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The effect of interfacial interactions on the rheo-optical behaviour of compatibilized polystyrene/low-density polyethylene/ styrene–ethylene–butylene–styrene copolymer blends

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The influence of styrene–ethylene–butylene–styrene (SEBS) triblock copolymers on the interfacial interactions in heterogeneous polystyrene/low-density polyethylene (PS/LDPE) blends was studied by simultaneous Fourier transform infra-red (*FT*i.r.) spectroscopic and stress–strain (rheo-optical) measurements. Values of the dichroic ratio (*DR*) for a specific absorption band of the dispersed LDPE phase were determined from the polarized spectra as a function of extension (λ), and were taken as a measure of the molecular orientation of the LDPE. A linear relationship between *DR* and ln λ was found, and the slope was interpreted as a reflection of the interfacial interactions in the heterogeneous blends. The slope increased with the amount of a low-molecular-mass SEBS which was added, but was less affected by the addition of a high-molecular-mass SEBS. The difference was explained by a lower concentration of the high-molecular-mass copolymer at the interphase. Copyright © 1996 Elsevier Science Ltd.

(Keywords: rheo-optical measurements; compatibilized blends; interfacial interactions)

INTRODUCTION

The mechanical and viscoelastic properties of polymer blends are strongly influenced by the properties of the interphase. The lack of strong interphases in most blends is due to the fact that most polymer pairs form heterogeneous systems with narrow interphases. However, this problem may be overcome by the addition of a compatibilizer, which is considered to locate itself mainly at the interface between the two immiscible polymers where it increases the interaction and enlarges the interphase volume between the phases. Compatibilization may thus be an effective way to increase the adhesion and stress-transfer possibilities across the phase boundaries in heterogeneous blends.

Simultaneous *FT*i.r. spectroscopic and mechanical (rheo-optical) measurements made during the deformation emerge as an informative probing technique for gaining information on the orientation, conformation and crystallization of the different polymers, as well as on the stress transfer in heterogeneous polymer blends[1]. Rheo-optical measurements have been used to study several homopolymers[1–12], copolymers[13] and miscible polymer blends[11,14–20] in detail. The *FT*i.r. rheo-optical technique has also been used to investigate heterogeneous systems[2,21,22], but studies of the effect of interface interactions on the orientation behaviour of compatibilized polymer blends have been very rare. Khoo *et al.*[22] used this technique to study heterogeneous blends of high-impact polypropylene with a matrix of polypropylene (PP) and a dispersed phase of polyethylene (PE) and ethylene–propylene copolymer (EP). They investigated the effect of the relative molecular masses of the constituents on the interfacial interactions through monitoring the orientation behaviour of both the matrix and the dispersed PE phase. It was observed that the maximum molecular orientation of the dispersed PE phase increased with the increasing molecular mass of PE, which correlated with the increasing fibril formation. The orientation behaviour was thus explained by the presence or absence of the PE fibrils which were responsible for the stress transfer from the PP matrix to the dispersed phase.

The aim of this present work is to study the influence of styrene–ethylene–butylene–styrene (SEBS) triblock copolymers on the interfacial interactions in heterogeneous polystyrene/low-density polyethylene (PS/LDPE) blends. The influence of styrene–ethylene or styrene–butylene copolymers on, e.g. thermal conductivity, stress relaxation and creep, stress and strain at break, morphology and dynamic mechanical properties, etc., has previously been extensively studied for various PS/PE systems[23–36]. The studies have shown that SEBS is an efficient compatibilizer in various PS/PE blends and that it increases the interaction between the phases. The interfacial interactions in the PS/LDPE/SEBS blends

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were studied in this work by monitoring the orientation behaviour of the dispersed LDPE during uniaxial drawing using the *FT*i.r. rheo-optical technique. Two SEBS copolymers with different molecular masses were compared.

EXPERIMENTAL

Materials

Some physical properties of the polymers used in this work are given in *Table 1*. The PS is a commercial grade obtained from Scientific Polymer Products Inc. (no. 845) and the LDPE was obtained from Borealis AB. Two SEBS triblock copolymers (SEBS-L and SEBS-H) with different molecular masses were used as compatibilizers. SEBS-H was obtained from the Shell Chemical Company (Kraton G 1651) while SEBS-L was obtained from Scientific Polymer Products Inc. (no. 452). The molecular mass distribution, dynamic mechanical behaviour and styrene content of SEBS-L were all comparable to a commercial SEBS triblock copolymer (Kraton G 1650) from the Shell Chemical Company. All polymers were used as received.

Blending procedure and film preparation

Blends were prepared in a Brabender AEV 330 with a chamber volume of 50 cm^3. The set temperature was 180°C (end temperature, 195–200°C), the blending time was 10 min, and a rotation speed of 40 revolutions per min was used. The blends were then cooled at room temperature. PS/LDPE/SEBS-L and PS/LDPE/SEBS-H blends with a common composition of 70 volume parts of PS and 30 volume parts of LDPE were prepared, with an additional amount of 0, 1, 5 and 10 volume parts (Φ_L and Φ_H) of the triblock copolymers. The volume compositions are based on the densities at room temperature. Since transmission *FT*i.r. spectroscopy is employed, the type of samples that can be used is restricted to thin films. These were prepared in a press at 180°C by preheating for 5 min and then applying a force of 50–150 kN for 5 min in order to obtain a film thickness of 20–60 μm. Samples were then cut from the pressed film to a width of approximately 5 mm and a length of 15–20 mm (the starting distance between the clamps was approximately 12 mm). The presence of approximately spherical LDPE particles dispersed in the PS matrix in the pressed films was verified by scanning electron microscopy (SEM).

Instrumentation

Dynamic mechanical spectroscopy (d.m.s.) experiments were performed with a Rheometrics Dynamic Analyzer RDA II, operating in the oscillatory mode, in order to study the viscoelastic properties of the constituents of the blends. Samples were prepared by compression moulding the blends into the shape of a rectangular parallelepiped with approximate dimensions of 30 × 12 × 2 mm^3. The samples were then subjected to a shear strain of 0.1% at temperatures ranging from 20 to 140°C and an angular frequency of 1 rad s^{-1}.

Table 1 Physical properties of the pure polymers

Polymer	M_n (kg mol^{-1})	M_w (kg mol^{-1})	$T_{(G''\max)}$[a] (°C)	T_m[b] (°C)	PS content (wt%)
PS	97[c]	212[c]	97		
LDPE	19[d]	80[d]	–	114	–
SEBS-L	36[d]	41[d]	83	–	29
SEBS-H	76[d]	94[d]	102	–	30

[a] Temperature at G'' maximum ($\omega = 1$ rad s^{-1}) in dynamic mechanical spectroscopy (d.m.s.) experiment

[b] Peak temperature determined by differential scanning calorimetry (2nd heating run)

[c] Determined by size exclusion chromatography (s.e.c.) with PS calibration

[d] Determined by s.e.c. with linear PE calibration

A Perkin-Elmer System 7 differential scanning calorimeter was used to determine the melt temperature (T_m) of the LDPE. The sample was first heated to 150°C, then cooled down to 10°C, and finally heated again to 150°C. The heating and cooling rates were 10°C min^{-1}.

Size exclusion chromatography (s.e.c.) was used to determine the molecular masses of the pure constituents. The samples were first dissolved in 1,2,4-trichlorobenzene and then examined with a Waters 150 CV machine, equipped with a RI detector, at 135°C.

A Zeiss DSM 940A scanning electron microscope was used to study the influence of the triblock copolymers on the morphology of the blends. The samples were first fractured in liquid nitrogen, then mounted on a sample holder, gold-sputtered and finally analysed under the microscope.

The experimental principle of rheo-optical vibrational spectroscopy has been described previously[1,10,22]. A schematic diagram of the technique is given in *Figure 1*. It is based on the simultaneous acquisition of spectra and stress–strain diagrams during deformation, recovery or stress relaxation of a polymer sample. The tensile machine, with an oven[1,10] fitted with KBr windows, is placed in one of the sample chambers of the *FT*i.r. instrument, which is surrounded by a box of a transparent material, so that the stretching can be performed at different temperatures and in different environments and can also be followed visually. The rheo-optical measurements in this study were performed at two different temperatures, 40 and 105°C, in a nitrogen environment. The strain rate was 1% min^{-1} for the 40°C measurements and 2% min^{-1} for the 105°C measurements, based on the original sample length. The *FT*i.r. spectroscopic measurements were carried out by using a Perkin-Elmer FTIR 2000 system, with an adjustable wire grid silver bromide polarizer (placed before the sample) and a liquid-nitrogen-cooled mercury-cadmium telluride

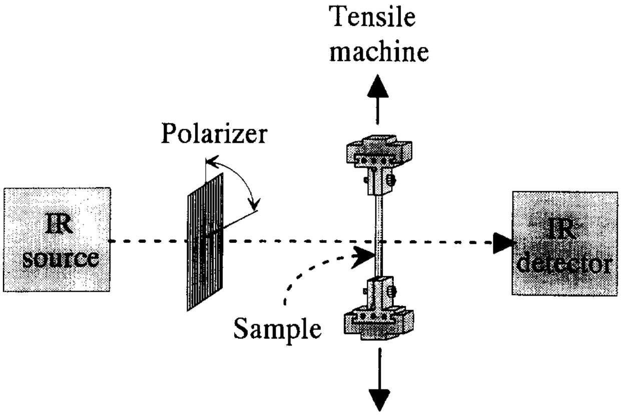

Figure 1 A schematic diagram of the experimental set-up used for the rheo-optical experiments

(MCT) detector. The resolution employed was $4\,cm^{-1}$, with each spectrum consisting of 10 scans. One spectrum was recorded every 22 s. The change-over between parallel (p) and perpendicular (s) polarization (relative to the stretching direction) was made automatically at the end of every 10 scans.

Data analysis

The analysis of the spectroscopic and mechanical data allow the correlation of macroscopic and microscopic changes in the sample during deformation. The macromolecular chains in a drawn polymer are preferentially oriented in the direction of the strain, which leads to differences between the infra-red absorptions in the s- and p-directions. To study the molecular orientation behaviour of the dispersed LDPE phase in the PS/LDPE/SEBS blends, the PS absorption was first subtracted from each blend absorption spectrum (the same polarized direction and strain value was used for the blend and subtrahend). The subtracted spectrum should then correspond to the absorptions of the dispersed LDPE phase (plus SEBS, which could not be properly subtracted). The orientation behaviour as a function of strain of the crystalline and amorphous regions of different polyethylenes has been studied in detail previously[1]. In most studies, the absorption of the band doublet at 730/$720\,cm^{-1}$ (which is assigned to the methylene rocking mode[1]) has been followed quantitatively, which allows the determination of the orientation of the crystallographic *a*-, *b*- and *c*-axes relative to the stretching direction as a function of strain. Unfortunately, we found that it is difficult to accurately determine the absorption areas of the band doublet at $730/720\,cm^{-1}$ for the LDPE phase in the subtracted spectra, as these peaks are overlapped by overabsorbed PS absorptions (maxima at 757 and $702\,cm^{-1}$) in the blend spectra. Instead, we observed that the LDPE absorption height at approximately $1464\,cm^{-1}$ (which corresponds to the scissoring motion of the CH_2 group[37]) can be more accurately determined in the subtracted spectra of the blends (the absorption band at $1464\,cm^{-1}$ was not integrated as the accuracy was less satisfactory, but the conclusions are not affected by the use of the absorbance peak). To be able to estimate the molecular orientation of the dispersed LDPE phase of the blends in this work, we have therefore determined the peak absorption height at $1464\,cm^{-1}$ for each subtracted s- and p-polarized spectrum and defined the dichroic ratio, *DR*, as follows:

$$DR = \frac{h_p}{h_s} \qquad (1)$$

where h_p and h_s are the absorbance peak heights of the LDPE absorption at approximately $1464\,cm^{-1}$ in the subtracted blend spectra for a certain strain value, in the directions parallel and perpendicular to the strain direction, respectively. To determine the heights at the same strain, h_p was taken as the mean absorbance height of the two p-polarized spectra just before and after the polarized s-spectrum for a certain strain. The orientation of the chains in the stretching direction results in h_p becoming less than h_s, i.e. *DR* decreases with increasing strain from a value of 1 in the unoriented sample. The parameter *DR* is then a measure of the molecular orientation in the dispersed LDPE phase. The orientation behaviour of the PS matrix was not studied.

RESULTS AND DISCUSSION

The dynamic shear modulus, G_d, is given at different temperatures for the pure constituents in *Figure 2*. It can be observed that PS has the highest modulus at both 40 and 105°C and that the SEBS triblock copolymers have lower moduli than the homopolymers at both 40 and 105°C. At 105°C, SEBS-L and SEBS-H have approximately the same stiffness.

Rheo-optical measurements on the blends were first performed at 40°, which is far below the glass transition of PS and the melting range of LDPE (therefore it was only possible to stretch the samples to less than 10%). An example of the absorbed light in the parallel (p) and perpendicular (s) directions of the PS/LDPE/SEBS-L (70/30/10) blend at a strain of 7% is shown in *Figure 3* for the spectral region of $1520–1420\,cm^{-1}$. A small but detectable difference between the s- and p-polarized spectra can be observed for the LDPE absorption at $1464\,cm^{-1}$ (Siesler[1] also observed that it is possible to detect the orientation of HDPE at strains lower than 10%), which indicates a small molecular orientation of the LDPE phase, but no difference can be detected for the PS absorptions (maxima at 1493 and $1452\,cm^{-1}$). In *Figure 4*, the *DR* is plotted against the extension λ ($\lambda = L/L_0$, where L is the length at a certain time and L_0 is the initial length of the sample) at 40°C for the PS/LDPE/SEBS-L (70/30/0) and (70/30/10) blends. The figure shows that the *DR* decreases with increasing extension for both samples. It can also be observed that the *DR* decreases more for the PS/LDPE/SEBS-L (70/30/10) blend than for the (70/30/0) blend. This means that the increase in molecular orientation in the dispersed LDPE phase with increasing strain is larger when the SEBS-L compatibilizer is added, which indicates that stresses are better transferred to the dispersed phase when SEBS-L is added as compared to the situation when no compatibilizer is added.

In order to be able to more accurately determine the influence of the SEBS compatibilizers on the LDPE orientation in the ternary blends, we also performed experiments at a higher temperature (e.g. 105°C), for

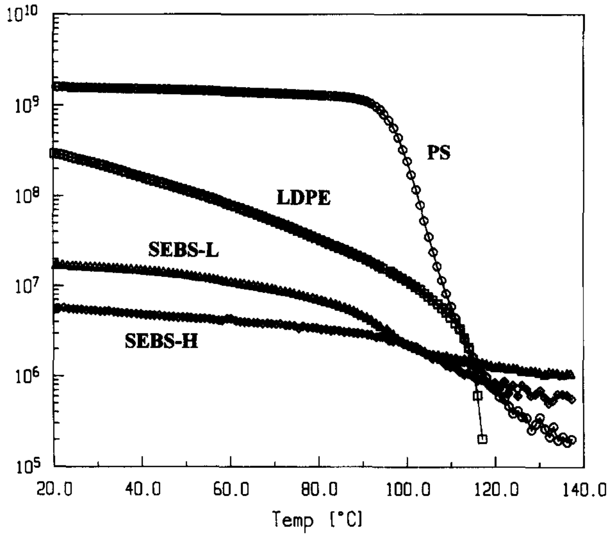

Figure 2 The dynamic shear modulus G_d as a function of temperature for the pure PS, LDPE, SEBS-L and SEBS-H polymers; a strain of 0.1% and an angular frequency of $1\,rad\,s^{-1}$ was used for all samples

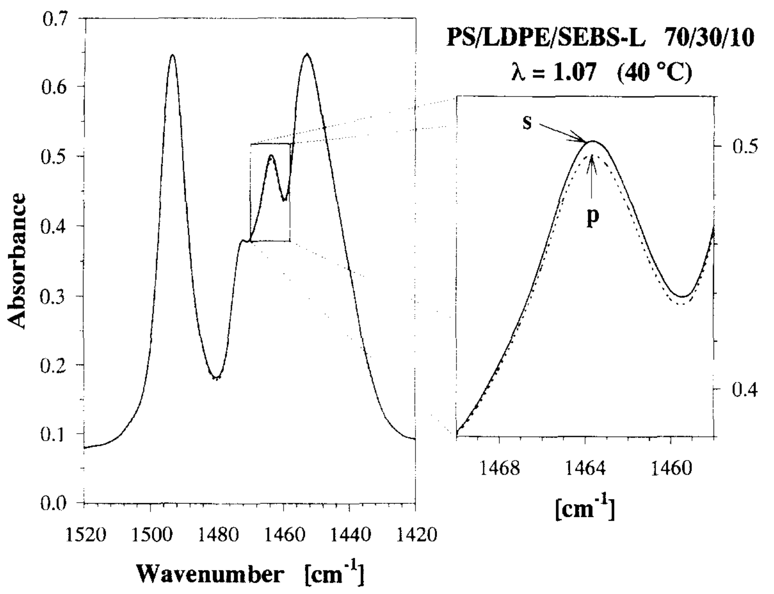

Figure 3 The absorbance at 1420–1520 cm^{-1} in the s- and p-directions (solid and dotted lines, respectively) of the PS/LDPE/SEBS-L (70/30/10) blend at an extension λ of 1.07 and a temperature of 40°C

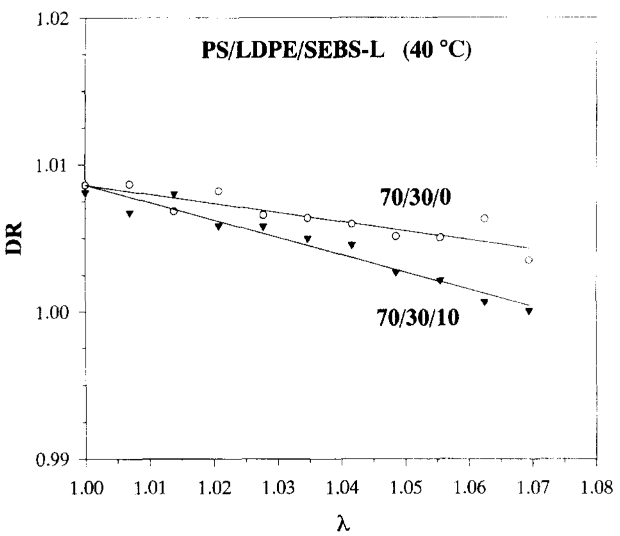

Figure 4 The DR as a function of λ for the PS/LDPE/SEBS-L (70/30/0 and 70/30/10) blends at 40°C

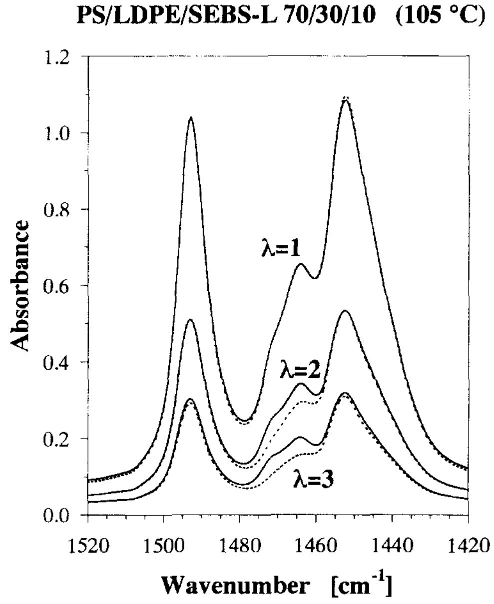

Figure 5 The absorbance at 1420–1520 cm^{-1} in the s- and p-directions (solid and dotted lines, respectively) of the PS/LDPE/SEBS-L (70/30/10) blend for extensions λ of 1, 2 and 3, at 105°C

which larger deformations are possible. This temperature is in the glass–rubber transition region of PS ($T_g = 97$°C), but still below the melting temperature of LDPE ($T_m = 114$°C). At 105°C, the blend samples showed a yield point below 10% strain, after which it was possible to draw the samples 150–250% with an approximately constant stress value (the stress–strain behaviour of the samples was qualitatively similar to the stress–strain behaviour of the PP/PE/EP blends presented previously[22]). The LDPE chains relax slowly at this temperature in relation to the time of the experiment (this was checked by holding the PS/LDPE/SEBS-L (70/30/10) blend stretched at $\lambda = 2$ and observing that the change in the DR of the LDPE phase was negligible after 1 h). An example of the orientation behaviour during the mechanical treatment of the PS/LDPE/SEBS-L (70/30/10) blend at 105°C is illustrated in *Figure 5*. It shows the absorbed light in the polarized p- and s-directions in the spectral region of 1520–1420 cm^{-1} at values of the extension λ of 1, 2 and 3. The molecular orientation in the LDPE phase is clearly detectable as a difference between the s- and p-spectra.

The results of the rheo-optical experiments at 105°C for the different PS/LDPE/SEBS (70/30/Φ_L) blends ($\phi_L = 0$, 1, 5 and 10) are given in *Figure 6*, where the DR is plotted against ln λ (the Hencky strain). The data for pure LDPE (at 105°C) are given by the dotted line. It can be observed that the data for the PS/LDPE/SEBS-L blends form approximately straight lines in the DR *versus* ln λ plot. This is different from the rheo-optical behaviour of both the pure LDPE and the PP/PE/EP blends[22], whose orientation *versus* strain curves have an S-shaped form. The difference can be explained by the fact that both LDPE and the PP/PE/EP blends show

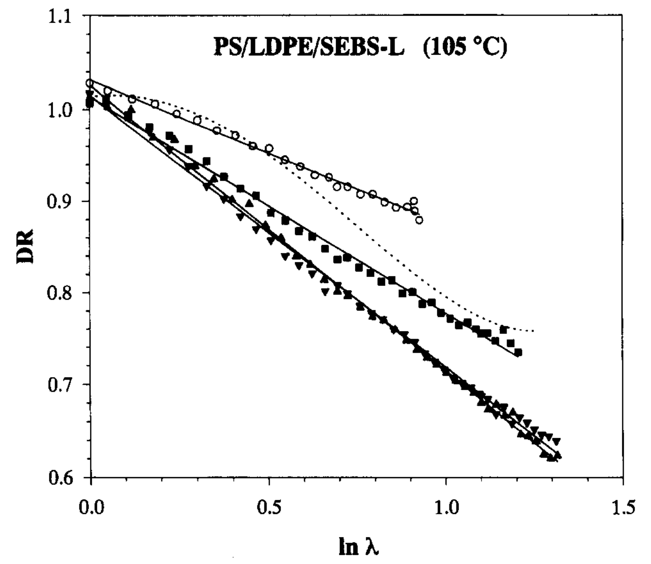

Figure 6 The *DR* as a function of ln λ for various PS/LDPE/SEBS-L blends at 105°C: (○) 30/70/0; (■) 30/70/1; (▲) 30/70/5; (▼) 30/70/10. The dotted line corresponds to the data for pure LDPE and the solid lines represent the linear regression of the experimental data points

necking during deformation, which was not observed for the PS/LDPE/SEBS-L blends (LDPE and PP show a clear necking behaviour, while PS does not). The PP/PE/EP blends could thus only be compared at their maximum orientation levels. The homogeneous deformation behaviour of the PS/LDPE/SEBS system allows us to follow and compare the orientation behaviour during the whole stretching procedure.

It can be observed in *Figure 6* that even a small addition of SEBS-L ($\Phi_L = 1$) increases the orientability, i.e. the degree of molecular orientation in the dispersed LDPE phase per unit strain. The orientability increases with an increasing amount of added SEBS-L up to a level of $\Phi_L = 5$, after which any additional amounts of SEBS-L do not further increase the orientability. As the *DR* is a measure of the internal strain in the dispersed LDPE phase, while λ is a measure of the external strain, the experiments thus show that the internal strain is empirically related to the external strain according to the following relationship:

$$DR = \alpha - \beta \ln \lambda \qquad (2)$$

where α and β are constants determined by linear regression of the experimental data points (the constants are given for the PS/LDPE/SEBS-L (70/30/Φ_L) system in *Table 2*). As the molecular orientation is approximately random in the unstretched samples ($\ln \lambda = 0$), α is close to zero for all samples. The reason why the α values are not exactly equal to zero is that there is a minor orientation of the dispersed LDPE phase originating from the pressing of the films. It can be argued that β is a measure of the orientability of the LDPE phase, which depends on the amount of SEBS-L that is added. As β increases with increasing amounts of SEBS-L, and as it is assumed that the compatibilizer exists primarily at the interphase[34], it can also be argued that β is a factor that reflects the effect of the interaction between the phases in the interphase. From this reasoning, it follows that it is likely that the adhesion between the phases increases continuously with the addition of up to 5 volume parts of SEBS-L, and then remains constant with further additions of the SEBS-L compatibilizer. It should be noted that β is also positive for the PS/LDPE (70/30) blend without any compatibilizer. This positive value of β cannot be assigned to the adhesion between PS and LDPE, but is instead an effect of the normal forces acting on the dispersed phase during stretching. The β values should thus be used as relative values, which can be compared for different compatibilized blends of a certain matrix/particle phase system under specific experimental conditions.

Figure 7 gives the corresponding *DR versus* ln λ data for the different PS/LDPE/SEBS-H (70/30/Φ_H) blends (Φ_H = 0, 1, 5, and 10). It can be observed that the data in *Figure 7* also follow the relationship given in equation (2) (the constants α and β are given in *Table 2*). However, two major differences can be observed when compared with the results obtained for the PS/LDPE/SEBS-L system. First, the effect of adding SEBS-H to the PS/LDPE (70/30) blend on the orientability of the molecules in the dispersed LDPE phase is much smaller than that obtained when adding SEBS-L. Secondly, the orientation behaviour of LDPE is approximately independent of the amount of SEBS-H which is added. *Table 2* shows that β increases when 1 volume part of SEBS-H is added, but then decreases slightly with increasing amounts of SEBS-H. The orientation behaviour of the PS/LDPE/SEBS-H system indicates, using the same argument as

Table 2 Values of the constants α and β as determined by linear regression from the *DR* vs. ln λ data

	PS/LDPE/SEBS-L (70/30/Φ_L)		PS/LDPE/SEBS-H (70/30/Φ_H)	
Φ	α	β	α	β
0	1.031	0.157	1.031	0.157
1	1.014	0.236	1.033	0.220
5	1.026	0.311	1.021	0.205
10	1.015	0.296	1.018	0.196

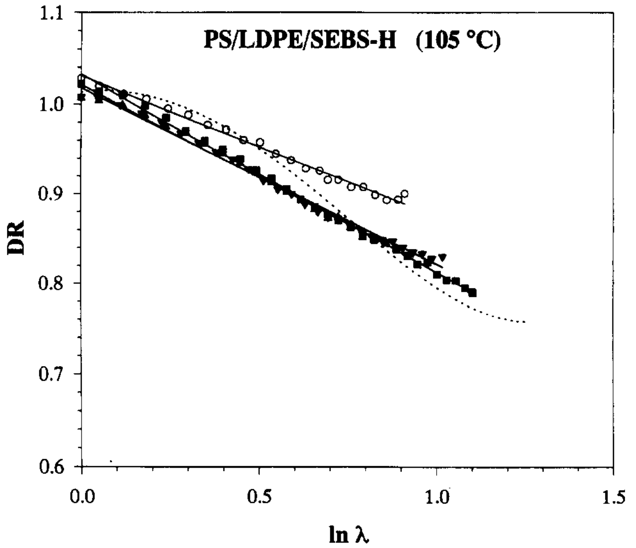

Figure 7 The *DR* as a function of ln λ for various PS/LDPE/SEBS-H blends at 105°C: (○) 30/70/0; (■) 30/70/1; (▲) 30/70/5; (▼) 30/70/10. The dotted line corresponds to the data for pure LDPE and the solid lines represent the linear regression of the experimental data points

above, that the adhesion between the phases reaches a maximum with the addition of 1 volume part of SEBS-H to the PS/LDPE (70/30) blend.

Previous studies[38,39] have shown that the ability of a compatibilizer to transfer stress across the phase boundaries depends on its molecular mass. Brown *et al.*[39] showed that the toughness (which reflects the efficiency of the coupling agent) of blends between PS and poly(methyl methacrylate) (PMMA), that were compatibilized by PS-PMMA copolymers, increases with an increasing molecular mass of the compatibilizer up to a certain level, after which the toughness remains constant. The amount of compatibilizer needed to reach the maximum toughness increases, however, with the increasing molecular mass of the compatibilizer, which means that there exists an optimum molecular mass of the compatibilizer in this system. It is possible that there also exists an optimum molecular mass for the SEBS in the PS/LDPE blends and that the molecular mass of SEBS-L is closer to this than the molecular mass of SEBS-H. However, we would then expect that the orientability would increase with Φ_H, but we observe instead that the orientability is almost constant when Φ_H increases from 1 to 10.

A more reasonable explanation for the differences between the PS/LDPE/SEBS-L and PS/LDPE/SEBS-H systems is instead a less efficient concentration of the copolymer at the interphase in the PS/LDPE/SEBS-H blends. This is in agreement with the conclusion of Schwarz *et al.*[33], who studied the effect of different SEBS triblock copolymers (Kraton G 1651, which is the same as the SEBS-H used here, and Kraton G 1652, which has a lower molecular mass than SEBS-L). They observed that the impact strength and the strain at break were larger when Kraton G 1652 was used as the compatibilizer, which was explained by the less efficient mixing of Kraton G 1651 as a result of its higher blending viscosity. A less efficient concentration of SEBS-H at the interphase can also be explained by the fact that the critical micelle concentration rapidly decreases with the increasing molecular mass of the compatibilizer[40]. The results thus indicate that SEBS-L is more concentrated at the interphase than SEBS-H, which results in a larger interfacial interaction in the PS/LDPE/SEBS-L blends, leading to an increased stress transfer between the phases.

The rheo-optical results are in agreement with SEM experiments. In the PS/LDPE (70/30) blend, dewetting of the LDPE particles is observed and fracture takes place between the phases. The dispersed LDPE phase size decreases with an increasing amount of SEBS-L, with the samples fracturing through both phases (and not at the interfaces) when SEBS-L is added. However, in the PS/LDPE/SEBS-L (70/30/10) blend, separate particles which are smaller than the dispersed LDPE phase can be observed in the PS matrix and the LDPE particles, which indicates that SEBS-L forms separate phases when the SEBS-L content is high. This may explain why the orientability, i.e. the interfacial interaction, does not increase when the SEBS-L content exceeds 5 volume parts. In contrast to the PS/LDPE/SEBS-L system, the PS/LDPE/SEBS-H system shows a different fracture behaviour, i.e. the blends have a stronger tendency to fracture at the interface in the PS/LDPE/SEBS-H system, which indicates that the interfacial interactions between the PS and LDPE phases are weaker in this system. The dispersed phase size is also not reduced as much when SEBS-H is added.

CONCLUSIONS

In this work, we used a *FT*i.r. rheo-optical technique to study the orientation behaviour of the dispersed LDPE phase in PS/LDPE/SEBS blends. The effect of the amount of the added SEBS copolymer was investigated. Two SEBS triblock copolymers with different molecular masses were used. The results show that the dichroic ratio is linearly dependent on the Hencky strain for all of the blends. The slope β of these straight lines is a measure of the orientability, i.e. the degree of molecular orientation of the dispersed LDPE phase per unit strain. For the PS/LDPE/SEBS-L (70/30/Φ_L) blends, the orientability, and thus the adhesion between the PS and LDPE phases, increases continuously when Φ_L increases from 0 to 5, but then remains constant with further addition of SEBS-L. This is in agreement with the SEM results. The orientability for the PS/LDPE/SEBS-H (70/30/Φ_H) blends is less dependent on Φ_H and less than the orientability of any of the blends when SEBS-L is added. This is primarily explained by the copolymer in the PS/LDPE/SEBS-H blends being less concentrated at the interphase. It can be concluded that this rheo-optical technique can be a valuable tool for studying the effect of compatibilizers on the orientation behaviour of the different phases in compatibilized polymer blends.

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