Adhesion of styrenic triblock copolymers to miscible blends of polystyrene and a phenylene ether copolymer

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The adhesion of a triblock copolymer having short styrene end-blocks and a hydrogenated mid-block to a polystyrene containing substrate was studied using both lap shear and peel test methods. The two approaches gave very similar results. Within the limits examined, the adhesive bond strength did not depend significantly on bonding temperature or time. However, the adhesive strength did increase substantially as a phenylene ether copolymer or PEC, essentially poly(phenylene oxide), was added to the substrate. This effect is believed to be the result of the exothermic mixing of PEC with polystyrene that causes an additional driving force, other than combinatorial entropy, for interpenetration of segments of the substrate and the styrenic phase of the block copolymer at the interface. Attempts to use a block copolymer having longer styrenic segments resulted in adhesive bond strengths so large that cohesive failure occurred first.

INTRODUCTION

Polymer–polymer interfaces and interphases have attracted a greal deal of interest recently[1,2] in large measure because of the obvious importance to multiphase blends. In this connection, the key consequence of the molecular interaction and organization in this region relates to interfacial tension in the melt (ability to disperse) and adhesion in the solid state (ability to transfer stress). The focus of this paper is the solid state adhesion between SEBS triblock copolymers, having styrene end-blocks with a hydrogenated butadiene mid-block, and miscible blends of polystyrene, PS, with a phenylene ether copolymer, similar to poly(phenylene oxide), that develops during juxtaposition in the melt state. The main variable is the effect of the content of phenylene ether copolymer, PEC, in the miscible blend phase, although time and temperature in the melt must be considered. The next section explains the reason for interest in this problem and places it into the context of related literature.

BACKGROUND

When two homopolymers form an interface in the melt state, interdiffusion of the two is possible and, in modern interpretation, the extent of solid state adhesion achieved as a result will depend on the number of chains traversing the interface and the depth of their interpenetration into each phase[2–5]. If the two polymers are chemically identical or miscible, interdiffusion will continue until eventually the segment density of each polymer becomes entirely uniform throughout space, as shown schematically in *Figure 1*. The strength of the adhesive bond formed is related to the extent that chains traversing the interface

are anchored into each phase. At some point the adhesion becomes as great as the cohesive strength of the bulk polymer. This is believed to occur when the interpenetration is greater than the distance between entanglement points[2]. A great deal of recent work has focused on experimental investigation of the diffusion process[3–11] and of the development of adhesion in such cases[2–7]. Theories involving the dynamics of chain movement, e.g., reptation motions, and thermodynamic forces, have emerged to describe available observations[12–14] although some areas of disagreement exist[8]. An important consequence of these theories is the intuitive notion that the stronger the affinity (or energetic interaction) between the two species the more rapid the diffusion[7,13–15]. For identical polymers or dissimilar ones that mix athermally, the only driving force for mixing is the combinatorial entropy of mixing which is quite small because of the high molecular weights. For dissimilar polymers that mix exothermically, there can be a much larger driving force for diffusion and this has been found to be manifested in higher diffusion coefficients[15] and more rapid development of adhesion[6,7] relative to comparable athermal systems. Studies of this type have generally been conducted at relatively low temperatures so that the time scale of the diffusion is lengthened, relative to normal fabrication conditions, for convenience of measurement.

For immiscible polymer pairs, recent theories[16–18] suggest that at equilibrium there is a concentration profile of segments across the interface not unlike that found at finite time for a miscible pair (see *Figure 1*). The thickness of this interfacial zone is predicted to vary inversely with the interaction energy for the polymer pair and typical numerical estimates range from 1 to 10 nm[17]. Therefore, only a relatively short time (of the order of a second) is needed for an immiscible polymer pair to form an equilibrium interfacial zone of this dimension even

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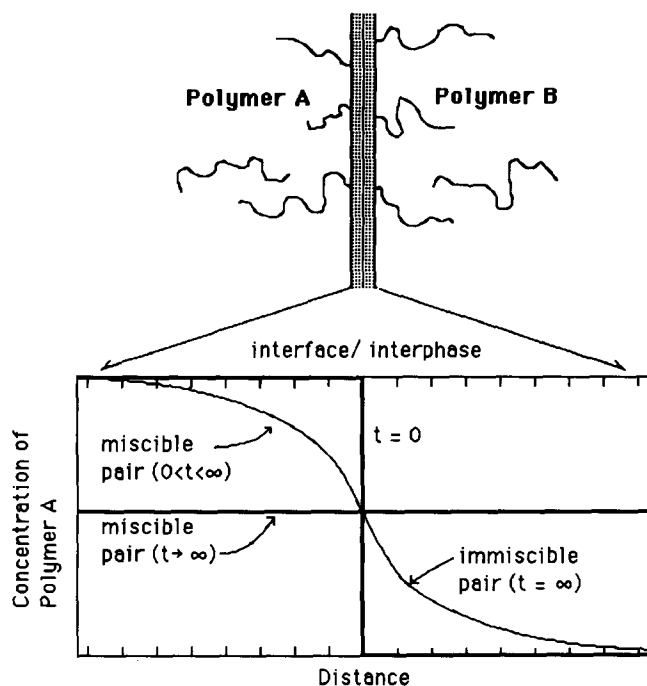
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Figure 1 Schematic diagram showing the concentration profile within the interfacial zone between two polymers

though the diffusion coefficient is small. Macroscopically, this means that adhesion development between immiscible polymer pairs is effectively independent of time at normal processing temperatures once good contact at the interface has been made.

Frequently, however, the interaction between the two polymers is strongly repulsive resulting in a high interfacial tension and poor adhesion. This situation leads to serious processing and property limitations of their blends that necessitates the use of some type of compatibilizer, e.g., a block copolymer that acts as a surfactant in the melt (lowers interfacial tension to give finer dispersion and stable morphology) and promotes adhesion in the solid state as a result of chemical bonds traversing the interface. The ideal 'compatibilizer' is generally believed to be a block copolymer whose segments are identical with those of the two homopolymer phases. This means that the only driving force causing mixing or interdiffusion between the homopolymer phase and the copolymer segments is the rather small combinatorial entropy of mixing. However, there can be an enthalpic driving force, in addition to entropy, for mixing of the homopolymer and copolymer chains if the two are not chemically identical yet form a miscible pair. This additional interaction is believed to be responsible for the improved compatibilizer efficiency seen in a recent study[19-21].

The compatibilization of polystyrene/polyethylene blends using styrene/hydrogenated butadiene block copolymers has been extensively studied[22]. As a variant of that theme our recent work[19-21] examined the addition of a poly(phenylene oxide) copolymer, PEC, to the polystyrene which caused an increase in the glass transition temperature and the ductility of this phase. An SEBS block copolymer was used to compatibilize blends of the PS/PEC phase with high density polyethylene, HDPE. For fixed amounts of HDPE and SEBS, the effectiveness of the compatibilization improved

as the proportion of PEC in the glassy phase increased based on these separate observations: scanning electron microscopy[19] showed smaller phase domains and more ligaments attaching the two phases; ductility of the blends increased[20], relative to that predicted by additivity from component properties; and mechanical dilatometry[21] suggested decreased interfacial debonding between the glassy phase and the HDPE caused by the compatibilizer.

A separate investigation in our laboratory[23,24] has shown that PPO is solubilized into the styrene microdomains of block copolymers to a much greater extent than is PS homopolymer and without the familiar molecular weight restrictions[25,26] associated with the latter. The reason for this is that the enthalpy of mixing polystyrene blocks with PPO is exothermic, or favourable, while mixing of these blocks with PS homopolymer is athermal. The latter process is then driven only by entropy while the former has an additional enthalpic driving force.

These observations taken together suggest that SEBS type block copolymers should adhere to PPO (or PEC) better than to PS because of this difference in driving force. One could reach this conclusion from either equilibrium or kinetic arguments based on the background given above. Here, we will test this hypothesis by examining the adhesion of SEBS materials to PS/PEC blends of varying PEC content using two different means of measurement. The issue of kinetics is also examined.

During the course of this work, Green *et al.*[9,10] have published interesting experimental measurements of diffusion of PS and PMMA homopolymers into S–MMA block copolymers above the T_g. The depth of the diffusion suggests for their materials that the microphases of the copolymer are co-continuous and connect to the interface in the general manner suggested by *Figure 2*. The diffusion rates into the copolymer were found to be lower than those into a homopolymer presumably because of the reduced volume for transport and the more tortuous path presented by the copolymer microphases[9]. The parallels with the present adhesion investigation should be obvious.

There can be significant differences between the surface

Homogeneous Phase
(including miscible blend)

Microphase Separated
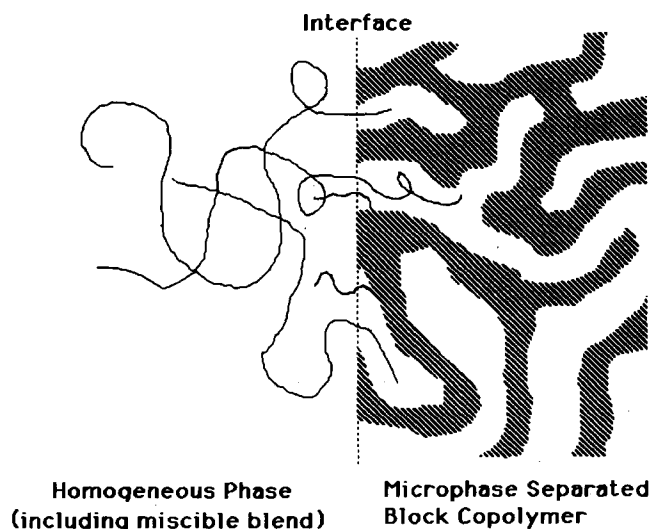**Block Copolymer**

Figure 2 Schematic diagram of the interface between a homogeneous polymer phase and microphase separated (arbitrary morphology) block copolymer. The block copolymer segments of the shaded microphase are not miscible with the polymer phase on the left

and bulk compositions of multicomponent polymer systems[27-29]. At equilibrium, one expects the component with the lower surface tension to be, to some degree, preferentially located at the surface. Such effects could have profound effects on the adhesion and needs to be addressed before interpreting the results of a study like the current one. For miscible blends of PS and PPO, Pan[30] found no significant difference between surface and bulk compositions using XPS which agrees with predictions made by the parachor method[31]. Very dramatic effects have been reported for block copolymers[29]. In the present case, the SEBS materials are prepared by melt preparation methods that certainly do not lead to equilibrium structure so calculations are meaningless. Measurement of surface concentration was considered but found to be very difficult. On the basis of the adhesion results presented here, it is clear that polystyrene domains extend to the SEBS surface, and we believe that the schematic picture given in *Figure 2* is adequate to represent the current systems.

EXPERIMENTAL

Materials

The polymers used in this research are identified in *Table 1*. PEC is a random copolymer of about 95 mol% 2,6-dimethyl phenol and 5 mol% 2,3,6-trimethyl phenol. PEC has almost the same properties as poly(2,6-dimethyl-1,4-phenylene oxide), PPO, including complete miscibility with PS over the full range of composition[32,33]. The triblock copolymers designated by SEBS are commercial products of Shell Chemical Co. with styrene end-blocks and a mid-block with structure similar to an ethylene–butene copolymer. Two molecular weight grades were used. Prior to any further processing, polystyrene and PS/PEC blends were dried in a circulation oven at 70°C overnight while the SEBS materials were dried in a vacuum oven at room temperature overnight.

The PEC was supplied to us through the courtesy of W. A. Pavelich of Borg–Warner in the form of blends (containing 80% and 60% by weight PEC) with polystyrene. To obtain other PS/PEC compositions PEC80 (PS 20%/PEC 80% blend) or PEC60 (PS 40%/PEC 60% blend) were melt blended with additional PS in a Killion single screw extruder.

The glass transition temperatures for the blends and triblock copolymers were measured using a Perkin–Elmer DSC7 at a heating rate of 40°C/min and a Polymer Laboratories DMTA at a heating rate of 2°C/min. *Table 2* shows the single glass transition temperatures observed for the PS/PEC blends and for the polystyrene blocks of SEBS copolymers.

Lap shear test

The lap shear test (ASTM D 3165) provides a convenient measure of the stress required to fracture the interface between two polymers. However, interpretation is complicated by the development of a steep stress distribution along the length of the joint as determined by Goland and Reissner[34]. Lap shear test specimens of the configuration shown in *Figure 3* were made by a compression moulding technique. First, thick outside substrates made of PS of PS/PEC blends were prepared by compression moulding between aluminium foil for 15 min at 250°C and 1.7 MPa followed by cooling using high pressure air circulation while maintaining pressure on the part. Aluminium frames were used to obtain the various sample thicknesses. The thickness of the substrates was 0.318 cm for the measurement of adhesion between PS/PEC blends and SEBS-L. However, substrates as

Table 2 Glass transition temperatures of materials used

Material	Composition	T_g (°C)	
		D.s.c.[a]	D.m.t.a.[b]
PS	Polystyrene	107	101
PEC20	80% PS/20% PEC	122.5	115
PEC40	60% PS/40% PEC	133.2	130
PEC60	40% PS/60% PEC	160.0	155
PEC80	20% PS/80% PEC	180.6	176
PEC	Phenylene Ether	[c]	[c]
	Copolymer		
	SEBS-H	98.6[d]	
	SEBS-L	80.3[d]	

[a] Midpoint temperature from second scan at 40°C/min in the differential scanning calorimeter
[b] Temperature at which the loss modulus, in dynamic mechanical thermal analysis, becomes a maximum at 3 Hz
[c] 100% PEC was not available
[d] Transition for the styrenic phase of the copolymer

Table 1 Characteristics and sources of materials

Polymer	Abbreviation	Source	Molecular weight
Polystyrene	PS	Fina Chemical Co.	$M_n = 100\,000$
			$M_w = 350\,000$
Phenylene–ether copolymer	PEC[a]	Borg-Warner Chemical Co	not available
SEBS triblock copolymer	SEBS-H	Shell Chemical Co.	PS blocks = 29 000
		(Kraton G1651)	EB block = 116 000
SEBS triblock copolymer	SEBS-L	Shell Chemical Co.	PS blocks = 7000
		(Kraton G1652)	EB block = 37 500

[a] This material was supplied as either a 60% or an 80% by weight blend with PS (Cosden 550). All other PS/PEC compositions were obtained by extrusion mixing of these blends with the appropriate amount of PS (Cosden 550). This PEC is believed to have the following structure:
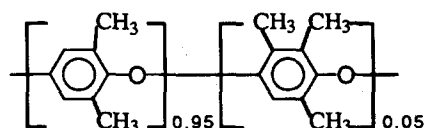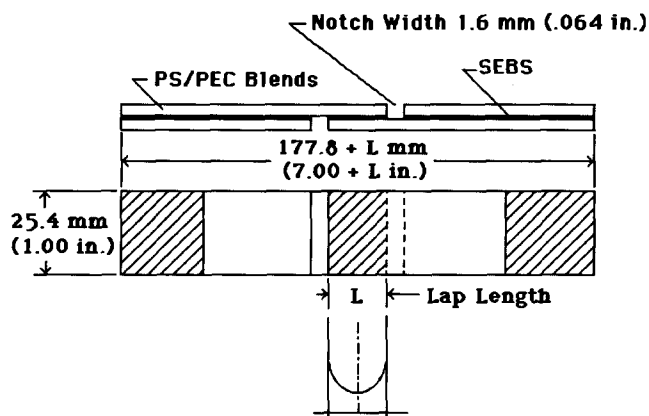
Figure 3 Description of the lap shear test specimens illustrating the stress profile along the lap length

thick as 1.27 cm were tried in the case of SEBS-H. Second, thin SEBS layers (0.08 cm) were compression moulded between Mylar films for 15 min at 170°C and 1.7 MPa followed by cooling as described above. By this procedure, a translucent but uniform sheet was obtained for both SEBS-L and SEBS-H. After peeling off the Mylar films, the moulded SEBS sheets were placed in a vacuum oven overnight at 130°C to release residual stresses.

Bonding between the PS/PEC blend substrates and SEBS sheets was performed for up to one hour at a constant pressure (c. 0.69 MPa). The bonding temperatures were 170°C, 200°C, and 230°C and were selected to be above the T_g values of the PS/PEC blends used and the PS segments of SEBS. The materials to be laminated were sandwiched between two 0.635 cm aluminium plates and thickness was controlled by an aluminium frame. This assembly was placed between the heated platens of a compression press. No pressure was applied until the temperature indicated by a thermo-couple embedded in the top aluminium plate reached within 10°C of the temperature of the preheated platens set at the desired bonding temperature. At this point, pressure was applied by the press and this defined the start of the bonding time.

The test specimens of the dimensions specified in ASTM D 3165 (see *Figure 3*) were made by cutting the 20 cm × 20 cm laminates using a band saw. The lap length for this test was fixed at 1.27 cm. The loads required to cause interfacial fracture were measured at room temperature on an Instron tensile tester with a crosshead speed of 0.51 cm/min and used to calculate the average shear stress at failure. It should be noted that this average shear failure stress depends on the lap length used owing to the stress distribution mentioned earlier.

Peel test

The work of adhesion may be obtained by peel tests. Hata[37] suggested the following relation between the peeling force and the work of adhesion:

$$f = W/(1 - \cos \theta) \tag{1}$$

where f is the peeling force per unit width of the substrate, W is the work of adhesion, and θ is the peel angle.

In this work, specimens like those illustrated in *Figure 4* (ASTM D1876) were tested with an ideal peel angle of 180°. The PS/PEC blend layer was prepared by pressing small amounts of pellets on a Kevlar cloth for 15 min at 250°C in a compression press at a pressure of 1.7 MPa.

This cloth backing was required because the PS/PEC blend layer is very susceptible to failure at cracks or flaws during tensile testing[38]. The procedure for the SEBS layer and bonding of the two layers is the same as used to form lap shear specimens. The actual peel angle between the PS/PEC blend and the SEBS layer was affected by the moduli of the two materials. Due to the severe shrinkage of SEBS-H during cooling, the test specimens for (PS/PEC)/SEBS-H were not able to be made. The average peeling force required for an adhesive failure of the interface was measured at a separation rate of 12.7 cm/min by the preset point technique on an Instron tensile tester. At least four average values were taken for each condition of bonding.

RESULTS AND DISCUSSION

Figures 5 and *6* show the lap shear adhesion results obtained for interfaces formed from the various PEC/PS blends and the SEBS copolymer with the lowest molecular weight, SEBS-L in *Table 1*. Note that 100% PEC could not be used in these experiments because this material was not available. In *Figure 5* the average lap shear stress from seven test specimens is plotted as a function of the bonding time. Within the experimental limitations there seems to be no effect of time or temperature on the adhesion development for blends containing 0%, 20%, and 40% PEC. At high PEC blends there may be some effects of bonding time or temperature but the trends are not entirely consistent.

Figure 6 shows the lap shear results plotted as a function of the weight percent PEC in the blends. The level of adhesion unambiguously increases as the weight percent of PEC in the blends increases regardless of the temperature or time of bonding within the limits examined
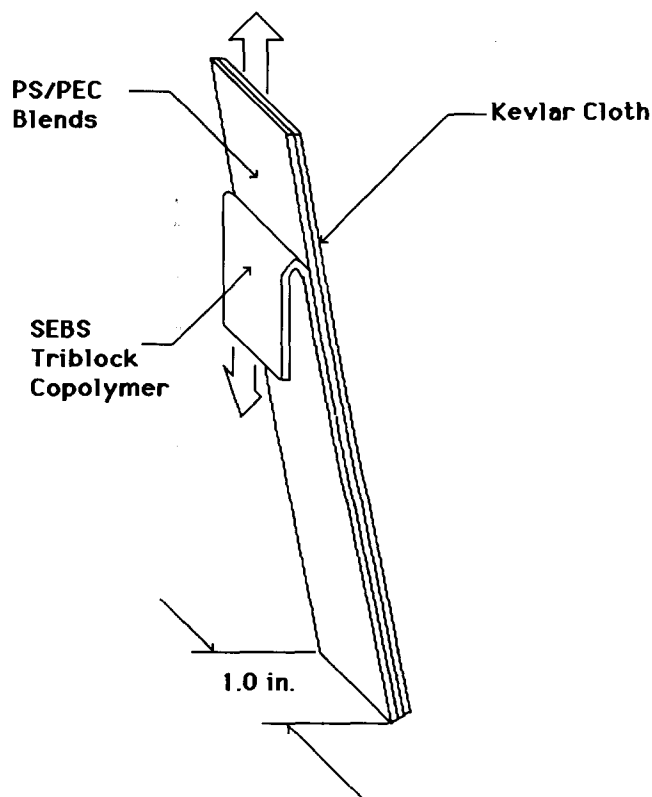

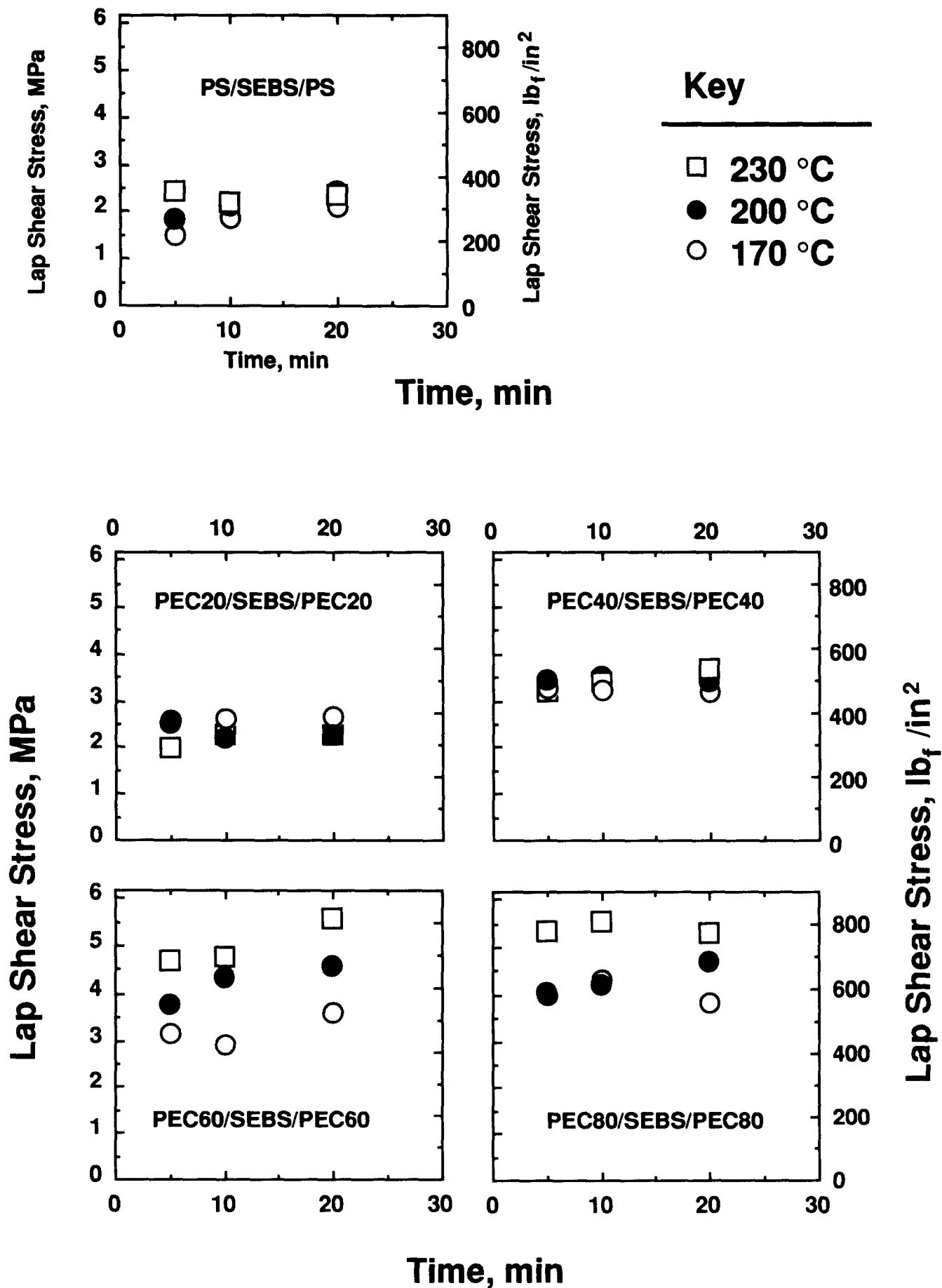**Figure 4** Illustration of the peeling test

Figure 5 Lap shear adhesive stress vs. bonding time between PS/PEC blends and SEBS-L with a lap length 1.27 cm at various bonding temperatures; (○) 170°C; (●) 200°C; and (□) 230°C
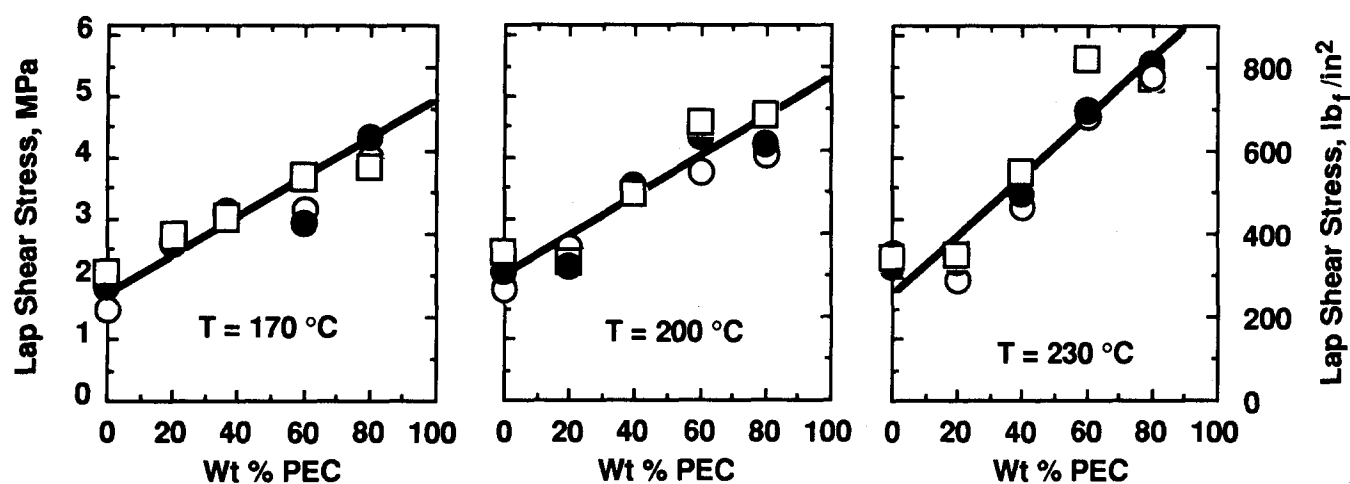
(PEC/PS)/SEBS/(PEC/PS)

Figure 6 Lap shear adhesive stress from *Figure 5* replotted vs. wt% of PEC in the PS/PEC phase for various bonding temperatures and times: (O) 5 min; (●) 10 min; and (□) 20 min

Table 3 Experimental attempts to measure the lap shear adhesion using SEBS-H

Outer layer	Thickness of outer layer (cm)	Load at failure (N)	Lap shear stress[a] (MPa)	Tensile stress in outer layer[b] (MPa)	Location of failure
PS	0.318	811	2.51	13.4	notch area of PS
	0.635	1527	4.74	10.1	notch area of PS
	1.27	2637	8.18	8.44	SEBS layer
HIPS	0.318	1118	3.47	15.8	notch area of HIPS
PS with Kevlar backing	0.318	823	2.55	13.6	notch area of PS
PS expoxied to brass reinforcing plate	0.318	807	2.50	13.3	notch area of PS

[a] Shear stress = load at failure/lap joint area
[b] Tensile stress = load at failure/cross section of outer layer
[c] The adhesion between the Kevlar cloth and PS was poor and the cloth backing did not prevent the progress of cracks
[d] The modulus of the epoxy that glued the brass plate to the PS substrate was much higher than that of the PS substrate so that the glue phase broke first

here. In other words, introducing a third component, PEC, which has a favourable energetic interaction with the styrene endblocks of the copolymers increases the macroscopically observed adhesive strength as proposed based on the reasoning outlined in the 'Background' section. We believe the enhancement of adhesion that occurs on addition of PEC is the result of more effective molecular bonding of the PS microphase to the PS/PEC homogeneous phase, because of more chains spanning this interface or because of more deep penetration of these chains or both, driven by the more favourable energy of mixing and has little to do with the EB microphase. While diffusional processes are no doubt involved, the lack of time dependence suggests that the results observed are more or less an equilibrium effect that is achieved rather rapidly.

The peel test results are shown in *Figures 6* and *7*. The peeling force showed an initial peak value *versus* time as pointed out by Igarashi[39], and then dropped quickly to a lower steady-state level. The steady-state peeling force was averaged over the duration of the test and used to compute the peeling force per inch. The trends seen

with the peel test are essentially identical with those from the lap shear method. There seems to be no effect of either time or temperature of bonding, except possibly at high PEC levels in the blend. Again, the adhesive bond improves with addition of PEC to the PS.

We were very interested in learning how molecular weight of the styrene end-blocks of the SEBS copolymer affects the adhesion. However, we were not able to quantify this effect. As mentioned earlier, we were not able to fabricate SEBS-H peel test specimens owing to the high volume shrinkage during cooling or casting of this high molecular weight copolymer. Lap shear specimens could be formed. However, the standard 0.318 cm outer layer always broke in the region of the notch. The same was observed when the outer layer was made 0.635 cm thick or when high impact polystyrene, HIPS, was used instead. Incorporation of Kevlar fabric as backing did not eliminate this problem. As a final attempt an outer layer of 1.27 cm of PS was fabricated. This specimen did not fracture in the PS phase but it failed cohesively in the SEBS phase. The results of these trials are summarized in *Table 3*. We can conclude that the
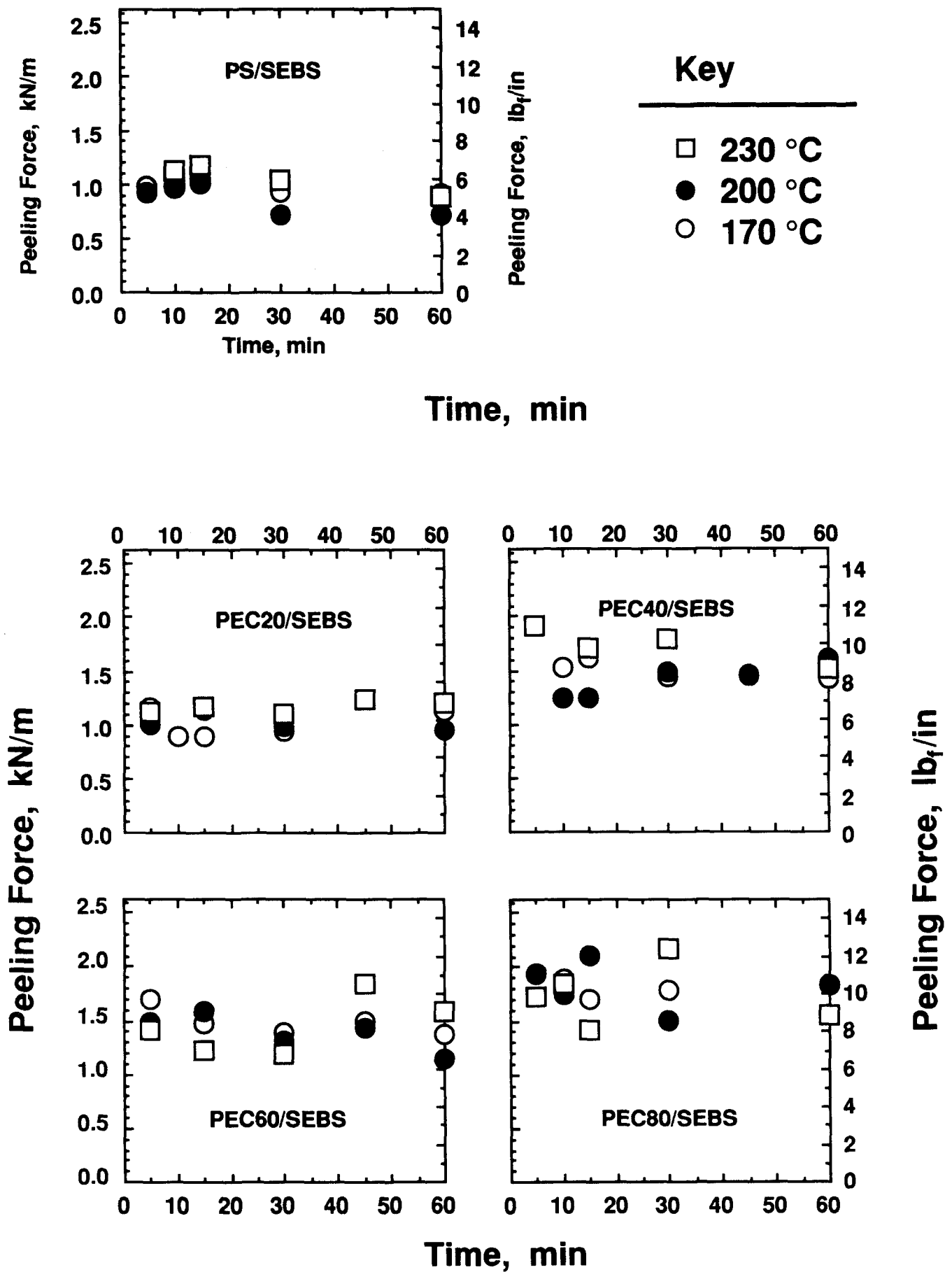
Figure 7 Peeling force vs. bonding time for the adhesion between PS/PEC blends and SEBS-L at a separation rate of 12.7 cm/min for various bonding temperatures: (O) 170°C; (●) 200°C; and (□) 230°C
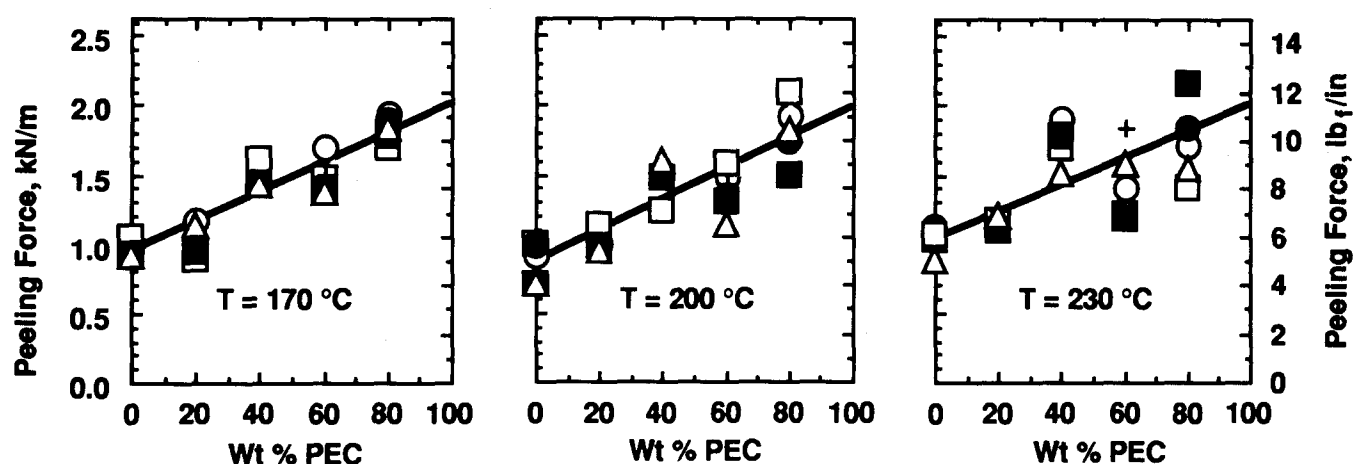
(PEC/PS) / SEBS

Figure 8 Peeling force from *Figure 7* replotted vs. weight percent of PEC in the PS/PEC phase for various bonding temperatures and times: (○) 5 min; (●) 10 min; (□) 15 min; (■) 30 min; (+) 45 min; and (△) 60 min

lap shear adhesion strength of SEBS-H with PS is greater than about 1200 psi. Clearly, increasing the molecular weight of the styrene block of SEBS dramatically increases the level of adhesion to PS.

CONCLUSIONS

The adhesion of SEBS copolymers to a polystyrene substrate was found to increase dramatically upon addition of a phenylene ether copolymer to the polystyrene substrate or by increasing the styrene block length of the copolymer. We believe the former is the result of the more favourable driving force for mixing at the interface caused by the exothermic mixing of PEC or PPO with PS relative to the strictly entropy driven process for segment mixing at the interface of a PS homopolymer with a styrene based block copolymer. We believe this is also the basis for the greater solubilization of PPO than PS in SEBS microdomains[23,40] and the more efficient compatibilization by SEBS copolymers of blends of polyolefins with PEC containing materials than PS[19-21]. The fact that the adhesion level does not significantly depend on bonding temperature or time implies that the adhesion is the result of a relatively fast diffusional process and more nearly reflects issues relating to the equilibrium nature of the system. From these results, it is not clear, however, whether the dominant cause of enhanced adhesion is penetration of styrene copolymer segments into the PEC/PS phase or the penetration of these chains into the PS-microdomains of the copolymer or both.

ACKNOWLEDGEMENTS

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