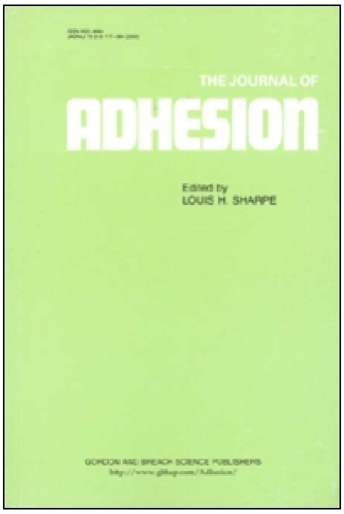

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Creating Smart Polymer Surfaces with Selective Adhesion Properties

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Creating Smart Polymer Surfaces with Selective Adhesion Properties

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A new concept for polymer surface modification is described that employs surface-active ω-functional block copolymers as additives to create polymers with smart sufaces. The block copolymers are composed of three components: a low surface energy block that causes the copolymer to segregate to the surface of the matrix homopolymer to which it is added, an anchor block that tethers the copolymer into that matrix, and a functional group located at the terminus of the surface-active block. The functional end group is selected to interact selectively with a complementary receptor on the target substrate. When the modified polymer surface and a substrate are placed in contact, adhesion is enhanced *only* if the functional end group senses an appropriate receptor on that substrate with which it can form the specific interaction. If a receptor is not present, the modified surface exhibits release properties. This class of copolymer additives can thereby be employed to create smart polymer surfaces with selective adhesive properties. We present preliminary results that demonstrate how this new concept can be employed to modify the surface of polystyrene and impart selective adhesion toward either poly(methyl methacrylate) or poly(dimethylsiloxane) substrates.

Keywords: Functional block copolymers; selective adhesion; surface-active block copolymers; asymmetric cantilever adhesion test; JKR adhesion test; smart surfaces

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INTRODUCTION

A polymeric additive of lower surface energy than its host matrix is known to adsorb preferentially at a free surface and, consequently, decreases the thermodynamic work of adhesion of that surface towards a particular substrate. A surface-active diblock copolymer, for example, can be formed from a low surface energy block that brings the copolymer to the surface of a polymer host matrix and a second anchor block that tethers the copolymer to the bulk matrix. Surface adsorption of the block copolymer brings about a controllable reduction in the surface tension [1] and, therefore, constitutes a valuable route for the preparation of surface with controlled release properties.

The question that then arises is whether a surface-active additive can be designed to enhance the adhesion of a polymer toward a particular substrate. While a surface-active adhesion promoter seems at first to be an oxymoron, we demonstrate in this communication that surface-active ω-functional diblock copolymers of appropriate molecular design can be used to create a smart polymer surface with selective adhesive properties. The key to the molecular design is proper sequencing of the anchor block, surface-active block and functional chain end.

Figure 1 illustrates schematically how surface-active ω-functional diblock copolymers can be employed as selective adhesion promoters. The first step in the overall approach is adsorption of the diblock copolymers at the matrix surface (Fig. 1a), a process driven by the surface tension reduction that occurs when the low surface energy copolymer sequences segregate to the air-polymer interface. The diblock copolymers form a layered structure at the surface, consisting of a top layer of the surface-active sequence (black chains) followed by a layer of the anchor block (white chains) entangled with the host matrix. The functional chain ends (filled rectangles) are carried to the surface along with the surface-active sequences and, if their surface energy exceeds that of the chain backbone, reside just below the surface. Terminal amine functional groups on a poly(dimethylsiloxane) backbone, for example, form a depletion layer at the surface [2]. Recent lattice model calculations [3] demonstrate that the surface depletion layer is followed by an excess of functional end groups

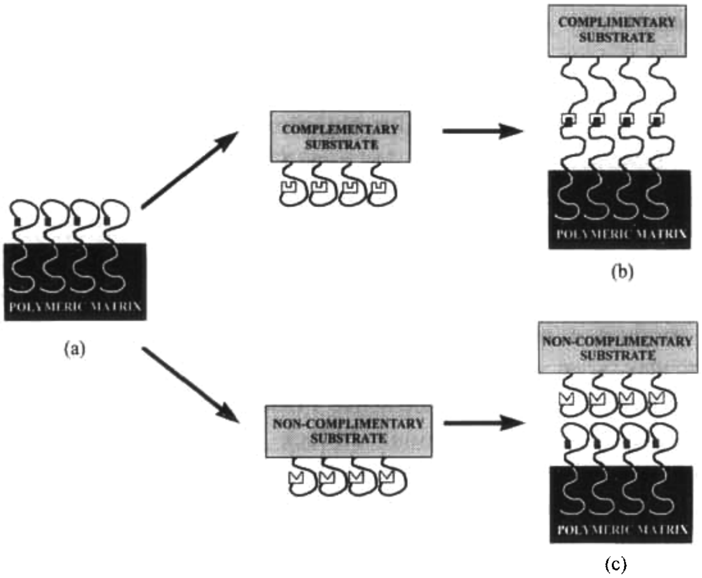


FIGURE 1 Schematic diagram illustrating the concept of surface-active ω-functional block copolymers as selective adhesion promotes. (a) The surface is nomially non-adhesive after preparation. (b) A target substrate constaining complementary receptors binds specifically to the polymeric matrix modified with a surface-active ω-functional block copolymer. (c) A target substrate with non-complementary receptors does not bind to the modified polymeric matrix.

buried only a few lattice layers beneath the surface due to connectivity between the functional end group and the chain backbone.

When the copolymer-modified surface is contacted with a substrate, the functional groups are exposed to a stimulus associated with the new thermodynamic environment imposed by the proximity of the substrate. Whether or not the functional groups respond toward this stimulus determines whether adhesion or release is promoted. If the functional end groups find complementary receptors on the substrate (Fig. 1b), specific interactions form that enhance the adhesive strength between the host matrix and the substrate. Possible specific interactions include hydrogen bonding, acid-base interactions, complexation and covalent bonding. If appropriate receptors are not found (Fig. 1c), the functional groups do not interact with the substrate. In this case, the low-energy surface layer on the matrix acts as a release coating that effectively separates the host matrix from the substrate and thereby minimizes any potential adhesive interactions that might occur between the two surfaces in contact.

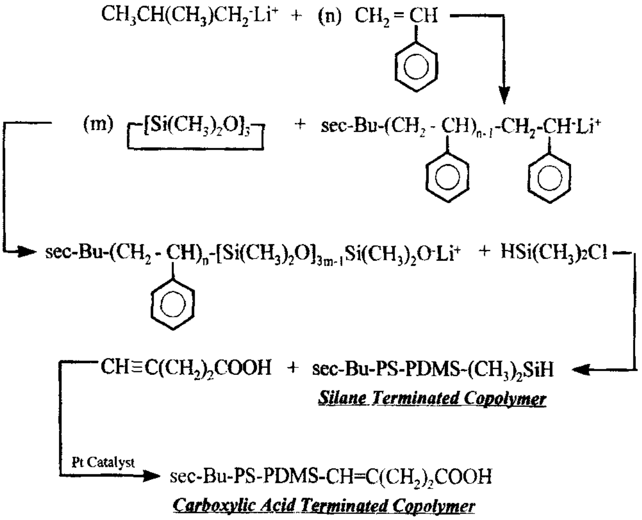
The model systems chosen to illustrate this new concept are ω-functional poly(styrene-*b*-dimethylsiloxane) diblock copolymers P(S-*b*-DMS)-X added to a polystyrene (PS) matrix, where X refers to the end group. It is well known that non-functional P(S-*b*-DMS) copolymers adsorb at the surface of PS with the low surface energy PDMS block located at the surface [4, 5]. The resultant PDMS-enriched surface exhibits release properties towards most substrates. To produce a selectively adhesive surface that sticks only to a particular target substrate, a specific functional end group is attached to the terminus of the surface-active PDMS block of the copolymer, thus creating a ω-functional diblock copolymer. The specific functional end group is selected so as to form a specific interaction *only* with appropriate receptors on the target substrate. In this report, we examine the adhesion enhancement of surface-modified PS matrices toward poly(methyl methacrylate) (PMMA) and poly(dimethylsiloxane) substrates in order to illustrate how selective adhesion behavior can be controlled by appropriate choice of the functional end group.

EXPERIMENTAL

A. PS/PDMS Adhesion Studies

Materials

A silyl-terminated poly(styrene-*block*-dimethylsiloxane) [P(S-*b*-DMS)-SiH] diblock copolymer with Si—H terminal groups on the PDMS blocks was synthesized by standard anionic techniques as depicted in Scheme I. The nominal molecular weight of the block copolymer is 110,000 as determined by gel permeation chromatography (GPC) using polystyrene standards and it is, thus, designated as [P(S-*b*-DMS)-SiH-110 K]. A PS composition of 54% by weight was obtained by Ultraviolet-Visible spectroscopy (UV). Trimethoxysilane end-functional PS homopolymer (Mn = 160,000 g/mole, polydispersity index = 1.05) was synthesized anionically by Dr. K. Shull of IBM. Divinyl-terminated PDMS with a viscosity of 100 c.s. (MW = 6000 g/



SCHEME I Anionic synthesis of ω-functional poly(S-*b*-DMS)-X diblock copolymers.

mole, Petrarch Systems) and poly(methylhydro siloxane-co-dimethyl siloxane) copolymer containing 30–35% methylhydro (182 curing agent, MW = 2000 g/mole, Dow Corning) were cured to prepare crosslinked PDMS lenses. The catalyst for the crosslinking reaction was PC075 (Petrarch Systems), a platinum-divinyltetramethyldisiloxane complex (3–3.5% platinum).

PS Substrate

The base substrates for adhesion studies were ultrathin PS films bound by end group interactions onto silicon wafers. End-functional PS solution (0.5% in toluene) was spin-coated onto silicon wafers at 2000 rpm., after which the wafer was heated in a vacuum oven at 170°C for 1 hr to complete the anchoring of the PS to the substrate through the terminal trimethoxysilane group. The wafer with the grafted PS film was then washed with toluene to remove unreacted residues until an optically-clean surface was obtained. The PS film thickness, measured by ellipsometry (Rudolph Research AutoEl-II automatic ellipsometer with a laser light source at 632.8 nm and incident angle of 70°) was about 13 nm.

Copolymer Film

Copolymer films were coated onto the PS base substrates by spin coating solutions of the copolymer in toluene. The film thickness was varied by using different copolymer concentrations and spin rates. After spin coating, the wafer was annealed in a toluene vapor for 1 hr. The total film thickness, including the PS and the copolymer layers, was measured by ellipsometry after annealing. The thickness of the copolymer film was obtained by substracting the PS thickness from the total film thickness and was subsequently used to calculate the areal density of the copolymer.

Adhesion Measurement

The interfacial energy release rate for the interface between a PDMS gel and both the PS base substrate and the copolymer modified substrates was measured by the JKR technique [6]. In this technique, a hemispherical PDMS lens was placed upside down on the substrates, which either had the copolymer or PS as the top layer. Four glass slides (18 gm) were used as a weight which was loaded on top of the lens. A thin, transparent PS film was sandwiched between the slides and the lens to prevent the lens from sticking on the slides after long loading times. A Zeiss optical microscope with calibrated eyepiece was used in reflection mode to obtain the radii of curvature of the lenses as well as the contact radii of the PDMS lenses on the substrate. When the load was released, the contact radius of the lens on the substrate was measured as a function of time until a steady state was reached. After the contact radius measurement, the modulus and the radius of curvature of the same lens were measured. For the radius of curvature measurements, the lens was placed vertically against the wall of a transparent holder. A photograph of the lens was taken in a transmission mode and the geometry of the hemisphere was analyzed to obtain the radius of curvature.

The moduli of the PDMS lenses were measured using a device designed by Dr. C. Creton as pictured schematically in Figure 2. Each

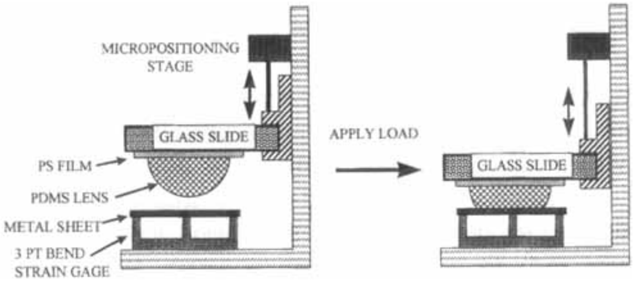


FIGURE 2 Schematic diagram of device used to measure moduli of PDMS lenses.

PDMS lens (upside down) was placed between a PS film and a thin metal sheet. A transparent glass slide placed onto the PS film was adjusted up and down to control the applied force on the lens. The deflection of the metal sheet under the applied force was measured by a strain gauge with a 3-point bending beam. The output readings were calibrated by a standard and converted into force units. The contact radius of the lens, as a function of applied force, was determined by the optical microscope and used to calculate [6] the modulus of the lens from the following equation:

$$a^3 = (R/K)\left\{P + 3\pi WR + \left[6\pi WRP + (3\pi WR)^2\right]^{1/2}\right\} \tag{1}$$

where a is the contact radius, R the radius of curvature, K the effective modulus ($K = 16E/9$, where E is the Young's modulus), P the weight on the lens, and W the work of adhesion of the lens and the substrate. Knowing the radius of curvature and the effective modulus of the lens, the fracture toughness of the interface (G_C) was calculated from the measured contact radius as a function of time as [7]:

$$G_C = \frac{1}{6\pi K a^3}\left[\frac{Ka^3}{R} - P\right]^2 \tag{2}$$

Lenses

PDMS lenses were prepared by an established procedure that employs an addition cure reaction [8]. The bond formation is *via* a hydrosilylation reaction between the Si—H group of the cure agent and the C—C group of the divinyl-terminated PDMS in the presence of a platinum complex. A glass slide was treated with hexane solution containing about 0.35% of a silane ((tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane) for 1 minute to produce a low surface energy. A solution which contained divinyl-terminated PDMS, 0.2% platinum complex and 9–18% 182 curing agent was dropped onto the pre-coated slide to form hemispherical lenses. High-contact-angle drops were obtained due to the low surface energy of the pre-coated slides. The lenses were then transferred to an oven and cured at 65°C. Some lenses were treated after cure with a thiol solution (0.5% 1-Dodecanethiol, $CH_3(CH_2)_{11}SH$, in toluene) for 2 hr. in order to poison the platinum catalyst contained in the lens. The thiol-treated lenses were then washed in toluene for 1 hr, dried in 50% methanol in toluene for 1 hr, and finally dried in air.

B. PS/PMMA Adhesion Studies

Materials

Polystyrene (PS) (Dow Research Inc., Mn = 115,000) and poly(methyl methacrylate) (PMMA) (Polysciences Inc., Mn = 100,000) were used as received. Molecular weights were characterized by size exclusion chromotography (SEC) in THF using a Millipore 150C SEC with four ultrastyrogel columns. Carboxyl-terminated poly(styrene-*block*-dimethyl siloxane) [P(S-*b*-DMS)-COOH] and SiH-terminated poly(styrene-*block*-dimethyl siloxane) [P(S-*b*-DMS)-SiH] diblock copolymers were synthesized by standard anionic techniques as described in Scheme I. The SiH end group was obtained by terminating the polymerization with dimethylchlorosilane and the carboxyl terminus was obtained by hydrosilylation of the terminal silane with pentynoic acid in the presence of platinum catalyst. The copolymers were characterized using SEC and end group titration. SEC was carried out in toluene with a Beckman 100A pump, an Altec 156 refractive index detector, and two Polymer Labs 10 μ mixed gel columns. P(S-*b*-DMS)-COOH end group titrations were performed using a measured amount of copolymer in propanol. Phenolphthalein was used as the indicator and titration to a purple end point was carried out using 0.1 normal alcoholic potassium hydroxide solution. The molecular weight of the P(S-*b*-DMS)-SiH-5.5K was 5,500 with a polydispersity of 1.13 and the molecular weight of the P(S-*b*-DMS)-COOH-5.1K was 5,100 with a polydispersity of 1.12 as determined by SEC. The molecular weight of the PS block for both copolymers was 2,900 with a polydispersity of 1.12 as determined by SEC. The carboxyl-terminated copolymer was determined, by end group titration, to have 50% carboxylic acid end groups.

Adhesion Testing

Measurements of the interfacial toughness for the glassy interface between PS and PMMA were made using the asymmetric double cantilever test [9]. In this test, a single-edged razor blade is used to drive a crack through the plane of the interface. The fracture toughness is determined by measurement of the crack length, a, according to

$$G = \frac{3ED^3\mu^2}{8a^4[1 + (0.64D/a)]^4} \tag{3}$$

where E is the Youngs modulus of the unadhered beam, D is the depth of the beam, and μ is the thickness of the razor blade. Since the failure of polymeric materials is highly time dependent, the crack length was measured 24 hours after it was initiated. The asymmetry in stiffness required by the technique was generated by bonding the PS substrate directly to a glass slide. Adhering the PS beam to the glass slide prevents the crack from jumping away from the interface [10] prior to use, the single-edge razor blade was cleaned ultrasonically for 5 minutes in both methanol and acetone. Multiple samples, typically 35 or more, were measured to obtain each value of interfacial toughness.

The sample geometry was a multilayer sandwich with a base layer that consisted of a 3.5 mm plague of PS on glass. The block copolymer layer of interest was spin coated onto the PS substrate and then a 3.5 mm PMMA plaque was placed on top. The PS and PMMA plaques (5 × 100 × 3.5 mm) were compression molded at 150°C and gradually brought to 10 metric tons of pressure. The molds were slowly cooled to room temperature in the press at 10 metric tons. To obtain a smooth surface, aluminum foil was placed between the molds and the platens. Care was taken not to touch the molded surfaces. Thin films of the block copolymers were prepared by spin coating ethyl acetate solutions of the block copolymer directly onto the PS slabs using a spin speed of 1000 rpm for 60 seconds. These coated PS slabs were then annealed overnight under vacuum at 100 °C. The PS and PMMA were brought into contact in a the compression mold for 3 hours at 150°C under 2 metric tons of pressure. The samples were then cooled to room temperature under pressure. The samples were released from the molds and allowed to stand for 24 hours before testing.

C. Surface Tension

Surface tension was measured by application of a modified pendant drop method employing digital imaging to determine the drop profile and robust shape analysis to compare this profile with predicted shapes for asymmetric fluid drop profiles. Details regarding similar apparatus and its utilization can be found elsewhere [11]. The density of PS required for the method was obtained from the Fox and Flory empirical correlation [12]:

$$\nu_{PS} = 0.913 + 5.5 \times 10^{-4} T + \frac{53}{M_n} \tag{4}$$

where ν is the specific volume of PS in ml/g, T is temperature in °C, and M_n is the number average molecular weight in g/mole.

P(S-*b*-DMS)-SiH or P(S-*b*-DMS)-COOH was mixed with PS by solution blending in THF. A microextruder with a vacuum line and a temperature controller was used to fill the mixtures into glass capillaries for pendant drop tensiometry. The material was heated at 180 °C under vacuum for one hour and then extruded into a capillary. The pendant drop cell was purged with argon to prevent degradation of the polymers. Pendant drop measurements were carried out at 140°C (±1°C), a temperature which is well above the glass transition of the components. Data were taken as a function of time until a stable surface tension was obtained.

RESULTS AND DISCUSSION

Modification of the PS/PDMS Interface

PS and PDMS will not normally adhere well to each other since they are highly immiscible and have a low thermodynamic work of adhesion. This is due in large part of the low surface tension of PDMS (20.4 dyne/cm at room temperature [13]). The strength of the interface can, however, be improved by the addition of an ω-functional poly(styrene-*b*-dimethyl siloxane) diblock copolymer to the poly(styrene) substrate. The choice of an appropriate functional end group for the surface-active copolymer is limited in this case because PDMS has no intrinsic functionality that can form hydrogen bonds or complexes. PDMS gels, however, do have some residual functionality associated with their synthesis. Crosslinking of the PDMS gel involves an hydrosilylation reaction between terminal vinyl groups on PDMS chains and crosslinking agents that contain silane functionality [*e.g.*, poly(hydromethyl siloxane)]. These reactions are promoted by a number of platinum catalysts. The gels normally contain some residual vinyl groups that remain unreacted after the curing reaction. Adhesion to the gel can, therefore, be promoted by the addition of silane-terminated poly(S-*b*-DMS)-SiH diblock copolymers. In the presence of residual platinum catalysts, the silane terminus can react *via* hydrosilylation with a vinyl group in the PDMS substrate leading to covalent coupling between the copolymer and the substrate. If the PS anchor block of the copolymer entangles with the PS matrix, the copolymer then forms a mechanically effective copolymer bridge across the substrate-matrix interphase. The overall mechanism of adhesion promotion is depicted schematically in Figure 3.

Measurements of the adsorption isotherm for the poly(S-*b*-DMS-SiH) copolymer in a PS matrix demonstrate that it is surface-active and that the surface concentration can be controlled by varying the bulk composition. The value of the minimum surface tension obtained demonstrates that an essentially pure PDMS layer can be formed at the PS matrix surface. Figure 4 demonstrates that the surface activity of the copolymers is essentially independent of the end group type. The surface active diblock copolymer, therefore, functions effectively as a vehicle to deliver the functional group to the substrate surface.

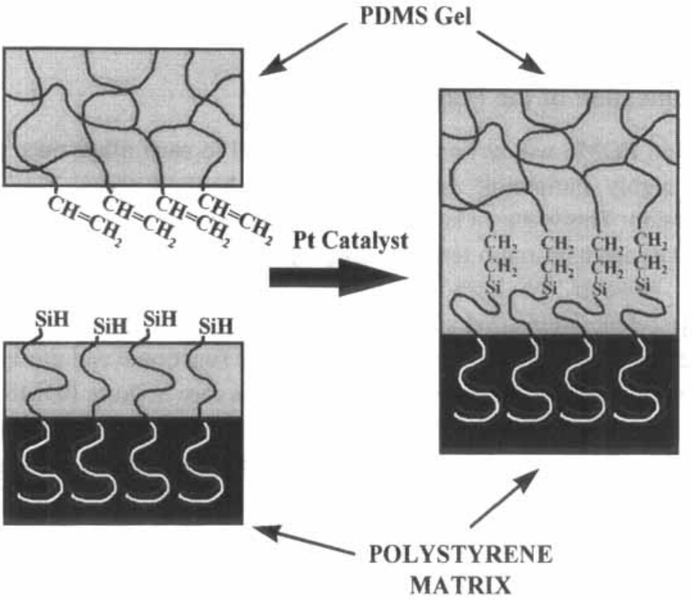


FIGURE 3 Schematic representation of the mechanism of adhesion promotion between a polystyrene matrix modified with a surface-active poly(S-*b*-DMS)-SiH block copolymer and a PDMS gel. Black chains are PDMS and white chains are polystyrene. The residual vinyl chain ends in the gel react with the silane termini of the block copolymers *via* an hydrosilylation reaction (in the presence of Pt catalyst) to produce chemical bridging across the interface.

The areal density of the copolymer may also be controlled by spin coating layers of the copolymer on top of the polystyrene matrix. Due to the simplicity and rapidity of this latter method, we have employed spin coating to prepared substrates varying in copolymer areal density. Figure 5 shows the enhancement in the threshold interfacial fracture toughness afforded by addition of the silane-terminated P(S-*b*-DMS-SiH) copolymer to the interface between a PDMS gel and a PS matrix. The adhesion enhancement is initially linearly dependent on the areal density of the block copolymer or, in other words, is directly proportional to the surface concentration of silane functional groups. Above a copolymer concentration associated with saturation of the PS surface, a plateau in the toughness is observed. Further copolymer addition beyond the plateau leads to the formation of copolymer multilayers that are ineffective in promoting adhesion, leading to an

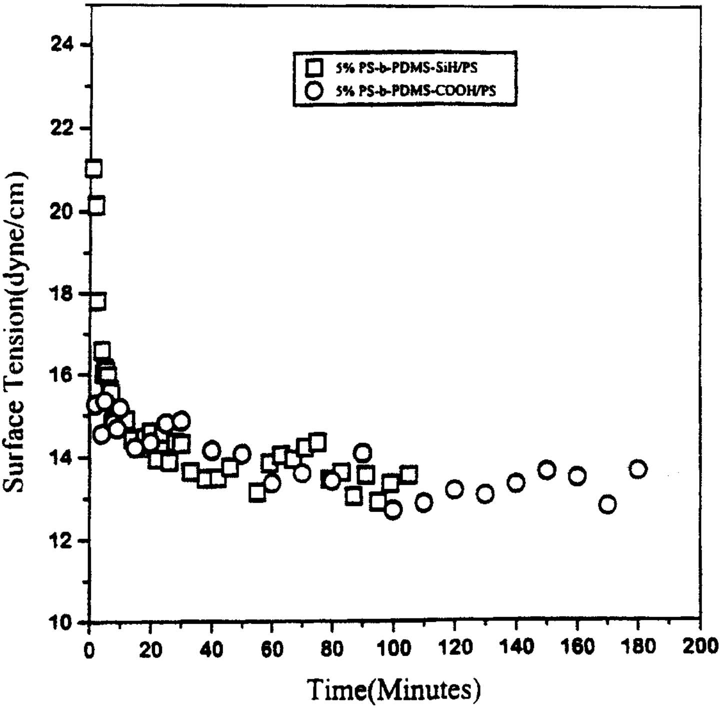


FIGURE 4 Surface tension at 140°C as a function of time for polystyrene melts ($M_n = 4000$) containing 5% diblock copolymer: poly(S-*b*-DMS)-COOH-5.1K (circles) and poly(S-*b*-DMS)-SiH-5.5K (squares).

eventual decrease in interfacial toughness. If the platinum catalyst is poisoned by addition of a thiol, the hydrosilylation reaction cannot occur and the copolymer does not enhance the adhesion. More detailed studies of these materials [14] demonstrate that the level of adhesion promotion obtained can be controlled by adjusting the surface concentration of silane groups (*i.e.*, areal density of the block copolymer), the concentration of residual vinyl groups in the gel, the presence of catalyst, and the molecular weight of the block copolymer. The results are consistent with predictions of the Lake-Thomas model [15] for failure of crosslinked elastomer networks and indicate that adhesion between the copolymer-modified PS matrix and the PDMS substrate is completely mediated by the specific interactions (*i.e.*,

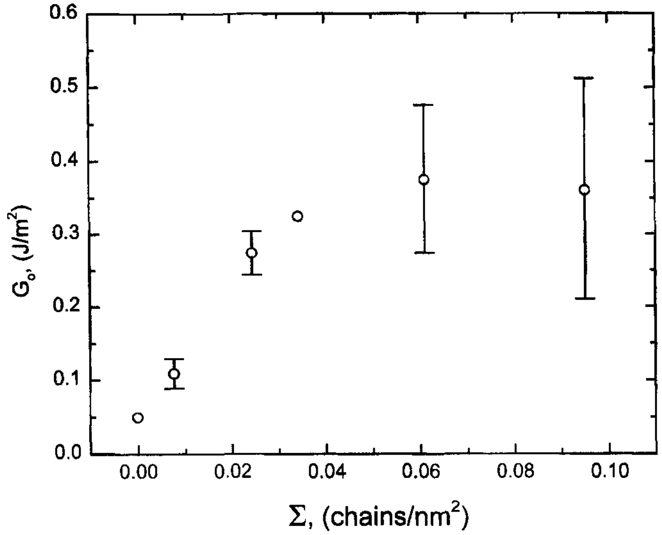


FIGURE 5 Threshold toughness of the interface between polystyrene and a PDMS gel as a function of the areal density of poly(S-*b*-DMS)-SiH-110K added to the interface.

covalent bonding) between the silane termini of the block copolymers and the vinyl groups in the PDMS substrate, as detailed in Figure 3. These details are discussed further in a forthcoming manuscript [14].

Modification of the PS/PMMA Interface

The selective nature of the adhesion promotion offered by this approach can be illustrated by examining how ω-functional P(S-*b*-DMS)-X copolymers can be used to affect the adhesion between a PS matrix and a PMMA substrate. For these glassy-glassy interfaces, the energy release rate or toughness associated with interfacial fracture is measured by application of the asymmetric double cantilever method. The errors associated with the use of this techniques are large, even when 35 samples are averaged for each measurement. The values we obtain are statistically different, however, allowing inferences to be made regarding the effects of the various block copolymer additives.

The fracture toughness (Fig. 6) of the PS/PMMA interface is approximately 2 J/m^2 and can be compared with cited values [16] of

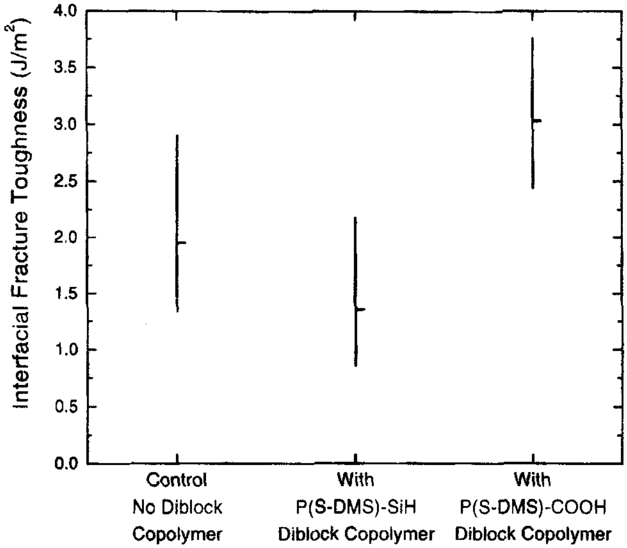


FIGURE 6 The effect of poly(S-*b*-DMS)-COOH-5.1K and poly(S-*b*-DMS)-SiH-5.5K copolymer additives on the toughness of the interface between polystyrene and poly(methyl methacrylate). The concentration of the spin coating solution used to prepare the films 2×10^{-3} g/l.

5–10 J/m^2. Assuming a surface tension of 30 dynes/cm for PS and PMMA and an interfacial tension value of 0.2 estimated from literature data contained in [17], the thermodynamic work of adhesion is estimated to be 0.058 J/m^2. Whereas a P(S-*b*-DMS)-SiH copolymer enhanced the adhesion of the PS-PDMS interface, a similar copolymer yields a small but discernible decrease in the toughness of the PS-PMMA interface. This result can be attributed to the fact that the silane functionality on the copolymer has no specific interaction with the PMMA substrate so that the PDMS layer on the PS matrix consequently functions as a release coating. The PS-PMMA interface is replaced by a relatively weaker PDMS-PMMA interface.

The adhesion between PS and PMMA can be enhanced, however, with a carboxylic-acid-terminated P(S-*b*-DMS)-COOH diblock copolymer. In this case, we recognize that PMMA is a Lewis base and, therefore, can form an acid-base interaction [18] with the carboxylic acid end group on the block copolymer. The carboxylic-acid-terminated copolymer leads to a statistically-significant increase in the fracture energy to approximately 3 J/m^2, reflecting the acid-base interaction between the carboxyl groups and PMMA. The dependence of adhesion enhancement on the areal density of block copolymer at the surface (*i.e.*, the coating thickness is proportional to the concentration of copolymer in the coating solution) is shown in Figure 7. Initially, additional copolymer loading increases the fracture toughness. When the copolymer layer thickness exceeds that corresponding to a saturated surface (*i.e.*, a complete monolayer) multilayers form. Multilayers are apparently ineffective in bridging the interphase and the toughness decreases.

The selective adhesion behavior of these additives is emphasized by the fact that a silane-terminated diblock copolymer enhances the adhesion between PS and a PDMS network by virtue of an hydrosilylation reaction between the silane group and residual vinyl groups in the PDMS gel, but causes a decrease in fracture toughness for the PS/PMMA interface. The carboxylic-acid-terminated P(S-*b*-DMS-COOH) diblock copolymer, on the other hand, is effective in promoting adhesion to PMMA, but would not promote adhesion to a PDMS substrate.

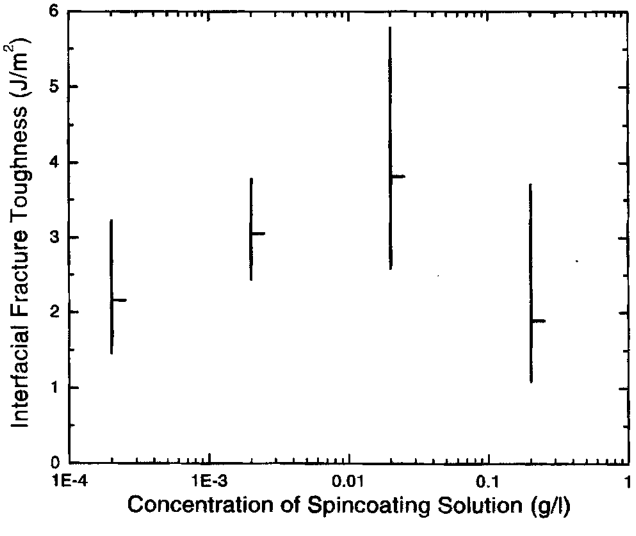


FIGURE 7 Toughness of the PS/PMMA interface as a function of the amount of poly(S-*b*-DMS)-COOH-5.1K added to the interface. The areal density of copolymer is directly related to the concentration of the solution used in spin coating.

Although the effects of the functional block copolymer are small, they are statistically significant and demonstrate the viability of the concept of surface active, selective adhesion promoters. The small magnitudes of the effects are due in large part to the use of low molecular weight (*i.e.*, ≈ 5000 Daltons) block copolymers that are well below the entanglement molecular weight. In the discussion below, we examine the possible origins of the adhesion enhancement in order to estimate the magnitude of adhesion enhancement that might be obtained if higher molecular weight block copolymers were utilized.

X-ray photoelectron spectroscopy (XPS) analyses [19] of the fractured surfaces suggest that pullout of the relatively short PS blocks is the dominant failure mechanism of the PS/P(S-*b*-DMS)-COOH/PMMA interface. The survey spectra (Fig. 8) of the fracture

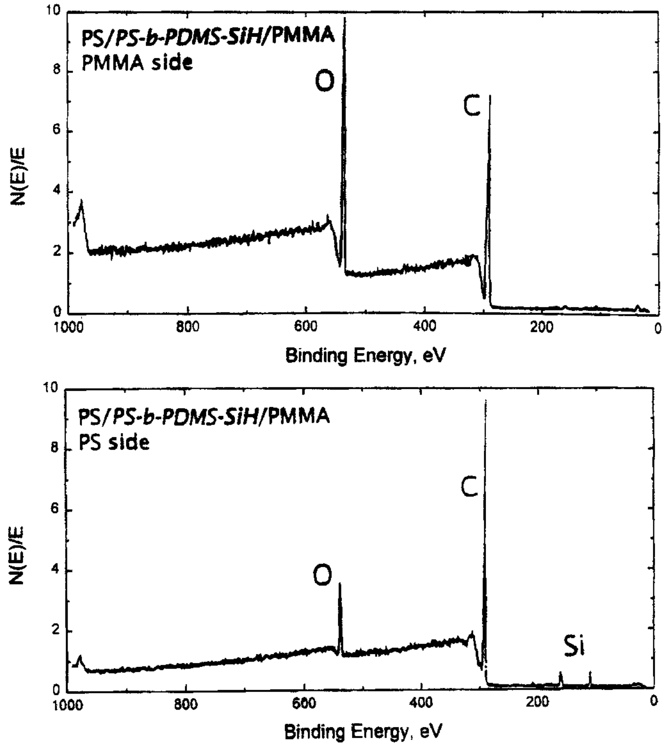


FIGURE 8 XPS survey spectra of the fracture surfaces from the poly(S-*b*-DMS)-SiH-5.5K copolymer-modified PS-PMMA interface.

faces show evidence of silicon on both surfaces; photoelectron signals from both the silicon 2p core level at 100.5eV and the silicon 2s core level at about 150 eV are clearly visible. This observation indicates that the acid-base interaction of the carboxylic acid end group with the PMMA is strong enough to pull some of the copolymer chains out of the PS homopolymer matrix. In contrast, the spectra for the PS/P(S-*b*-DMS)-SiH/PMMA fracture surfaces (Fig. 9) show evidence for silicon only on the PS side, indicating that this copolymer has no significant adhesion to the PMMA substrate.

Failure of the PS/P(S-*b*-DMS)-COOH/PMMA interface can occur by one of three mechanisms: pullout of the PS copolymer sequence

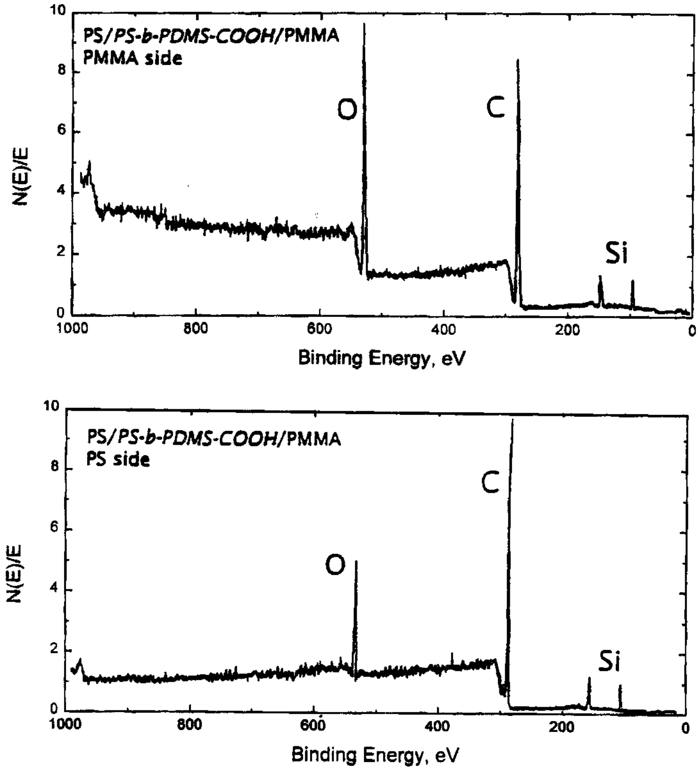


FIGURE 9 XPS survey spectra of the fracture surfaces from the poly(S-*b*-DMS)-COOH-5.1K copolymer-modified PS-PMMA interface.

from the PS matrix, breakage of the PDMS elastomeric copolymer sequence, or disruption of the acid-base interactions between PMMA and terminal carboxylic acid groups. Considerations of the force applied on each chain and the energy requirements for various modes of failure suggest that pullout of the PS copolymer sequence is the dominant failure mechanism. In the simplest model, the force to pull a chain out of a glassy polymer is equal to the total frictional force, Nf_{mono}, where N is the degree of polymerization of the pulled-out chain (*i.e.*, 29 for the PS sequence) and f_{mono} is the monomeric friction factor [20, 21, 22]. Entanglement effects can be ignored, since the molecular weight of the PS sequence length (*i.e.*, 2900) is well below the reported entanglement threshold of 18,000–20,000 [23]. If the friction factor for PS is assumed to be that of polyvinylpyridine, about 6×10^{-12} N/monomer, the calculated force for chain pullout is about 1.7×10^{-10} N. This number is smaller that the PS chain scission force of about 2×10^{-9} N, suggesting that failure occurs by pullout rather than scission. If the saturation chain density at the interface is assumed to be 0.5 chains/nm^2, then the failure energy dissipated in the pullout process, using the same model allowing for some plastic deformation [19], can be estimated at about 1.6 J/m^2, similar to the value observed. If the failure mode is breakage of the elastomeric PDMS sequence, the failure energy can be estimated using the Lake-Thomas model [14]. In this model, breakage of the elastomer occurs when the energy of each bond exceeds the bond rupture energy. The total failure energy per chain is equal to the total number of bonds times the rupture energy of a single bond. Assuming a bond energy of 6×10^{-19} J for the weakest covalent bond (Si—C), the fracture toughness associated with breakage of the PDMS sequence, calculated from literature values for the bond rupture energy and an estimate of the area per chain at the interface [19] is about 9 J/m^2, much larger than that observed. The fracture energy accompanying disruption of the acid-base interactions between the carboxyl group and the PMMA matrix is estimated to be in the 4.7 to 14.7 J/m^2 range [19], also larger than that observed. Calculations of fracture energies, therefore, suggest that failure occurs by pullout of the short PS copolymer sequences from the PS matrix and that the fracture toughness could be improved by the use of copolymers with longer PS blocks. Longer PS blocks could change the failure mechanism to either chain scission of the PDMS block or disruption of the acid-base interactions and could, therefore, generate additional increases (*i.e.*, by a factor of 3–6) in the interfacial fracture energy.

SUMMARY

The two examples described herein demonstrate a new molecular design concept for the creation of surface-active additives that impart selective adhesion properties to polymeric substrates. The design involves the synthesis of ω-functional diblock copolymers with proper sequencing of three constituents along the polymer chain. The first component is an anchor block that is composed of monomers that interact favorably with the matrix and, consequently, tether the copolymer into the matrix polymer. The sequence that follows comprises low surface energy monomers and serves as a vehicle to deliver the copolymer to the surface. The third component is a specific functional group attached to the terminus of the surface-active sequence. The functional terminus is selected to have a highly specific interaction with *only* the target substrate. While we have illustrated the concept here for adhesion promotion toward two synthetic polymeric substrates, we believe that the approach is a general one that can be used to design and create a wide variety of smart polymer surfaces that also have selective binding affinities for inorganic substrates, non-polymeric organic materials and biological substrates, including cells and proteins. Such smart material surfaces have tremendous value as model substrates and a myriad of potential applications in fields such as sensors, biomaterials and separation media.

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