-S also exhibits effective particle size reduction, in particular with PS / HDPE=30 / 70. However, S-EB-S is somewhat inferior to S-E, consistent with the mechanical properties observed. The diblock copolymer S-EP shows similar morphology in 30 / 70 blend but the least efficiency in 70 / 30 blend.

With PS / LDPE blends, effect of three block copolymers on the particle size of dispersed phase is not strong as with PS / HDPE blends. The particle size of PS / LDPE appears to be controlled by the composition ratio : the smaller particle size for the higher LDPE level. The phase morphology seems to be dependent on the composition ratio and block copolymer. In other words, PS / LDPE=70 / 30 exhibits co-continuous morphology which does not change with 1 or 2 wt. % block copolymer addition. PS / LDPE=30 / 70 blends, however, shows that PS is the dispersed phase.

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