Effect of Surface Segmental Mobility on Adhesion of Acrylic Soft Adhesives

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ABSTRACT: The dependence of adhesion on the surface segmental dynamics of polymer substrates in thin-film poly(methyl acrylate) (PMA)− and poly(methyl methacrylate) (PMMA)−adhesive tape systems was probed via tape peel tests. From 90° angle tape peel experiments at 28 °C of very thin films of PMA adsorbed on glass slides, it was found that the peel velocities varied linearly with applied force and the force−velocity curves were dependent on film thickness. Extrapolation of the peel−velocity curves to zero velocity yielded an estimate of the fracture energies, which varied from about 50 to 20 J/m^2 for thicknesses from 50 to 2000 nm. The fracture energies were also found to depend exponentially on film thickness with a decay length of 110 nm. In contrast to the behavior of PMA, PMMA films showed larger fracture energies but no thickness dependence. The differences in the behavior of the two types of films are believed to be due to differences in segmental mobilities in the films which give rise to differences in the motions of the "anchoring sites" across the interface. For PMMA, the glassy polymer was rigid at the interface, regardless of the thickness, and hence, no thickness dependence was observed. For PMA, a rubbery polymer at room temperature, the segments at the adhesive interface were influenced by the restrictions posed by interactions of the polymer with the glass surface. A model based on differing thicknesses of the polymer interphases is proposed to account for the behavior observed.

Introduction

Adhesion between two materials results from molecular attractions acting across an interface. The interaction between two polymer layers, especially the adhesion between them, is critical in many applications, especially for pressure-sensitive adhesives (PSAs).[1] Considerable effort has been devoted to developing methods for measuring adhesion because of its importance and also its complexity.[2,3] Detailed knowledge of the molecular structure and dynamics of polymer interfaces, and how they relate to macroscopic mechanical properties, should help in the understanding of adhesive systems.

In principle, the measured fracture energy, G_c, associated with the separation of two surfaces in contact, is expected to be greater than, or equal to, the thermodynamic work of adhesion, W_A. The thermodynamic work of adhesion may be estimated as the difference in the surface energies (interfacial tensions) of the free surfaces (γ_1 and γ_2), less that of the combined interfaces (γ_{12}) or $W_A = \gamma_1 + \gamma_2 - \gamma_{12} \le G_c$. The inequality arises from viscoelastic or other processes which occur at the interface during the separation. It has been found that the measured fracture energies are typically orders of magnitude greater than those given by the surface energies alone through a magnification factor.[3−5] It has also been suggested that a term representative of the rupture of interfacial interactions, such as hydrogen bonds, be added to account for adhesion.[6]

Despite the inequality mentioned above, it has been shown phenomenologically that the work of adhesion can still be important and may be amplified by viscoelastic factors or $G_c = W_A(1 + \phi)$, where ϕ is a function of variables, like velocity and temperature, and accounts for the other processes.[4,5,7] It has also been clearly demonstrated that the "dynamic processes at the interface" play an important role in adhesion.[8] Consequently, both the nature of the interaction and its modification by the dynamics at the interface control the adhesion in elastomeric systems. To fully understand these effects, knowledge of the microscopic nature of the interfacial region is required. The interplay of the chemical, physical, and mechanical nature of polymeric substrates has received some attention,[8−11] but these effects are complex and need further study.

In an attempt to clarify, at least in part, the role of the dynamics of polymer chains on adhesion, we have chosen to use peel tests to compare the behavior of two different, yet similar, glass-supported thin polymer films. Specifically, poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) were chosen because they have similar chemical structures and surface energies but, at measurement temperatures, very different segmental dynamics. Under the measurement conditions used, bulk PMA was rubbery and bulk PMMA was glassy. In addition, previous studies from this laboratory of these two systems allow us to relate this behavior to differences in the microscopic dynamics of the polymers in the interfacial region.

The surface dynamics of PMA-d_3 at the silica−polymer−air and silica−polymer−polymer interfaces have been studied using deuterium NMR.[12−14] These studies indicated that the adsorbed polymer at the air interface exhibited a motional gradient perpendicular to the silica surface. A very small number of polymer segments, with segmental mobilities that were greater than bulk (faster), were found and assigned to segments near the polymer−air interface. In contrast, most seg-

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ments had mobilities that were less than those in bulk (slower) due to the interaction of the polymer with the silica at the polymer−substrate interface. The mobility of most of the PMA segments was observed to decrease as the adsorbed amounts decreased.[12] Thus, for very thin films of PMA, *thinner films have slower dynamics than thicker films*. In addition, when another layer of polymer was lightly compression-molded over the polymer adsorbed on silica,[13,14] the highly mobile polymer segments, at the polymer−air interface, lost their extra mobility. The mobility of the PMA segments, now at the PMA−polymer interface, depended on the mobility of the polymer in the overlayer. This dependence was found even if the two polymers were incompatible, e.g., polystyrene on PMA. One would expect this kind of interaction to occur at the interface in systems such as those reported here.

The aforementioned NMR studies can also be interpreted in terms of a local glass-transition temperature (T_g), which we define as the onset of cooperative segmental motion. Clearly, there is an intimate relationship between significant increases in both the rates and amplitudes of segmental motions and the onset of the T_g.[15] The collapse of the deuterium powder pattern was indicative of significant amounts of segmental motion and could be considered the NMR T_g.[12,16] The NMR T_g is related to the T_g measured with calorimetry by the time scale of the experiment. It was evident that the glass-transition region was broadened (heterogeneous) for the adsorbed polymer, and the local T_g increased from the air interface to the substrate interface. The T_g also increased with decreased adsorbed amounts, especially near the air−polymer interface.

The thermal behavior of the PMMA on silica was studied with modulated differential scanning calorimetry (MDSC).[17] It was observed that the T_g of the adsorbed polymer increased as the thickness of the polymer layer decreased. It was also found that the width in the transition broadened as the amount of adsorbed polymer decreased. These results were consistent with the direction of the shift in T_g for thin layers of PMMA on silica as observed via ellipsometry.[18] Importantly, this behavior was observed in the region of the bulk T_g, i.e., >100 °C, and not at temperatures close to those where our measurements were taken. On the basis of these results, it is reasonable to suggest that in their respective glass-transition regions the PMA and PMMA adsorbed systems behave similarly. However, around room temperature, they behave very differently, especially in terms of their segmental dynamics.

Little is known about how changes in dynamics relate to certain mechanical properties of polymers, such as adhesion between two polymer layers. Although much research has been done to quantify the adhesion strength between films and substrates, many questions remain unanswered. For example, does adhesion strength depend on the mobility of polymer segments on the surface? If so, it should depend on the thickness of the polymer layer under some conditions. We believe we can address this question through the results of the tape peel tests reported and our knowledge of the microscopic dynamics of the systems.

Experimental Section

Poly(methyl acrylate) (PMA) was synthesized via bulk radical solution polymerization of methyl acrylate (Aldrich) with AIBN (Aldrich), recrystallized before use with methanol, as an initiator. Methyl acrylate was stirred overnight with CaH_2 and then vacuum-distilled. Methyl acrylate (25 mL) was mixed with 0.03 g of AIBN, and the reaction vessel was then heated to 60 °C and held for 5 h. The resulting polymer was dissolved in toluene and precipitated with methanol. PMMA (Aldrich) was used as received. Molecular masses of both polymers were measured using size-exclusion chromatography on a DAWN EOS light scattering instrument (Wyatt Technology, Santa Barbara, CA) with an Optilab refractive index detector (Wyatt Technology). The glass-transition temperature (T_g) for both polymers was measured using modulated differential scanning calorimetry (MDSC) (TA Instruments, New Castle, DE). The PMA and PMMA molecular masses and T_g's are given in Table 1.

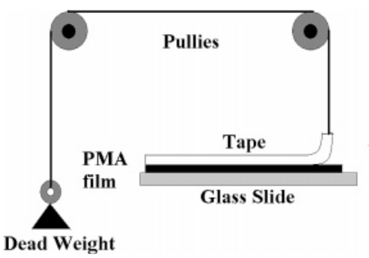

Figure 1. Experimental apparatus for peel experiments.

Table 1. Characterization of PMA and PMMA

polymer	T_g (°C)	M_w (g/mol)	polydispersity
PMA	10	620 000	2.27
PMMA	104	90 000	1.55

A variety of different conditions were evaluated to determine how to reproducibly obtain continuous films on the glass slides.[19−24] The glass slides (Corning Micro Slides 2948, single frosted) were first washed with methanol and then dried under vacuum. Thin polymer films were applied from PMA or PMMA solutions in toluene, using a spin-coater. Polymer solution concentrations greater than 1% (w/w) were used because, when the concentration was below 1%, holes were observed in the films. The coating process usually was done in 30−120 s, with higher adsorbed amounts resulting from higher initial solution concentrations. After the initial coating, the samples were briefly dipped in toluene, to remove excess polymer from the substrate and reduce surface roughness, and then air-dried. The samples were annealed for 10 h in a vacuum oven at 70 °C.

Adhesive tape (Scotch Magic Tape 810, 3M, Minneapolis, MN) was applied to the samples after they cooled. A lightweight wooden rod was rolled over the tape after it had been placed carefully on the coated glass slides. The samples, with tape applied, were kept in desiccators at room temperature for 2 days to allow the polymers to relax before the mechanical studies were conducted. For our samples, the results did not depend on the pressure applied by hand or the exact time the samples were allowed to set. A similar independence was found in other acrylic adhesives.[6]

The tape was peeled at a 90° angle with a string that was run over pulleys, as shown in Figure 1. Peel velocities were controlled by hanging different dead loads in a basket on the free end of the string. The measurements reported were the average of at least four individual measurements. The peel tests were conducted at 28 °C.

The coated slides, bare glass slides, and tape were probed with atomic force microscopy (AFM) using a Nanoscope III (Nanoscope Digital Instruments, Santa Barbara, CA). Randomly selected samples from some batches of coated slides were sacrificed before and after the peeling experiments to determine the surface profiles and polymer layer thicknesses. The slides were scored and broken by hand, attached to the instrument, and probed using tapping-mode AFM with a silicon nitride tip coated with Au. The thicknesses were usually determined by making a fine scratch on the polymer films with a medical scalpel across the 2.5 cm side of the glass slide. The AFM tip was then put in the vicinity of the side and the sample scanned near the scratch. The scoring process produced a

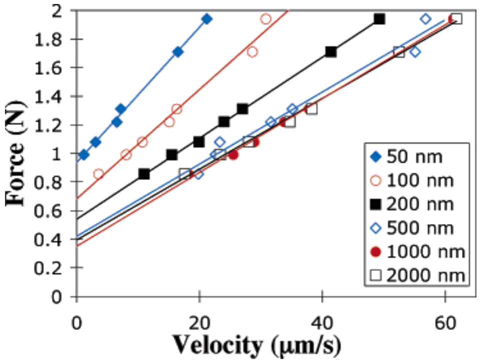

Figure 2. Peel force (N) vs peel velocity (μm/s) for various film thicknesses of PMA. The experiments were conducted at a 90° peel angle.

plateau of excess polymer parallel to the scratch. The thickness of the polymer film was determined to be the depth of the "trench" carved out by the scratch. This depth was measured relative to the height of the polymer past the plateau. We believe that this region was relatively unaltered by the scratch. The thickness measurements were also confirmed in several test cases by dipping part of the coated glass slide in toluene for about $^1/_2$ h. Under these conditions, most of the excess polymer desorbed in the dipped region of the slide, except for a very small amount of directly bound polymer (on the order of a few nanometers thick). The profile of the polymer from the dipped region to the undipped region was followed to estimate the thickness of the original film. These measurements were quite close to those made by the scratch method.

Results

The peel force vs peel velocity data on PMA for various film thicknesses are shown in Figure 2. The uncertainties, as determined from multiple measurements, were found to be roughly the size of the symbols used in the figure (always less than 3% error). The data did not depend, to any significant extent, on the force used to attach the tape or the amount of time the tape was allowed to mate with the substrate, as long as it was at least a couple of days. It was observed that peel velocities increased as the amount of force used to separate the two surfaces increased. The relationship between peel force and peel velocity was observed to be linear. The force, extrapolated to zero velocity, can be considered the amount of force required for initiation of crack propagation. For forces that are higher than this, the additional energy is used in the propagation of the crack. It was also observed that the force required to separate the polymer layers increased as the film thickness decreased, except at the larger thicknesses, where the forces were roughly independent of thickness.

The peel force vs peel velocity data for PMMA films of various thicknesses are shown in Figure 3. For comparison, the lines for the PMA data are shown in this figure without symbols. The uncertainties for single PMMA measurements were found to be higher than those for PMA, on the order of 6% error. The dependence on peel velocity was similar to that for PMA, but there were no distinct, systematic differences in peel force as a function of film thickness for PMMA. The points for the different thicknesses roughly fell on the same line, as distinct from the behavior of PMA. Thus, for PMMA, it was observed that the force required to separate the polymer layers did not depend on the thickness of the polymer film on the substrate in the range studied. Because of the lack of dependence of the PMMA peel data on film thickness, and its expected behavior (vide infra), we did not feel it was necessary to make any additional measurements on the PMMA system. For PMMA, the force required to separate the two polymer layers was also significantly greater than that observed for PMA (on the order of 3 times).

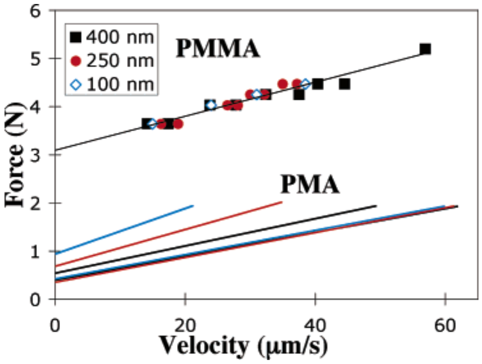

Figure 3. Force (N) vs peel velocity (μm/s) for different film thicknesses of PMMA. Peel experiments were conducted at a 90° peel angle. The lines drawn from the data in Figure 2 for PMA are also included for reference.

Table 2. Extrapolated Forces and Fracture Energies for PMA as a Function of Film Thickness

thickness (nm)	force (N) ($v = 0$)	fracture energy (J/m^2)
50	0.94 (±0.01)	49.3 (±0.7)
100	0.68 (±0.04)	36 (±2)
200	0.54 (±0.01)	28.4 (±0.5)
500	0.42 (±0.07)	22 (±4)
1000	0.35 (±0.02)	18 (±1)
2000	0.39 (±0.03)	21 (±1)

Peel experiments with untreated glass slides (bare glass), performed for comparison, showed that the amount of force required to initiate a crack in the system was approximately 6 times that observed in peel experiments with PMMA. The reproducibility with bare glass was much worse than for the polymer-coated slides, but the trend was certainly clear.

The tapping-mode AFM micrographs of the surface structure of representative samples of unpeeled and tape-peeled PMA films (120 nm) on glass slides are shown in Figure 4. The darker regions on the left-hand sides of both samples indicate the location of the scratch. Moving to the right of the figure, the bright regions, consisting of PMA piled up during the scratching process, are from the plateaus, parallel to the scratches. Both of the plateaus shown were about 2.5 μm wide and 200 nm high. The height was measured relative to the more uniform part of the polymer film on the right-hand side. It is apparent that the unpeeled samples (Figure 4a) had a flatter surface than the peeled samples (Figure 4b). The peeled samples did not show pinholes or any significant differences in thickness compared to the unpeeled samples. The peeled samples did exhibit more roughness than the unpeeled samples as well as the presence of some higher "hills", likely resulting from the peeling process. The rms surface roughness of the unpeeled substrates was typically 30 nm compared to 60 nm for the pealed samples. This compares to about 20 nm for the bare glass slide and 75 nm for the tape.

The extrapolation of the peel forces to zero velocity (intercepts given in Table 2), divided by the width of the tape (1.9 cm), yields the fracture energies per unit length, G_c (J/m^2). The values of G_c for PMA are shown in Figure 5 as a function of the thickness of the PMA

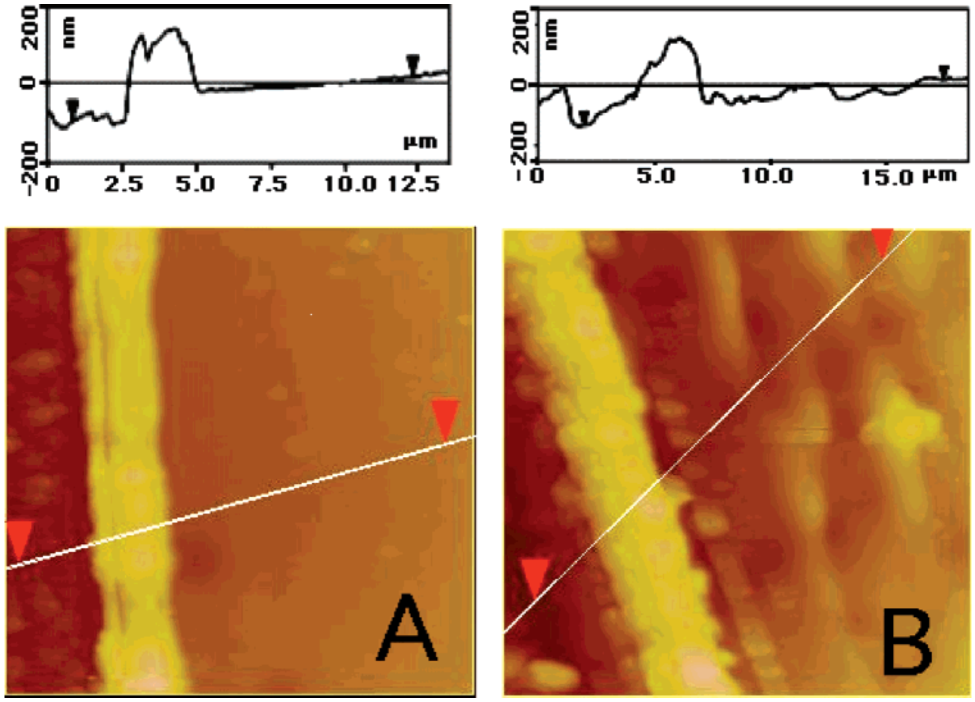

Figure 4. AFM images of PMA on glass slides (13.5 × 13.5 μm) for (A) unpeeled and (B) tape-peeled films (120 nm thick). Top: image heights across the traverse line in the bottom images. Bottom: from left to right in each micrograph are the regions associated with the scratch, plateau (bright portion), and flat film (see text).

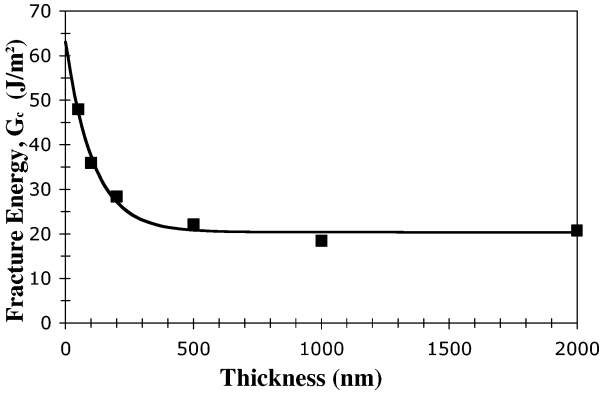

Figure 5. Fracture energies as a function of film thickness of PMA. The curve drawn is an exponential fit to the data as in eq 1.

layer. The data were fit to exponential thickness dependence with

$$G_c = A \exp(-t/t_c) + G_{c,\infty} \tag{1}$$

where A is a preexponential factor, t the film thickness, t_c the decay coefficient, and $G_{c,\infty}$ the bulk fracture energy. The values determined from a least-squares fit yielded a preexponential constant of $A = 42.6 \pm 1.5$ J/m^2, a bulk fracture energy of $G_{c,\infty} = 20.4 \pm 0.4$ J/m^2, and a decay length of $t_c = 109 \pm 4$ nm. The values reported are those yielding a minimum least-squares error, (predicted − experimental)^2, from eq 1. The uncertainties are given as the values which, when added to the best-fit values, give a 10% change in the sum of the squares of the residuals.

For PMMA, the extrapolation of the peel forces to zero velocity, and the corresponding G_c values are shown in Table 3. Within experimental error, as expected from data, these values were independent of the PMMA film thickness. The value of the fracture energy for the extrapolation of all of the data together is 163 ± 3 N/m^2. This value is roughly 3 times that for a 50 nm PMA film or 2.5 times the extrapolated value for a PMA film of zero thickness.

Table 3. Extrapolated Forces and Fracture Energies for PMMA as a Function of Film Thickness

thickness (nm)	force (N) (v = 0)	fracture energy (J/m^2)
100	3.14 (±0.06)	165 (±3)
250	2.86 (±0.08)	150 (±4)
400	3.1 (±0.1)	163 (±5)
all	3.09 (±0.06)	163 (±3)

Discussion

Fracture energy is defined as the amount of energy applied to a system, per unit extension of the crack area, when a fracture takes place, according to the Griffith energy balance criterion.[25] For our data, a linear extrapolation to zero velocity was appropriate and accurate and has been observed by others,[26] although we recognize that rather complicated rate and time dependencies have also been observed.[27,28] The fracture energies were calculated from the load, P, at zero velocity, after Kendal for the separation of an elastomeric film from a rigid substrate:[8,29]

$$G_c = (P/b)^2(1/2Eh) + (P/b)(1 - \cos\theta) \tag{2}$$

where b is the width of the tape, E is its Young's modulus, h is its thickness, and θ is the peel angle. The first term in eq 2 gives the amount of recoverable strain energy. For high peel angles (e.g., 90°), the first term of eq 2, which represents the elastic strain energy term, becomes insignificant. Ideally, at angles near 90°, the lateral stress on the film is negligible, and there should be no slip at the interface (of course the angle will not be exactly 90° for a flexible tape). Then, the fracture energy is simply given as[29−31]

$$G_c = P/b \quad (3)$$

In practice, the peel angle will not be exactly 90° at the interface due to the curvature of the tape. Thus, the fracture energy only approximates the peel force per unit width of film. The intercepts of the peel force vs peel velocities of PMA in Figure 2 yield the value of the energy required to initiate cracking. For PMA, the fracture energy increased as the film thickness decreased.

Fractures can be cohesive or adhesive. If fracture occurs in the bulk of the polymer film, then it is called a cohesive fracture, while fractures occurring at the interface are called adhesive. Fracture at the interface is often a rate-dependent quantity due to chain pullout, chemical reactions, or viscoelastic processes at the interface. Consequently, we looked for manifestations of chain pullout[27,32] or other effects such as cavitation or fibril formation[33,34] in the AFM pictures, but we found none in either the PMA or PMMA (not shown) systems. In addition, there were no significant changes in film thickness beyond that which might be ascribed to the roughness of the slide. Although the distortions in the peeled films may indicate some minor distortions in either the substrate or tape, we concluded that the failure was primarily adhesive in nature.

The following observations require explanations: (i) the adhesion of PMA films is thickness dependent and that of PMMA films is not, (ii) thinner PMA films have greater fracture energies than thicker ones, and (iii) PMA thin films have smaller fracture energies than PMMA thin films. These effects should be related to the fundamental nature of the interaction at the interface and/or the dynamic and mechanical properties of the film. Clearly, all of these may be interrelated.[9]

PMA and PMMA have similar functional groups, and as expected, their surface energies are similar. The surface energy, at ambient temperature, for PMMA[35] (γ = 38.5 ± 0.5 mJ/m^2) is lower than that for PMA[36] (γ = 42.7 mJ/m^2). In principle, on the basis of these criteria, and assuming the tape−polymer interactions (γ_{12}) are similar, it should take slightly more energy to create an exposed PMA surface than a PMMA surface. While it is difficult to measure the surface energy of a rubbery polymer with great accuracy, this ordering is in opposition to that expected on the basis of the measured fracture energies for PMA−tape and PMMA−tape. Therefore, we expect that the surface energies of the free surfaces alone do not play a dominant role in the differences observed.

Over the past several years, several studies have focused on the role of viscoelasticity in adhesion of PSAs with rubbery polymers with low adhesion.[7,9,10,26] Newby et al.[7,8,26] found that the adhesion between tape and either a fluorocarbon or poly(dimethylsiloxane) (PDMS) grafted on glass was dominated by the differences in dynamics of the two grafted polymers. More slippage at the interface was proposed to be the primary cause of the lower adhesion of the more mobile PDMS.[8] Amouroux et al.[10] used a similar technique with PDMS elastomers (60 μm films on glass), with different amounts of a filler resin. They attributed lower adhesion, in systems with no or little filler resin, to slippage at the interface. At higher filler resin contents, shear deformations, distributed within the elastomer, became dominant. The latter mechanism, based in part on the mating time dependence of the adhesion, was supposed to be due to a stronger interaction (which the authors refer to as "anchoring sites") of the filler resin with the tape adhesive. In the absence of a slip mechanism, the adhesion increased substantially.

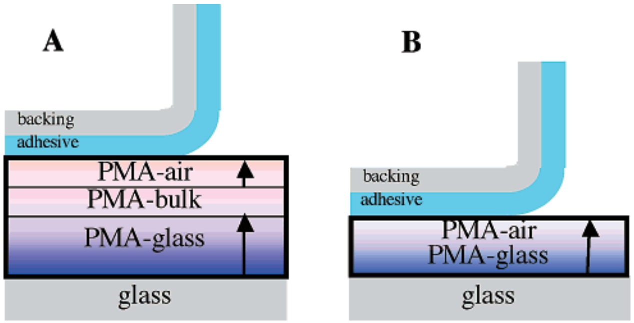

Figure 6. Schematic representations of the adsorbed polymer films on a glass substrate showing the polymer−air and polymer−glass interphases (not to scale) when they are (A) well separated (thick films) and (B) in close proximity (thin films). The motional gradients (from lower to higher mobility) are indicated by the arrows.

Other studies have focused on the effect of the chemical composition of the components.[6,9] In adhesion tests based on a poly(n-butyl methacrylate) (PNBA) adhesive, Ahn and Shull found differences based on the polymer used as the substrate.[6] With the PNBA adhesive, a PMMA substrate was found to have about twice the adhesion as a 10 nm PNBA substrate. This factor is similar to what we found for PMMA and PMA. The thickness dependence of the adhesion with the PNBA substrate was not probed by Ahn and Shull, but a slight thickness dependence was found for a PMMA/PNBA/PMMA triblock polymer.

The polar nature of the PMA and PMMA and their more favorable interaction with the acrylate-based adhesive in the tape are responsible for the larger fracture energies found for these polymers compared with PDMS.[8,10] We believe that the differences in adhesion (and the thickness dependences) in the PMMA− and PMA−tape systems are due to differences in the segmental mobility of these polymers. The polymer film acts as a boundary layer for the tape. Unlike earlier works, where chemical modifications were made to change the adhesion in model systems, *our modification is physical.* For PMA, the chemical composition of the thin films remained constant while the mechanical/dynamical properties of the films were changed. These changes were due to the proximity of the glass surface to the mating (adhesion) surface with thinner films exhibiting more limited segmental dynamics than thicker films.

We propose a model for our polymer films with two interphases: one near the air−polymer interface and the other near the polymer−glass interface. Between them, if the films are thick enough, lies bulklike polymer. The interphases are the regions of the polymer where the presence of the interface (i.e., polymer−air or polymer−glass in this case) modifies the properties (e.g., segmental mobility) of the polymer. Each of the interphases has a characteristic distance scale (depth) over which its influence is effective. A schematic of this situation is shown in Figure 6. We believe that this simple model can be used to provide the answers to some of the questions posed. The features of the model are similar to those proposed by others and reviewed by Forrest and Dalnoki-Veress.[37]

The dependence, or independence, of the adhesion on thickness for either the PMA or PMMA system may be rationalized on the basis of the depth of the polymer−air (and polymer−adhesive) interphases at the temperature studied. The lack of a thickness dependence for glassy PMMA films can be explained if the depth of that interphase is very small. A thin interphase for a glassy polymer would be expected since only very short-range motions may take place on the time scale of our measurements. In contrast to the small depth of the air−polymer interphase for glassy PMMA, our present results estimate the depth of the interphase for rubbery PMA as on the order of 110 nm (as per the exponential decay, τ_c, of the adhesion measurements). We know of no comparable measurements of this length scale for rubbery PMA around its glass transition; however, there are measurements for PMMA near its glass transition. The PMA and PMMA comparison is reasonable as long as each is around its own T_g. Keddie and Cory[18] have used ellipsometry to make such measurements for rubbery PMMA on silica, near its glass-transition temperature (i.e., on the order of 100 °C). They estimate very similar decay lengths for rubbery PMMA as we have found for our rubbery PMA. In addition, since the adhesive in the tape is lightly cross-linked and the tape adhesive and PMA are immiscible, we believe that there is likely little interpenetration of the PMA layer and the tape adhesive. Little interpenetration of the tape adhesive and PMA plus the rough interphase width compared to the thicknesses of our PMA films would both be consistent with possible thickness dependence on segmental dynamics and, ultimately, adhesion.

The rationale developed for the differences in adhesion in the other systems discussed above[7,8,26] can be applied to the PMMA− and PMA−tape systems. That is, substrate mobility gives rise to more slippage in more mobile systems. If the interfacial energies in the PMMA and PMA systems are not significantly different, the higher adhesion in the PMMA system would be due to its lower mobility. If the nearness of the polymer−silica interphase also lowers the mobility of the polymer−air (and polymer−adhesive) interphase (vide infra), it would also be consistent with the thickness dependence shown for the PMA system.

It is well-known that mechanical/viscoelastic responses of polymers are related to molecular motions of polymer segments.[15] Our group has used deuterium NMR to study how the presence of a silica interface modified the segmental dynamics of PMA at very small adsorbed amounts. We demonstrated the presence of a graded interface in terms of segmental motions.[12,13] The schematic in Figure 6 also shows this motional gradient. Segments at the air−polymer interface were found to have faster molecular motions than bulk−polymer segments, while those segments at the polymer−silica interface had motions slower than those in bulk. The latter reduction in mobility was due to the hydrogen-bonding interaction between the carbonyl group of the polymer and the surface silanols. Most importantly, the dynamics for thinner films at the air interface were the slowest in the films. In addition, a similar thickness dependence was also found, by differential scanning calorimetry, for adsorbed PMMA on silica, but only near its T_g.[17]

We believe that the differences in the segmental dynamics of the PMA films, as a function of film thickness, are ultimately responsible for the thickness dependence found in the adhesion measurements. We believe that slippage, and maybe other mechanical effects, are related to the dynamics of the "anchoring sites"[10] (also referred to as "sticker groups"[11]) and their interaction across the interface. In thinner PMA films, where the polymer−glass and polymer−air interphases overlap, slower dynamics and longer-lived interactions across the interface allow less slippage and result in greater adhesion. As the polymer−glass and polymer−air interphases become separate, as in thicker PMA films, the physical properties level off. Relatively mobile polymer−adhesive interphases, such as those found in thicker PMA films, would be expected to give rise to more rapid making and breaking of secondary bonds at the interface, which would then allow slippage at a local level. This is clearly a simplification of a very detailed process, but it might well be a useful one.

Unfortunately, we have not yet been able to characterize the details of how the dynamics vary as a function of thickness, nor are we able to relate the details of the dynamics to a quantitative model for adhesion; so detailed modeling of the system is not possible at this time. Nevertheless, the exponential dependence on thickness of the adhesion in very thin films of PMA at room temperature is novel and striking.

Conclusions

The adhesion of ultrathin films of PMMA and PMA on glass slides with tape showed remarkable differences at room temperature. Both systems showed a linear dependence of velocity on force over the range probed. For PMMA films on the order of 100−400 nm, higher adhesion and *no* thickness dependence were found. For PMA films from 50 to 2000 nm, lower adhesion and an exponential thickness dependence were found. The exponential decay constant for the PMA film was found to be about 110 nm, suggesting a distance scale for the decay of the influence of the polymer−glass interphase on the polymer−air or polymer−adhesive interface.

We believe that the differences in the behavior of the two polymer thin films are based in their dynamics at a segmental level. The glassy PMMA at the polymer−air (or polymer−adhesive) interface has a relatively small interfacial length and is rigid. This gives rise to longer-lived interactions than in the case of PMA. If interfacial slippage or another similar mechanism occurs, it is likely to be minimal for rigid PMMA and, consequently, will enable larger fracture energies to occur. On the other hand, the segmental dynamics of the more rubbery PMA are much faster and one might expect more slippage when PMA is used, thereby reducing the fracture energies. The much larger thickness of the polymer−air (or polymer−adhesive) interphase in rubbery PMA and its concomitant interaction with the polymer−glass interphase are responsible for the thickness dependence observed for this system. The exponential decay of the fracture energy gives a significant estimate of the distance scale for this interaction.

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Supporting Information Available: Tables of velocities for the peel tests for PMA as a function of force (Table 4) and velocities for the peel tests for PMMA as a function of force (Table 5). This material is available free of charge via the Internet at http://pubs.acs.org.

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