Morphology and deformation of compatibilized polystyrene low density polyethylene blends

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Abstract: This investigation deals with the morphology and tensile behavior of polystyrene/low density polyethylene blends compatibilized by hydrogenated styrene-b-butadiene-b-styrene triblock copolymer. The stress-strain measurements indicate that blends with excellent toughness were achieved, due to the compatibilizing role of the triblock copolymer in the system. The morphology of the blends was observed by scanning electron microscopy (SEM), and the results show that the state of polystyrene changes from continuous phase to dispersed phase with increasing LDPE content. The correlation between mechanical properties and morphology is discussed. The morphologies of the tensile bars were also examined by SEM, and the deformation mechanisms of the blend were further analysed according to fractography.

INTRODUCTION
Polyethylene (PE) and polystyrene (PS) are the most widely used plastics. PS possesses high modulus and high tensile strength; however, it is brittle and easy to crack. On the other hand, PE shows high toughness and good impact performance even at low temperature. Therefore, combining two polymers to form a heterophase system is a very attractive route to produce a new toughened PS material. It is known that the addition of a block or graft copolymer acting as a compatibilizer to phase-separated blends of immiscible homopolymers will significantly improve their mechanical properties. The effects of PE-g-PS copolymers on the microstructure and mechanical properties of PS/PE blends were reported in the 1970s. The blends modified by copolymers exhibited higher strengths, whereas the elongation at break remained rather low. From the early 1980s, Fayt and Teyssie tried to improve the properties of PS/PE blends by adding block copolymers. They systematically studied the effects of the structure, architecture, molecular weight and content of block copolymers on the emulsifying efficiency in the system. The results showed that the mechanical properties of PS/PE blends compatibilized by block copolymers were greatly improved when compared with those compatibilized by graft copolymers. However, little attention was paid to the compatibilizing role of tri-block copolymers, especially of hydrogenated poly(styrene-b-butadiene-b-styrene) (SEBS). These copolymers were prepared by anionic polymerization of styrene (S) and butadiene (B) followed by hydrogenation of the PB block.

In our study, low density polyethylene (LDPE) was blended with polystyrene to reduce its brittleness, and SEBS (G1652) was chosen as a compatibilizer to increase the interfacial adhesion and mechanical properties of PS/LDPE blends. In this paper, first, we shall discuss the effects of processing conditions such as compounding equipment, blending temperature and shear stress, on the mechanical properties of PS/LDPE blends. Then, we shall report the relationship between mechanical properties, blend composition, and morphology of the blends.

EXPERIMENTAL
Materials
Two kinds of polystyrene homopolymers were used in this study, that were denoted PS (Yanshan Chemical 666D, MFI of 6.9 g/10 min, $M_w = 230000$, $M_n = 97000$, $M_w/M_n = 2.4$) and PS-2 (Fushan Chemical GPS 130, MFI of 4.9 g/10 min, $M_w = 273000$, $M_n = 125000$, $M_w/M_n = 2.2$). Low density polyethylene was purchased from Jinshan Chemical (LDPE, 2F2B, MFI of 1.8 g/10 min). The tri-block copolymer SEBS (G1652) was kindly supplied by Shell Chemi-
cals with respective molecular weights of PS blocks and central EB block being 7500 and 37500, the PS weight fraction being 28.6%.

Blending
All materials were dried overnight at 60–80°C in a vacuum oven prior to melt blending. The samples were pre-mixed by tumbling at room temperature, then were compounded in a mixer (Haake 90) under the given conditions. As a rule, a blend was denoted by the weight ratio of polystyrene to low density polyethylene (such as: PS/LDPE 80/20); the percentage of added copolymer (SEBS) was defined with respect to the total weight of the blend.

Stress-strain measurements
After mixing, the blends were compression moulded into 120 × 100 × 0.5 mm³ sheets under a pressure of 5 MPa at 180°C, then quenched in cold water. The sheets were then stored in a desiccator at room temperature for two days to ensure that all samples were subjected to the same thermal history prior to testing.

The dumbell bars with 20 × 4 mm² dimensions were machined from the sheets. Stress-strain measurements were performed at room temperature on a tensile tester at a crosshead speed of 10 mm min⁻¹. At least five specimens were tested and the average values were reported.

Observation of the morphology
Three kinds of sample surface were observed, ie the surface of the blends fractured in liquid nitrogen, the fracture surface of tensile bars at room temperature and the surface of the tensile specimens fractured in liquid nitrogen along the stretching direction. All the samples were coated with a thin layer of gold in a sputtering unit before morphology observation with a Hitachi Model S-450 scanning electron microscope, operating at 25kV.

RESULTS AND DISCUSSION
Effect of processing conditions
Table 1 shows the mechanical properties of blends with the same composition (PS-2/LDPE 80/20, 5 wt% SEBS) prepared by a two-roll mill and the mixer of a Haake-90 Rheometer respectively. The blending conditions are the same, ie at 200°C and with a rotor speed of 30 rpm for 10 min. The data in the table show that the blend prepared in the Haake Rheometer exhibits higher elongation at break and tensile strength, which implies that the rheometer possesses higher compounding efficiency than the two-roll mill.

The mechanical properties of blends of a given composition (PS-2/LDPE 80/20, 10% SEBS), prepared at five different temperatures using the Haake Rheometer mixer at the rotating speed of 35 rpm for 10 min, are shown in Table 2. It can be seen that the blend prepared at 200°C exhibits better tensile properties.

Usually, in a mixing process, higher rotating speed provides stronger shearing leading to better blending. However, high shearing can result in cleavage of molecular chains and decrease of the molecular weight of the polymers. Therefore, a preferential rotor speed has to be determined experimentally. The effect of rotor speed on the mechanical properties of the blends is shown in Table 3 (the blending time is 10 min and the temperature is 200°C). It shows that the blend obtained at 35 rpm has the highest elongation and fracture strength.

Based on the above results, the optimum processing conditions have been determined as following: mixing at 200°C with a rotor speed of 35 rpm for 10 min.

The effect of the molecular weight of polystyrene on the mechanical properties of the blends was also examined and it was found that the blend containing polystyrene of low molecular weight exhibited much better toughness in the tensile testing. Therefore, in the following discussion, all of the blends were prepared using low molecular weight PS unless otherwise stated.

**Table 1. Effect of the compounding equipment on the mechanical properties of a blend**

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>Blending equipment</th>
<th>Elongation at break (%)</th>
<th>Fracture strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-2/LDPE 80/20</td>
<td>Two-roll mill</td>
<td>11</td>
<td>26</td>
</tr>
<tr>
<td>5 wt% G1652</td>
<td>Haake Rheometer</td>
<td>19</td>
<td>29</td>
</tr>
</tbody>
</table>

**Table 2. Effect of temperature on the mechanical properties of a blend**

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>Blending temperature (°C)</th>
<th>Elongation at break (%)</th>
<th>Fracture strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-2/LDPE 80/20</td>
<td>170</td>
<td>23</td>
<td>29</td>
</tr>
<tr>
<td>190</td>
<td></td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>200</td>
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<td>27</td>
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</tr>
<tr>
<td>210</td>
<td></td>
<td>24</td>
<td>28</td>
</tr>
</tbody>
</table>

**Table 3. Effect of rotor speed on the mechanical properties of a blend**

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>Rotating speed (rpm)</th>
<th>Elongation at break (%)</th>
<th>Fracture strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-2/LDPE 80/20</td>
<td>25</td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td>10 wt% G1652</td>
<td>35</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>45</td>
<td>24</td>
<td>24</td>
<td>27</td>
</tr>
</tbody>
</table>
Effect of blend composition
A series of blends with the same SEBS content (10%) and different PS/LDPE ratios (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90) were prepared under the conditions mentioned above, and the tensile mechanical properties of the blends and homopolymers were measured and are presented in Figs 1–3.

Figure 1 is a plot of the modulus ratio of the blends (EB) to LDPE (ELDPE) versus blend composition. It can be seen that the modulus of PS is about 20 times higher than that of LDPE. The modulus of the blends generally decreases with increasing LDPE content (ie the weight fraction of LDPE) over the entire composition range. However, the modulus varies slowly over the two LDPE content ranges, ie from 0 to 30wt%, and 60 to 100wt%, while it decreases sharply in the range from 30wt% to 60wt% LDPE. As expected, the ultimate tensile strength (σB) of the blends is generally decreased as the LDPE content increases (Fig 2). However, for contents of LDPE in the ranges of 10wt% to 40wt% and 60wt% to 90wt%, little change is observed.

It can be seen from Fig 3 that the elongation at break (εB) of the blends increases with increasing content of LDPE, but that it hardly changes in the range of 10wt% to 40wt% LDPE. When the content of LDPE exceeds 50wt%, the elongation increases very sharply. It is interesting to note that the elongation at break of the blends is obviously higher than that of PS even in the presence of only 10wt% of LDPE. This result confirms the success in toughening PS by blending it with LDPE. Compared with the results reported in the literature,16 we observe that the PS-rich blends

Figure 1. Variation of relative elastic modulus with LDPE content for PS/LDPE blends compatibilized by 10wt% SEBS.

Figure 2. Variation of fracture strength with LDPE content for PS/LDPE blends compatibilized by 10wt% SEBS.

Figure 3. Variation of elongation at break with LDPE content for PS/LDPE blends compatibilized by 10wt% SEBS.
prepared in this work, using selected materials and under optimum processing conditions, exhibit better toughness.

It was reported that simple PS/LDPE blends without compatibilizer usually exhibit the behaviour of incompatible blends, ie very poor ultimate mechanical properties. Meanwhile, the curves of both strength and ductility against blend composition commonly exhibit a minimum value smaller than that of either component.\textsuperscript{14,19} However, in the present case, the PS/LDPE blends containing a tri-block copolymer exhibit higher fracture strength than LDPE and much higher elongation at break than PS over the whole composition range (Fig 3). These results convincingly demonstrate that a tri-block SEBS copolymer strengthens interfacial adhesion between PS and LDPE, playing the role of a compatibilizer. Although the apparent ultimate strength of the PS-rich blends is obviously lower than that of pure PS (Fig 2), it may not reflect the variation of true ultimate strength, because the cross-sectional area of the tensile bar was greatly reduced in the tensile process after the yield point of the sample. This was not considered in measuring the strength.

Fayt and Jerome\textsuperscript{16} studied the effect of copolymer structure on the mechanical properties of PS/PE blends and concluded that a block copolymer is preferable to a graft one. However, their experimental results demonstrated that the improvement in the mechanical properties (\(\sigma_B\) and \(\varepsilon_B\)) upon addition of a triblock copolymer (SEBS, Shell chemicals, G1651) was limited and generally lower than that of di-block copolymers. Considering the lower conformational constraint of that of a diblock copolymer than a tri-block one in the interfacial area, it seems reasonable that a di-block copolymer possesses better emulsifying effect than a tri-block one. However, in our study, although a triblock SEBS copolymer was used as compatibilizer, the blends exhibited greatly improved mechanical properties. In our opinion, the great difference in the molecular weight of the tri-block copolymer used by Fayt \textit{et al} (\(\bar{M}_w=287,000\)) and by us (\(\bar{M}_w=52,500\)) can probably explain the different results. Obviously, further work is needed to elucidate the factors that determine the emulsifying efficiency of block copolymers.

**Morphology of the blends**

The SEM micrographs of cryofracture surface of blends covering a broad composition range of PS/LDPE and containing 10 wt% of SEBS are shown in Figs 4(a)–(e). In Fig 4(a), it can be seen that there exist a great many fine white particles dispersed in a matrix of PS/LDPE 80/20 blend. Based on the composition, we could assign the dispersed particles to a LDPE phase, whereas the continuous matrix is a PS phase. The average diameter of the dispersed particles is about 0.5 \(\mu\)m. As the LDPE content of the blend is increased to 30 wt\%, the micrograph reveals the formation of a co-continuous structure with interpenetrating network (Fig 4(b)). The co-continuous structure seems to exist in the PS/LDPE 60/40 blend as well (Fig 4(c)), but there are also many round particles dispersed on the surface. With an increase of the LDPE content of the blend to 60 wt\%, phase inversion appears (Fig 4(d)), ie LDPE becomes the continuous matrix, whereas PS disperses in the matrix as round particles. Similar morphology is observed in PS/LDPE 20/80 blends (Fig 4(e)).

In PS/LDPE 80/20 blends, the low-modulus LDPE component is dispersed as discrete particles anchored into the PS matrix, similarly to rubber-toughened PS in which rubber particles are dispersed in a polystyrene matrix,\textsuperscript{20} so that the mechanical behaviour of modified PS/LDPE blends is expected to be close to that of a classical toughened PS, ie higher elongation but lower modulus than those of PS.\textsuperscript{21} However, it is interesting to note that PS/LDPE 80/20 blends present only a small loss (about 20\%) in terms of modulus compared with PS, showing a much higher value than that of the usual rubber-toughened plastics. Meanwhile, the blend exhibits elongation at break as high as 60\%, higher than ABS.\textsuperscript{22}

In many cases it is well known that when SEM is used to observe the morphology of a blend,\textsuperscript{23} the image contrast can be enhanced by etching the surface of the sample. Etching can be conducted by selectively dissolving one component. However, one should be careful to avoid any artifact arising from etching. For example, when the continuous phase of a blend is etched, the dispersed phase can be lost or aggregate together, leading to a false appearance of the blend morphology.

In our study, tetrahydrofuran (THF) was chosen to extract the PS phase from the blends. Figures 5(a)–(d) show SEM photographs of the etched blends. We can see that the morphologies of the blends are clearly revealed after etching in all of these blends. Obviously, the white area associated with the remaining PE component forms the continuous phase. However, with increasing content of LDPE from 30 wt\% to 80 wt\%, the PS phase varies from an interlocked two-continuous (Fig 5(a)) structure to a semi-continuous structure (Fig 5(b)), and finally to dispersed particles (Figs 5(c) and (d)). In addition, the PS particles become finer when the content of LDPE changes from 60 wt\% to 80 wt\%.

The dependence of the mechanical properties on composition of the blends discussed previously reflects the change of morphology. It is well known that the modulus is very sensitive to the morphology variation of the blends. PS is continuous when the content of LDPE is less than 30 wt\%, so that the modulus of the blends is relatively high and does not depend strongly on the composition. When the content of LDPE exceeds 60 wt\%, LDPE becomes the continuous phase, which leads to a much lower modulus of the blends with less composition dependence. Since in the range of 30 wt\%~60 wt\% LDPE, the continuous phase changes from PS with high modulus, to LDPE
with low modulus owing to phase inversion, the modulus decreases sharply in this range.

Figure 6(a) shows the fracture surface morphology of a PS/LDPE 80/20 blend containing 10 wt% SEBS after tensile testing. The rough surface indicates that plastic deformation occurred, which is obviously different from the brittle mode of pure PS. This suggests that toughening of PS has been achieved by blending it with LDPE and adding the compatibilizer SEBS. This result is in accordance with the observations on PS/LDPE blends modified with a di-block copolymer.\textsuperscript{19} Differing from the morphology of the

\textbf{Figure 4.} SEM micrographs showing cryofracture surfaces of blends compatibilized by 10\% SEBS, (a) PS/LDPE 80/20, (b) PS/LDPE 70/30, (c) PS/LDPE 60/40, (d) PS/LDPE 40/60, (e) PS/LDPE 20/80.
cryofracture surface of the blend shown in Fig 4(a), the spherical particles of LDPE on the fracture surface cannot be found as a result of the large deformation of LDPE. This argument is further evidenced by Fig 6(b) showing the cryofracture surface of a PS/LDPE 80/20 blend along the tensile direction, after stretching. It can be clearly seen that the dispersed LDPE particles have been fibrillated along the stretching direction. Such behaviour can be explained in terms of adhesion between the LDPE particles and the PS matrix. When the sample is deformed, the stress can be transferred to the dispersed LDPE particles through the strong interface area strengthened by the compatibilizer SEBS, so that the LDPE particles deform by shearing.24

Figure 7(a) shows the fracture surface of the PS/LDPE 20/80 blend (SEBS 10 wt%) after tensile testing. The surface is covered by bunches of ruptured polymer fibrils. It is interesting to note that a number of spherical particles are dispersed among the fibres. According to the observation on the morphology of the blend without stretching (Fig 4(e) and Fig 5(d)), these spheroids are PS particles. This observation implies that the plastic deformation of LDPE predominantly contributes to the blend elongation. Figure 7(b) shows the cryofracture surface of a PS/LDPE 20/80 blend along the tensile direction after tensile test; it can be clearly seen that PS particles hardly deform and maintain spherical shape. It can be seen from Fig 1 that the modulus of PS is much larger than that of LDPE, so that PS particles are still within their elastic region even when LDPE yields. During yielding deformation of the matrix, the stress applied on PS particles depends mainly on the interfacial adhesion. As the interfaces are not strong enough to make PS particles break or produce plastic deformation (such as crazing), the PS particles maintain elastic deformation up to the breakage of the interfaces. When the external stress disappears, the PS particles recover their original shape.

The deformation mechanism of thin films of PS/LDPE/SEBS blends has been extensively studied in our laboratory by in-situ TEM observation. The samples were prepared by a solution-melt procedure.25–28 For PS/LDPE 80/20 blends, during stretch-
ing, the matrix produced great many crazes and the dispersed LDPE particles deformed by shear bands. For PS/LDPE 20/80 blends, the localized yield producing microbands within the matrix became the main deformation mechanism, whereas deformation of the dispersed particles was not observed. In addition, many voids were produced at the interfaces between the dispersed particles and the matrix when the sample was strained to a larger extent. Obviously the present observation of deformation by SEM is in good agreement with the results observed by TEM on thin films.

CONCLUSIONS

From the above discussion, the following conclusions can be drawn for blends composed of LDPE and PS with a SEBS compatibilizer:

1. The mechanical properties of the blends depend on the processing conditions such as temperature, rotor speed etc. It was found that blending at 200°C and rotating speed of 35 rpm for 10 min led to a good combination of properties.

2. The tensile tests show that the PS-rich blends compatibilized by a triblock copolymer (SEBS)
exhibit excellent toughness and elongation at break higher than that of ABS. This suggests that the triblock copolymer SEBS is an effective compatibilizer for the system.

3. SEM examination reveals that the compatibilized PS/LDPE blends exhibit a two-phase structure. For blends containing less than 30 wt% of LDPE the LDPE particles are dispersed in the PS matrix. When the LDPE content is increased to 60 wt%, phase inversion occurs, and PS becomes the dispersed phase. When the content of LDPE lies in the range 30 wt% to 60 wt% PS exhibits an interlocked co-continuous or semi-continuous structure.

4. Observations on the morphology of tensile bars show that there exist different deformation mechanisms in the blends of different compositions. For PS/LDPE 80/20 blends, plastic deformation of the dispersed LDPE particles takes place in the tensile process, whereas in PS/LDPE 20/80 blends, the dispersed PS particles hardly deform and remain spherical in shape, which is in accordance with the results detained previously by TEM.

REFERENCES