

EFFECT OF SEBS COPOLYMERS ON THE INTERFACIAL STRENGTH BETWEEN POLYSTYRENE AND LOW DENSITY POLYETHYLENE

Chatchai Kunyawut^{1,*} and Julia S. Higgins²

Abstract

The relative interfacial strengths of poly(styrene-*block*-ethylene/*butylene-block*-styrene) triblock copolymers (SEBS) modified interfaces of immiscible polymers, polystyrene (PS) and low density polyethylene (LDPE), has been studied using peel test. Specimens were prepared by spin coating thin SEBS triblock copolymer films from solution onto LDPE slab. After spin coating and drying in a vacuum oven at 40°C for several days, the LDPE slabs were placed on top of them, forming the "sandwich" arrangement. The 90° peel test arrangement was employed because the PS is stiff at room temperature whereas the LDPE is flexible. For thin copolymer layer (expected to leave the interface unsaturated), the trend in variation of interfacial strength with copolymer molecular weight was observed. However, for thick layers (oversaturating interface) the interfacial strength became in one case too large to separate the layers in the peel test. This may suggest a different mechanism for increasing interfacial strength when at least one of the copolymer blocks is crystallisable. Moreover, The microstructure morphology of the copolymers at the interface is expected to change during annealing time since it was found that the interfacial strength changed with annealing time.

Keywords: AFM, SEBS, interfacial strength, peel test.

Introduction

The use of a compatibilizer, normally a block copolymer, is necessary to improve the interface when an immiscible polymer blend exhibits poor mechanical properties due to weak adhesion between the phases. Preferably, the block copolymer chosen should have not only a good emulsifying ability (reduction of the interfacial tension leading to a finer morphology) but also a good interfacial activity (penetration of the segments of a block copolymer into its respective homopolymer leading to an improvement in the adhesion between the phases). There are no direct means to measure interfacial strength of immiscible blends (Brown and Yang, 1992). Over the years, a simple technique called the peel test has been, therefore, employed to evaluate the interfacial strength of immiscible blends (Setz *et al.*, 1996; Heck *et al.*, 1997; and Hermes *et al.*, 1998b). Peel tests are commonly used to measure the adhesive strength between thin films. However, since peel tests cause macroscopic deformation of the specimen, the adhesive strength measured is a practical adhesion and does not represent the true interfacial strength (Kim *et al.*, 1989).

¹ Department of Chemical Engineering, Rajamangala University of Technology Thanyaburi, Pathumthani, 12110, Thailand.

* To whom correspondence should be addressed

² Department of Chemical Engineering and Chemical Technology, Imperial College, London, SW7 2BY, UK.

Over the years, a number of studies on the effect of block copolymer on the interfacial strength between immiscible homopolymers have been carried out by several workers (Brown, 1989; Cho *et al.*, 1990; Creton *et al.*, 1990, 1992; Washiyama *et al.*, 1993b, 1994; Brown *et al.*, 1993; Char *et al.*, 1993; and Hermes and Higgins, 1998a). Using an asymmetric cantilever beam test, Brown, Creton, Kramer and co-workers have shown in glassy systems that diblock copolymer film can considerably increase the adhesion between immiscible polymer interfaces. These authors have also generally found that the principal variables governing the interfacial strength of diblock copolymer-modified interfaces are the areal chain density, Σ , of the block copolymer at the interface and the molecular weights of the copolymer blocks. For a symmetric diblock copolymer, Σ can be estimated from the copolymer layer thickness (or copolymer amount at the interface) by assuming that one diblock polymer chain contributes only one joint across the interface due to well organised structure near the interface (Char *et al.*, 1993). Hence, $\Sigma = \rho t N_A / M_w$, where ρ is the density of the diblock copolymer, t is the thickness of the copolymer, N_A is Avogadro's number, and M_w is the weight average molecular weight of the copolymer.

For copolymers with a high molecular weight ($M_w \gg$ molecular weight of entanglement, M_e), two failure mechanisms are possible depending on the areal chain density of a copolymer at the interface. If copolymer areal densities are less than a critical value Σ_c chain scission of the block copolymer chains near the junction between the two blocks is likely to occur as at these areal densities the total stress required to break the copolymer chains $\sigma_{scission}$ is less than the crazing stress of the homopolymers, σ_{craze} . On the other

hand, if areal densities of copolymer are greater than Σ_c , $\sigma_{scission}$ exceeds σ_{craze} , and it is expected that the interface will fail by crazing in the homopolymer with the lowest crazing stress. It has been reported for copolymers with high M_w that the strength of the interface is proportional to Σ^2 (Char *et al.*, 1993). For copolymers with intermediate degree of polymerisation, a transition from chain pullout to crazing is expected to occur. Washiyama *et al.* (1993a) have shown in the PS/Poly(2-vinylpyridine) (or PS/PVP) system with PS-b-PVP copolymer film placed at the interface that this transition occurred at 0.04 chains/nm².

For copolymers with a low molecular weight, i.e. $M_w < M_e$, the failure mechanism is expected to arise mainly from chain pullout when S is less than the saturation areal density, S_{sat} . This is because the total stress required for chain pullout, $S_{pullout}$, is less than S_{craze} . Creton and co-workers found that for $S < S_{sat}$, the strength of the interface is proportional to S . Note that when copolymer thickness is greater than half of the lamellar microdomain morphology of the copolymer in the bulk, $0.5L_o$, the interface becomes saturated with copolymer (Russell *et al.*, 1991b). If the copolymer areal density exceeds S_{sat} , additional copolymer chains form micelles, lamellae or some other structure at the interface leading to secondary interfaces which are weaker than the original saturated homopolymer one (Washiyama *et al.*, 1993a). This was the case for symmetrical diblock copolymers which formed lamellae at the interface when $\Sigma > \Sigma_{sat}$. Washiyama *et al.* (1993a) also found, however, that for asymmetrical diblock copolymers, which formed spherical micelles on one side of the interface at high copolymer areal densities, the interfacial strength remained constant at the maximum value attained when $\Sigma \approx \Sigma_{sat}$. The effects of block copolymers on

glassy-semicrystalline and glassy-rubbery interfaces have been less widely studied especially for the case of triblock copolymers. Thus, the correlations between block copolymer molecular weight and interfacial strength are not as well understood as for glassy-glassy systems (Hermes and Higgins, 1998a).

The objective of this study is to investigate an improvement in adhesion when a SEBS triblock copolymer film is placed at the PS/LDPE interface using the peel test.

2. Materials and Methods

Materials

The polystyrene (PS) used was provided by BP Chemical Company ($M_w = 250,000$, polydispersity = 2.2). The low-density polyethylene (LDPE) (Stamylan LD2100 TN00) is a commercial product of DSM, The Netherlands ($M_w = 121,000$, polydispersity = 12.3). The molecular weights of the homopolymers were determined using GPC technique performed by RAPRA Technology Ltd., UK. All homopolymers were obtained in pellet form. The SEBS triblock copolymers used are commercial products of Shell Development Company: Kraton G1651 and Kraton G1652. The number average molecular weight, M_n , values of the SEBS were obtained from the supplier and are shown in table 1.

Table 1 Molecular characteristics of SEBS

SEBS	Total M_n	Mid-Block (PEB) M_n	End-Block (PS) M_n	PS (%)
G1651	240,000	160,000	39,000	33
G1652	55,000	39,000	8,000	29

Methods

The ellipsometry technique was employed to determine the thickness of the SEBS copolymer films prepared by spin coating from solution onto silicon substrates. The solvent used was toluene and the spin speed of 2,000 rpm was used. The effect of the spin

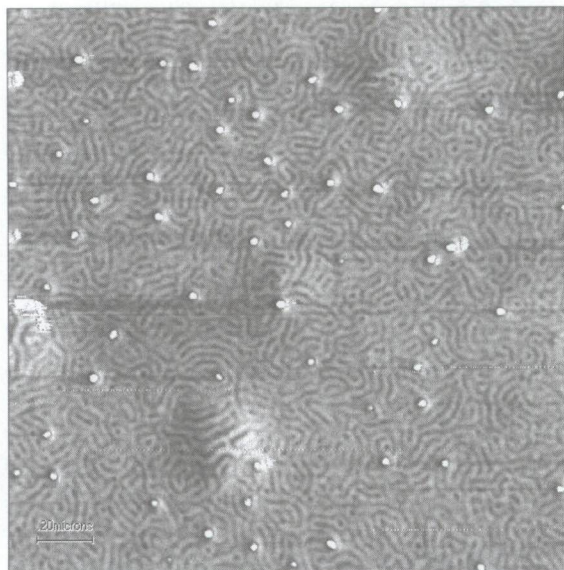
speed on the thickness of the films prepared was studied by Hermes (1996). Concentrations of copolymer solution used for preparing thin films with different thicknesses were 0.5, 1 and 2 wt/vol%. The ellipsometry measurements were carried out on a null ellipsometer (I-Elli200, Nanofilm Technology GmbH: Newark, USA) at the ISIS facilities of the Rutherford Appleton Laboratory (RAL): Oxon, UK. By using software provided by the manufacturer, only one parameter which is the refractive index of the sample is required for calculation of the phase difference and amplitude ratio which fit the measured data. The thickness of copolymer film obtained is shown in table 2 for each concentration. The thickness of the copolymer films is an average value of the thicknesses obtained from several areas of the sample surface.

Table 2 Copolymer film thickness.

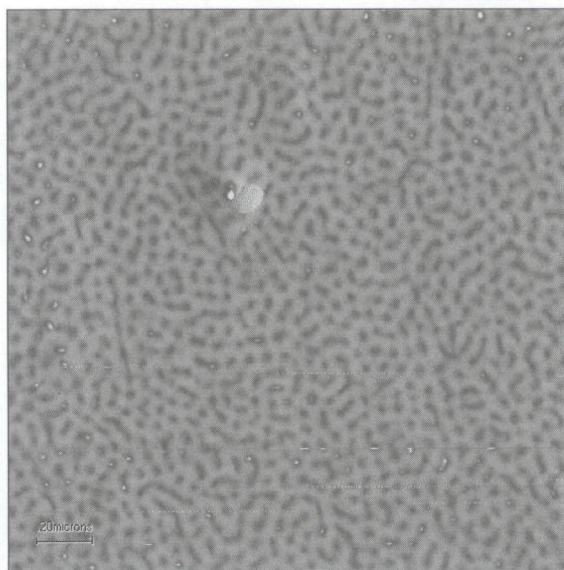
Concentration wt/vol%	Film thickness (Å)	
	SEBS(G1651)	SEBS(G1652)
0.5	230.0	240.0
1.0	411.3	403.3
2.0	1,572.0	1,540.0

Before conducting peel test experiments, the microstructure and microphase domains of the SEBS copolymer films were first investigated using AFM technique. This is necessary in order to determine whether the PS/LDPE interface is saturated with the block copolymer as the interfacial strength is strongly dependent on the areal chain density of the block copolymer. Assuming that segments of a symmetric diblock copolymer will be well miscible with the corresponding homopolymer phases, Russell *et al.* (1991a, 1991b) suggested that the interface becomes saturated with copolymer when the copolymer film thickness placed between the homopolymers exceeds the half

period of the lamellar microdomain morphology of the copolymer in the bulk, 0.5L.



(a) SEBS(G1651)



(a) SEBS(G1652)

Figure 1 AFM topographic images of thin films of (a) SEBS(G1652) (29 wt% of PS Blocks), (b) SEBS(G1651) (33 wt% of PS Blocks)

In this work, the tapping mode atomic force microscopy (TMAFM) was used to investigate the microstructure and microphase domains of the SEBS copolymer films. The SEBS films were prepared by dissolving each SEBS in toluene with a concentration of 2 wt/vol% and then coating on fresh glass slides at a spinning speed of 2,000 rpm after filtering the solution through a Millipore Teflon filter (0.2 μm). The films were annealed at 100°C for 72 hours under vacuum (0.5 torr) and cooled down to room temperature. The AFM experiments were performed using an atomic force microscope model: NanoScope IIIa MSP, Digital Instruments Company: Santa Barbara, California, USA. The film thickness thus obtained was about 1500 Å. Figures 1a and 1b show AFM topographic images of the SEBS films.

The relative interfacial strengths of the SEBS triblock copolymers modified interfaces were determined by using the peel test in the same fashion performed by Hermes (1996) with the constant peel rate and sample dimensions. The properties of the peel arm (LDPE) and peel substrate (PS) were constant, since these were the same in all cases. The variations in the samples were the molecular weight of the SEBS triblock copolymers, thickness of the copolymer layer placed between the PS and LDPE and the annealing times. Therefore, the measured peel force can be used to rank the copolymers in terms of their effectiveness as interfacial strength improvers. It should be noted that because a considerable portion of the peel energy is dissipated as plastic bending of the interface, there is no simple correlation between the measured peel force and the absolute strength of the interface, though the characteristics of the peel arms and the peel rate are kept constant (Kinloch *et al.*, 1994).

Specimens were prepared by spin coating thin SEBS triblock copolymer films from solution onto the LDPE slab. Concentrations of copolymer solution used for preparing thin films were the same as for the case of ellipsometry measurements. After spin coating, the LDPE slabs were placed in the petri dishes with the coated side up, and then placed in a vacuum oven at 40°C for several days to ensure that all the residual toluene had been removed. The LDPE slabs were then removed from the petri dishes and PS slabs were placed on top of them, forming the "sandwich" arrangement. A piece of mylar film was placed between the PS and the LDPE at one end of the "sandwich" to prevent adhesion at this point, and provided a starting point for the peel test. The sample was then placed in a mould which was approximately 0.2 minutes thinner than its total uncompressed thickness. The mould was then placed in the preheated hot press (at a temperature of $150\pm 3^{\circ}\text{C}$) and heated for approximately 3 minutes without applying any pressure. A load of 100 kN was then applied to the mould. The annealing time was measured from this point and varied from 100 to 200 minutes to allow studying the effect of annealing time on the interfacial strength. The annealing temperature of 150°C was chosen partly because most experiments reported in the literature use an annealing temperature of 50°C above the highest glass transition temperature of the sandwich components ($T_g(\text{PS}) \approx 100^{\circ}\text{C}$). After annealing under pressure for the required length of time, the heating was switched off and cooling water was used to cool the specimens as rapidly as possible while still in the press. The specimen temperature dropped to below the T_g of the PS within 5 minutes. Once the plate temperature had reached approximately 15°C , the mould was removed from the press. The peel specimens were then carefully

removed from the press and placed in drawstring plastic bags. They were stored in a dark place until required for testing (storage time ≈ 1 month).

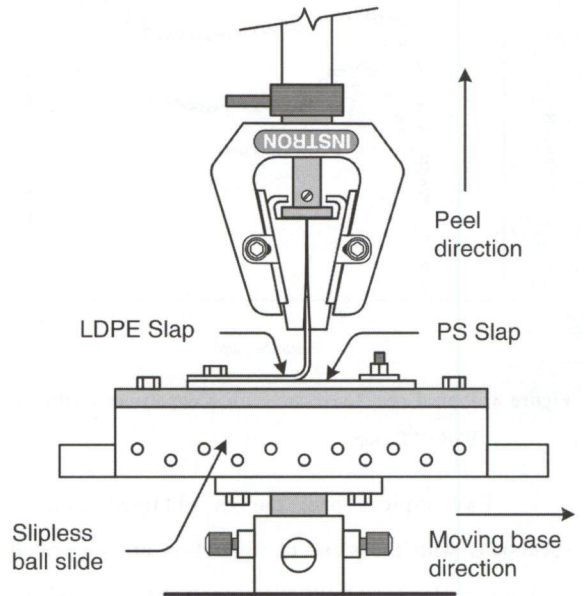


Figure 2 Peel test arrangement used (adapted from Hermes *et al.*, 1998).

The 90° peel test arrangement shown in figure 2 was used because the PS is stiff at room temperature whereas the LDPE is flexible. The peel specimens were mounted on a slipless ball slide which was attached to the base plate of an Instron Model 1185 apparatus. The slipless ball slide ensures that the angle between the PS base and the LDPE peel arm is maintained at 90° . The peel specimen was held in place by a single screw through one end of the specimen and a plate across the front of the PS slab, as shown in figure 2. The peel arm was attached to the force-measuring head via the clamp shown. The measurements were all carried out at room temperature (approximately 20°C). The experiment was performed by moving the force-measuring head upwards at a constant speed of 1

mm/min. For each specimen configuration, five repeat specimens were measured.

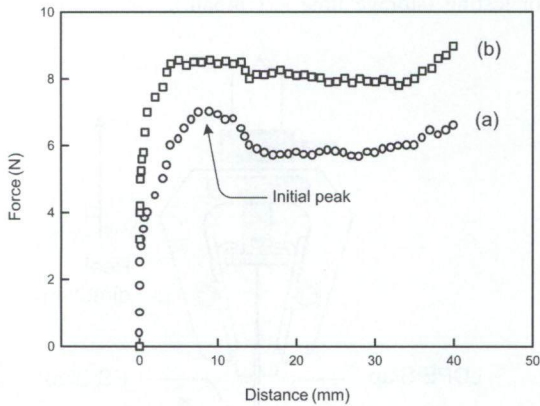


Figure 3 Typical peel force curve for a copolymer reinforced PS/LDPE slab.

Two typical peel curves obtained from 2 specimens with the same configuration are illustrated in figure 3. Hermes (1996) also reported these kinds of peel curves found on PS/LLDPE samples with diblock copolymers. The horizontal axis is the distance that the force-measuring head has moved upwards. This is equal to the length of interface that has been peeled apart, if no extension of the peel arm occurs. The vertical axis is the force recorded on the peel arm as this is related to the interfacial strength of the specimen. In figure 3, curve (a) exhibits an initial peak. This is caused by the development of the peel arm, i.e. the formation of the 90° bend, and is a result of the elastic and plastic bending of the peel arm. The peel force dropped to a constant level when the peel arm had developed and the interface started to separate. This drop is due to elastic recovery of the peel arm (Hermes, 1996). Curve (b) does not exhibit this initial peak because the PS and LDPE slabs had been separated more than case (a) during set-up of the experiment. The peel arm was, therefore, already developed prior to measurement. After

development of the peel arm, both curves have a similar shape: an initial approximately flat part from which the peel force is taken followed by an increase in the force. The increase is due to the crack tip beginning to interact with the screw holding the sample in position. The force necessary to separate the PS and LDPE slabs was determined from an average of the force obtained from the flat part of the curve for those specimens that exhibited a reasonable peel trace. The average peel force was normalised by the width of the specimen to calculate the peel strength (N/mm). Due to some of the measurement errors described below, the results for all 5 specimens were not always included in the average peel force quoted in results and discussion section.

There were several sources of error, which might invalidate the peel test results. The most dramatic of these was the effect of temperature. If the test specimens were stored and tested at different temperatures, the measured peel force could be different from those stored and tested at the same temperature. This source of error was minimised by placing the test specimens in a test room at least over night prior to testing. Another significant source of error arose from the sample preparation method used. It was found that there was some overlap of the top layer leading to a significant increase in the measured peel force. This problem was remedied by separating the overlap from the PS substrate at the edge of the sample using a scalpel. The toluene used to deposit the copolymer onto the LDPE may in itself improve the adhesion between the PS and LDPE layers. Therefore, in order to investigate this, a sample was prepared in the same manner as described above, but using pure toluene instead of copolymer in toluene solution. No improvement of the interfacial adhesion was found, i.e. as in the case where no copolymer

is presented, the act of removing the test specimen from the annealing mould was sufficient to separate the PS and LDPE slabs.

3. Results and discussion

As seen in figures 1a and 1b, the AFM topographic images reveal that there are two types of SEBS films. The characteristic morphologies consisting of hills (bright portions) and valleys (dark portions) were obtained. Such a topography is a result of the difference of the free surface energies (surface tension) between PS and PEB (Motomatsu *et al.*, 1997). Generally, in the formation process of the surface phase-separated structure, segments with low surface free energy tend to cover the air-polymer interfacial region in order to minimise the interfacial free energy. However, Tanaka *et al.* (1996) have found experimentally in thin films (~1,000 Å) of immiscible blends prepared by spin coating that the phase having lower surface energy is preferably spread out over the film surface. This is because the time required for the formation of surface structure is fairly short (i.e. less than 30 seconds) due to a rapid evaporation of solvent from the surface (prepared by spin coating) in comparison with that of the thick film (normally prepared by solvent casting). Therefore, if the total surface area of the thin film remains constant, the phase with higher surface energy will protrude from the film surface. Considering the SEBS films studied, the hills correspond to PS and the valleys to PEB as PS segments have higher surface tension (~39-43 mN/m@20°C) than PEB segments (~30-34 mN/m@20°C) (Hermes *et al.*, 1998b and Motomatsu *et al.*, 1997). Moreover, this is also confirmed by the fact that with increasing ratio of the PS component, the hills grow from long worm-like to mesh-like microphase domains as seen in figures 1a

and 1b. According to the AFM topographic images of the SEBS films illustrated in figure 1, the interdomain distance between the PS microdomains, L_o , (defined in figure 4) can be estimated using an AFM software and is approximately 555 Å and 333 Å for the SEBS(G1651) and SEBS(G1652) respectively.

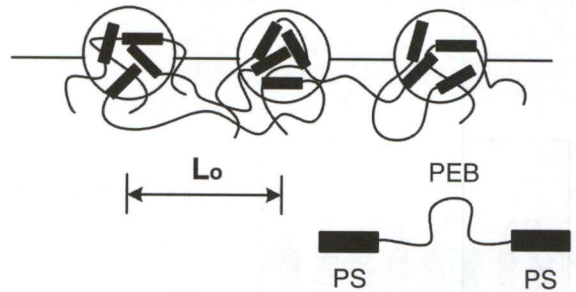


Figure 4 Schematic drawings of the surface structure of SEBS films showing the formation of self-organised structure of PS (cross sectional view). The hard segment of PS is represented as rectangular blocks and the rubbery segment of PEB as strings. (adapted from Motomatsu *et al.*, 1997).

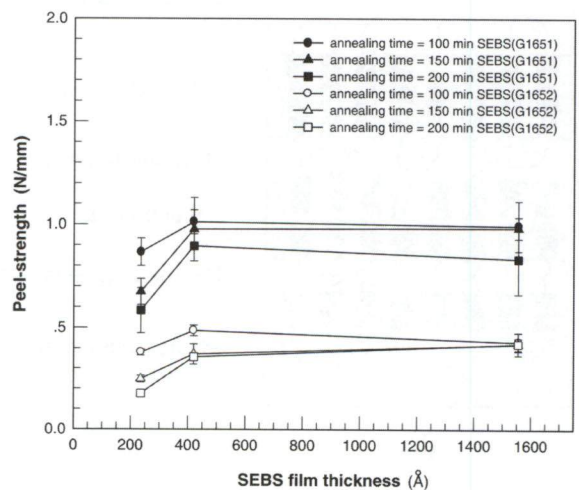


Figure 5 Peel strength as a function of film thickness of SEBS(G1651) and SEBS(G1652) placed between PS and LDPE bars.

Figure 5 summarises all results of the peel tests. The film thickness used for plotting is an average value of the thickness of films prepared from solution of each SEBS having the same concentration. A temperature of $150 \pm 3^\circ \text{C}$ was used for annealing the test specimens. Note that unless specified otherwise, the interfacial strength of the test samples is presented in

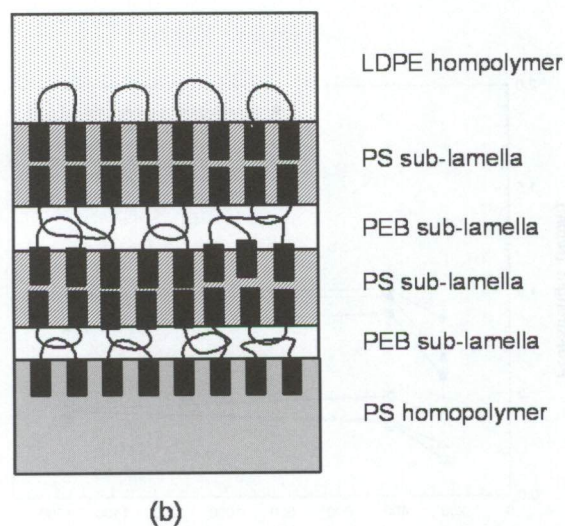
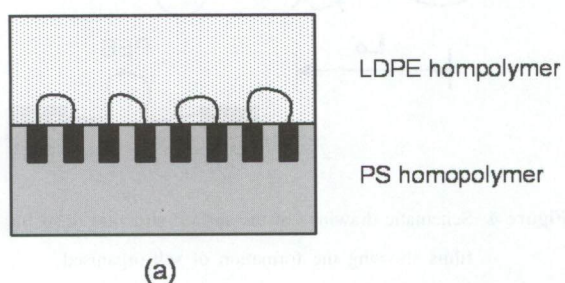


Figure 6 Schematic representation of chain conformation of SEBS (a) unsaturated interface, and (b) saturated interface PS/LDPE.

terms of peel strength throughout this section. Measuring the interfacial strength between PS and LDPE without addition of copolymer was not possible because removing the specimen from the annealing mould was sufficient to cause the two layers to separate (Hermes, 1996). As seen in the figure, the peel strength for the PS/SEBS(G1651)/LDPE systems is found to be higher than that of the PS/SEBS(G1652)/LDPE systems. This is attributed to the longer segments of copolymer blocks of SEBS(G1651) which have higher ability to form a junction across the interface through which stress can be transferred. According to the work of Tanaka *et al.* (1991), the miscibility of a copolymer with homopolymer will increase if the molecular weight of the blocks of copolymer is close to that of the corresponding homopolymer.

Since the thickness of the SEBS films prepared is equal to or exceeds $0.5L_o$, the PS/LDPE interface is expected to be saturated with the copolymer that is $\Sigma \geq \Sigma_{\text{sat}}$. Note that if the "staple structure" illustrated in figure 6 is well organised at the interface, Σ_{sat} of a triblock copolymer will be half of Σ_{sat} of a diblock copolymer. Therefore, a failure mechanism at the PS/LDPE interface by chain scission or chain pullout of the SEBS copolymers where the PEB blocks are miscible with the LDPE phase and the PS blocks are miscible with the PS phase, as described in the literature section for the case of $\Sigma < \Sigma_{\text{sat}}$, is no longer applicable directly to this study (see figure 6a). However, failure by chain pullout is expected occur at the LDPE/SEBS interface (see figure 6b). This can be explained by the fact that uncrosslinked rubbery polymers above their T_g are relatively mobile and chain pullout may still occur relatively easily although the molecular weights of the PEB blocks of the copolymers (see table 1) used

are much greater than $M_c(\text{PB})$ ($\sim 2,000 \text{ gmol}^{-1}$) (Hermes *et al.*, 1998b). At the PS/SEBS interface, as the molecular weights of the PS blocks of the SEBS(G1652) are lower than $M_c(\text{PS})$ ($\sim 20,000 \text{ gmol}^{-1}$) (Hermes and Higgins, 1998a), chain pullout from the PS homopolymer phase is expected to occur easily. By contrast, the molecular weight of the PS blocks of the SEBS(G1651) is greater than $M_c(\text{PS})$, so that the PS blocks are expected to be strongly anchored in the homopolymer phase. Therefore, the interface for this case would fail by crazing. However, the peel strength of the SEBS(G1651) system illustrated in figure 5 is significantly lower than that expected for crazing, thus the interfacial failure can only be expected to arise from chain pullout.

It can be seen in figure 5 that an increase in the peel strength was observed when the film thickness was increased from 235 to 407 Å. This may be because the PS/LDPE interface is not fully saturated with the copolymers as expected based on the criterion of $0.5L_0$, when the SEBS film of about 235 Å thickness was placed at the PS/LDPE interface; and the peel strength is still proportional to Σ (chain pullout). Further increase in the film thickness (from 407 to 1,552 Å) provided no increase in the peel strength. These data indicate that the SEBS films of 407 Å and 1,552 Å thickness fully saturate the PS/LDPE interface and $\Sigma \geq \Sigma_{\text{sat}}$. Hence, the peel strength is no longer dependent on Σ . This behaviour was found in both SEBS(G1651) and SEBS(G1652) films.

It has been reported that the peel strength which is in turn the interfacial strength increases with an increase of annealing time for bilayer specimens of PP ($M_w = 46.5 \times 10^3 \text{ gmol}^{-1}$) with SEBS(G1652) at an annealing temperature of 165°C (Setz *et al.*, 1996; Heck *et al.*, 1997) and poly(2,4-dimethylphenylene ether) (PPE)

($M_w = 53.0 \times 10^3 \text{ gmol}^{-1}$) with SEBS(G1652) at an annealing temperature of 225°C (Heck *et al.*, 1997). However, Heck *et al.* (1997) have also found that the peel strength of bilayer specimens of PS ($M_w = 158.0 \times 10^3 \text{ gmol}^{-1}$) with SEBS (G1652) is not strongly influenced by the annealing time and it was shown to be significantly lower than that of the bilayer specimens of PP with SEBS (G1652) and PPE with SEBS (G1652). Note that the annealing times used for these studies were at least 14 hours. Heck *et al.* (1997) suggested that these results should be attributed to the high miscibility of the PEB block with the PP and PPE while this is not the case for the PS. This was revealed by TEM that the PS blocks of the copolymer diffused into the PS homopolymer phase. However, as the M_w of the PS blocks of the SEBS (G1652) used here is below the $M_c(\text{PS})$, the interfacial strength is not significantly reinforced as found for the PP and PPE systems. Considering the trilayer specimens used in this study (see figure 6b), it can be expected that the peel strength of these samples will be strongly dependent not only on the miscibility of the PEB block with the LDPE layer but also the PS block with the PS layer. As the M_w of the PS blocks of both the SEBS (G1651) and SEBS (G1652) used in this study is lower than that of the PS homopolymer, failure would mainly arise from chain pullout from the interface side where the PS sub-lamella contacts with the PS homopolymer layer. As seen in figure 5, the peel strength decreases with increasing annealing time and this behaviour was more pronounced in the systems with the film thickness of 235 Å of both SEBS (G1651) and SEBS (G1652) systems. It is possible that when the longer annealing time is used the film of the copolymers may form a different microstructure which results in lowering the

peel strength. A change of the microstructure of the bulk morphology of SEBS (G1652) from cylindrical to lamellar at the interface of bilayer specimens of PS with SEBS(G1652), PP with SEBS (G1652) and PPE with SEBS(G1652) after annealing for 2 hours has been reported by Setz *et al.* (1996) and Heck *et al.* (1997). This behaviour would enable the blocks of copolymer to diffuse efficiently into the respective homopolymer phases. During spin coating the SEBS onto LDPE bars, the PEB blocks are likely to locate close to the LDPE surface while the PS blocks protrude into air as seen in figures 1a and 1b. However, due to rapid evaporation of the solvent, many of the PEB blocks may be frozen and not reach the LDPE surface to the level expected. Together with the relatively thick films of the copolymers obtained, changes in the surface microstructure of these films during annealing may take place especially for the case of the film prepared from the 2 wt/vol% of each SEBS solution. Further investigations on the microstructure of the SEBS after annealing for a given time are required in order to check this hypothesis.

4. Conclusion

Presumably as a result of the penetration of the copolymer blocks into the respective homopolymers, the films of SEBS triblock copolymers were found to increase the strength between the PS and LDPE. Due to the higher anchoring ability to the respective homopolymer phases of the relatively longer segments of the copolymer blocks, the high molecular weight copolymer was shown to be superior to the low molecular weight one in terms of the increase of the interfacial strength. Once the interface between the PS and LDPE became saturated with copolymer, addition of further copolymer resulted in only a slight increase

in the interfacial strength. It is believed that the annealing times used for preparing the peel test specimens were not long enough to allow the interface to attain its equilibrium state. The microstructure morphology of the copolymers at the interface is expected to change during annealing time since it was found that the interfacial strength changed with annealing time.

5. Acknowledgement

The authors would like to acknowledge and thank sincerely the Rutherford Appleton Laboratory (RAL): Oxon, UK, for research grants. Dr. Simon A. Butler, Department of Chemical Engineering, University of Cambridge, Dr. M. Sferrazza, RAL, for generous help with the ellipsometry experiments, Dr. Sergei Magonov, Digital Instruments Company, for AFM analysis.

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About the Authors



Chatchai Kunyawut is a lecturer in Department of Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology

Thanyaburi. He received his Ph.D. degree in Chemical Engineering from Imperial College of Science, Technology and Medicine, University of London, UK. Dr. Kunyawut has edited two books, Industrial Process Control and Process Dynamics and Control.

Julia S. Higgins is a Professor of Polymer Science at Imperial College of Science, Technology and Medicine, University of London, United Kingdom. Dr. Higgins served on the editorial boards for Polymer Journal. She has published extensively in the fields of polymer science and engineering, and chemical engineering. She is the author of numerous research papers in the area of polymer blends.

