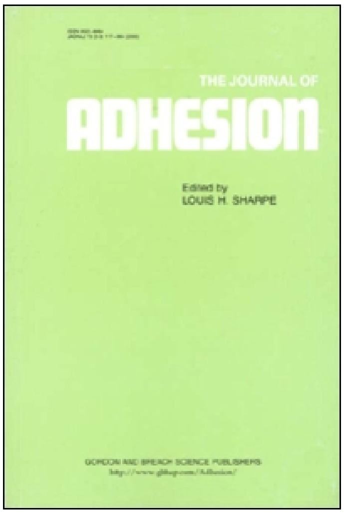

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Surface Segmental Mobility and Adhesion—Effects of Filler and Molecular Mass

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Surface Segmental Mobility and Adhesion—Effects of Filler and Molecular Mass

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The adhesion of thin films of poly(methyl acrylate) (PMA) on glass slides in contact with tape has been measured as a function of thickness, molecular mass, and amount of silica-based filler. In all cases studied the polymer thin-film, tape-peel tests resulted in linear force-velocity plots. The best-fit lines were extrapolated to find the fracture energies at zero velocity. For thin layers of rubbery PMA on glass slides the PMA-tape fracture energies were found to decrease (from 55–20 J/m^2*) with increasing PMA thickness (50–1000 nm). Thin films made from glassy poly (methyl methacrylate) (PMMA) were found to have no thickness dependence and much higher fracture energies (*$\sim$*140* J/m^2*). The effect of PMA molecular mass was found to be smaller than the effect of film thickness. Including silica in the films at low levels dramatically increased the fracture energies, with a maximum (182* J/m^2*) found with 5.2% silica. With larger amounts of silica, the fracture energy declined significantly.*

Keywords: Filler effects; Peel tests; Poly(methyl acrylate); Segmental dynamics; Silica filler; Tape peel test; Thickness effect; Thin-film adhesion

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INTRODUCTION

The adhesion of thin polymer films to various substrates is critical in a wide variety of technologies, especially in pressure sensitive adhesives [1]. The broad range of mechanisms that may play a role in adhesion, and the great differences in the strength of adhesion in different systems, make adhesion difficult to understand from a single point of view [2–4]. Consequently, a number of different techniques have been used to study adhesion and these techniques have been very useful in helping us understand many of the issues related to adhesion.

One area of interest to us is the behavior of soft adhesives (above their glass transition temperatures, T_g). It appears that these materials are clearly affected by the dynamics of the polymer segments at an interface [5–6]. Some studies have been made of the nature of the relationships between the physical and chemical properties of these polymers, their dynamics, mechanical properties, and adhesion [5–9], but there is still much more to be learned about how segmental dynamics affects adhesion.

Over the last few years we characterized the dynamics of interfacial polymers, how those dynamics affected the physical properties of adsorbed polymers, and, ultimately, their effects on the properties of composite materials. To this end we have used deuterium nuclear magnetic resonance (NMR) to study the dynamics of adsorbed poly (vinyl acetate)-d_3 [10] and PMA-d_3 [11–13] on silica. These polymers form hydrogen bonds with silanol groups on silica *via* their carbonyl groups. Consequently, the polymer dynamics of those adsorbed polymers are such that a motional gradient is established with the more mobile segments (lower T_g) present at the air interface and the more rigid segments (higher T_g) near the silica surface. Motional gradients in adsorbed rubbery polymers can affect the adhesion if the layers are thin enough [6].

In this work we report studies related to how the dynamics in thin films of PMA on glass slides affect the adhesion in the tape peel tests. Of specific interest are the effects of polymer molecular mass and the effect of a silica filler. Having previously established relationships between thickness and molecular mass for the segmental dynamics in PMA, it should be possible to determine if effects from these arise in the adhesion between PMA and tape.

EXPERIMENTAL

Poly(methyl acrylate) (PMA) was synthesized by atom transfer radical polymerization [14], similar to other PMA samples previously reported

[15]. Methyl acrylate (Aldrich, Milwaukee, WI, USA), N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) and ethyl 2-bromopropionate (2-EBP, Aldrich, 99%) were used as received. CuBr (Aldrich, 98%) was added to a 50-ml round-bottomed flask and the flask was sealed with a rubber septum. The flask was then purged with nitrogen to remove any oxygen. Degassed toluene, methyl acrylate monomer, and PMDETA were added with nitrogen-purged syringes. The mixture was purged with nitrogen for 10 min. Initiator (2-EBP) was added with nitrogen-purged syringes and the flask was immersed in an oil bath at 90°C for 8–24 h. The ratio of monomer/initiator was changed for each reaction, depending upon the molecular mass targeted. The polymers with relatively low polydispersity and molecular masses of 38, 41, 68, 77, and 165 kD were prepared.

A higher molecular mass PMA sample (384 kD) was synthesized *via* bulk radical solution polymerization of methyl acrylate (Aldrich) with AIBN (recrystallized before use with methanol) as an initiator. Methyl acrylate was stirred overnight with calcium hydride (CaH_2) and then vacuum distilled. Methyl acrylate, 25 ml, was mixed with 0.03 g of AIBN and the reaction was carried out at 60°C for 5 h. The polymer was dissolved in toluene and precipitated with methanol.

PMMA (Aldrich) and silica (Cab-O-Sil, M5, specific surface area, 200 m^2/g, Cabot Corp., Tuscola, IL, USA) were used as received. Molecular masses of the polymers were measured using size-exclusion chromatography on a DAWN EOS light scattering instrument (Wyatt Technology, Santa Barbara, CA, USA) with an Optilab refractive index detector (Wyatt Technology). The glass-transition temperatures (T_g's) for the polymers were measured using modulated differential scanning calorimetry (MDSC) (TA Instruments, New Castle, DE, USA). The PMA and PMMA molecular masses and T_g's are given in Table 1.

Different conditions were used to determine how to reproducibly obtain continuous films on the glass slides. The glass slides (Corning

TABLE 1 Characterization of PMA and PMMA Samples

Polymer	M_w (Da)	Polydispersity	T_g (°C)
PMA	38,000	1.15	3.5
PMA	68,000	1.29	10.6
PMA	77,000	1.26	12.3
PMA	165,000	1.42	13.4
PMA	384,000	1.50	14.2
PMMA	90,000	1.55	104

Micro Slides 2948, single frosted, Corning Corp., Corning, NY, USA) were first washed with acetone and then dried under vacuum. Thin polymer films were applied from PMA, PMA-silica, or PMMA solutions/dispersions in toluene using a spin coater. For individual systems 12–15 slides were coated in a batch.

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 completed in 30 to 120 s with thicker layers resulting from higher initial solution concentrations. After the initial coating the samples were washed by dipping them in toluene and then air-dried. The samples were kept for 10 h in a vacuum oven at 70°C. A few coated slides were randomly selected from a batch and probed with atomic force microscopy (AFM) using a Nanoscope III (Nanoscope Digital Instruments, Santa Barbara, CA, USA). The thickness of the polymer layer (before the peeling experiment) was measured by tapping-mode AFM using a silicon-nitride tip coated with Au. The thicknesses of the films with silica were about 2,000 nm for all of the samples studied. These thicknesses are in the range where the adhesion of the unfilled-PMA films shows adhesion to be independent of thickness (*i.e.*, in the large thickness limit).

Adhesive tape (Scotch Magic Tape® 810, 3 M, St. Paul, MN, USA) was applied to the samples after they had cooled down. 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. The tape was peeled at a 90° angle with a string that was run over pulleys, as previously reported [6].

Peel velocities were controlled by hanging different dead loads in a basket on the free end of the string. Peel velocities were calculated using the time taken to strip the tape off the coated slide for a fixed length (for different loads). The measurements reported were the average of at least four individual measurements. Experiments were conducted at 28°C. A few of the peeled slides were again randomly selected to probe with AFM to measure the thickness.

RESULTS

The peel force *vs.* peel velocity data for the PMA (384 kD) films of various thicknesses are shown in Figure 1. The uncertainties, as determined from multiple measurements, were roughly the size of symbols used in Figure 1 (less than 3% error). It was observed that the peel velocities increased as the amount of force applied to separate the surfaces increased. The relationship between peel force and peel velocity was observed to be linear. The force, extrapolated to zero velocity,

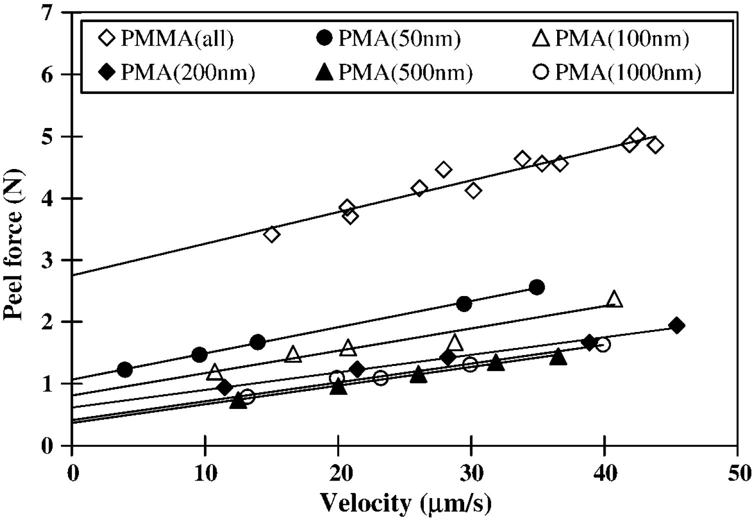


FIGURE 1 Peel force *vs.* peel velocity for PMA and PMMA of different film thicknesses. The individual PMMA thicknesses are not labeled because PMMA showed no thickness dependence.

gives the amount of force required to initiate crack propagation. The additional energy derived from excess force further accelerated the crack propagation. Also, it was observed that the force required to separate the two surfaces decreased as the PMA thickness increased until velocities (or energies) became independent of film thickness.

Force-velocity data were also collected for PMMA samples with thicknesses between 100 and 400 nm. The PMMA data are shown without labeling of the specific samples (thicknesses) in Figure1 because PMMA did not show a thickness dependence [6]. The composite line for the different thicknesses is considerably above those for the PMA samples indicating the stronger adhesion in the PMMA-tape system. The uncertainties of the PMMA measurements (less than 5% error) were found to be larger than those of PMA, but lower than those of PMA-silica films.

The extrapolation of the peel forces to zero velocity divided by the width of the tape (19 mm) yields the fracture energies per unit length, G_c (J/m^2). The least square fits to the data are also shown in Table 2. A definite dependence on thickness was found for the PMA samples. This is in contrast to that found for the PMMA. The G_c value for the PMMA samples was considerably higher, by a factor of about 3, than those for the PMA samples.

TABLE 2 Force-Velocity Analysis and Fracture Energies (at Zero Velocity) for PMA and PMMA at Different Thicknesses

Polymer	Thickness (nm)	Slope*	Intercept*	G_c (v = 0) (J/m^2)*
PMA	50	0.0423 (+/−0.0007)	1.06 (+/−0.02)	56.0 (+/−0.8)
PMA	100	0.0360 (+/−0.0045)	0.815 (+/−0.117)	42.9 (+/−6.1)
PMA	200	0.0284 (+/−0.0014)	0.616 (+/−0.044)	32.4 (+/−2.3)
PMA	500	0.0301 (+/−0.0088)	0.366 (+/−0.024)	21.3 (+/−2.4)
PMA	1000	0.0304 (+/−0.0020)	0.414 (+/−0.054)	21.8 (+/−2.8)
PMMA	100–400	0.0514 (+/−0.0043)	2.75 (+/−0.14)	144.5 (+/−7.3)

*Uncertainties given as +/− 1 S.D.

The peel test data for different molecular mass polymers for PMA films of 100 and 200 nm are shown in Figure 2. The behavior of the more narrowly dispersed masses was quite similar to that of the more polydisperse samples. The numerical results from the fits to the curve are shown in Table 3. The 200-nm films had fracture energies around 34 J/m^2 and their behavior appeared to be fairly independent of molecular mass. The 100-nm samples seemed to show some molecular mass dependence centered around 48 J/m^2; however, this dependence seems to be fairly small when the estimated experimental errors are taken into account. It is observed that the role of thickness seems to be more important than the role of molecular mass.

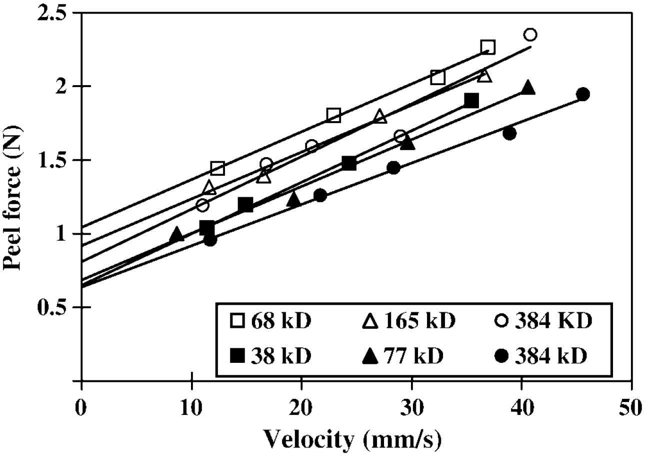


FIGURE 2 Force-velocity curves for 100-nm (open symbols) and 200-nm (closed symbols) PMA films as a function of molecular mass.

TABLE 3 Force-Velocity Analysis and Fracture Energies (at Zero Velocity) for PMA with Different Molecular Masses and Thicknesses

Molecular mass	Slope*	Intercept*	G_c (v = 0) (J/m^2)*
		100 nm Thick	
384,000	0.0360 (+/−0.0045)	0.815 (+/−0.117)	42.9 (+/−6.1)
165,000	0.0318 (+/−0.0019)	0.919 (+/−0.048)	48.4 (+/−2.5)
68,000	0.0324 (+/−0.0014)	1.046 (+/−0.039)	55.0 (+/−2.0)
		200 nm Thick	
384,000	0.0284 (+/−0.0014)	0.616 (+/−0.044)	32.4 (+/−2.3)
77,000	0.0318 (+/−0.0019)	0.684 (+/−0.051)	36.0 (+/−2.7)
38,000	0.0350 (+/−0.0011)	0.650 (+/−0.026)	34.2 (+/−1.4)

*Uncertainties given as +/−1 S.D.

The peel force *vs.* peel velocity data for PMA (41 kD)-silica films at various silica concentrations are shown in Figure 3. The line showing PMA with no silica was drawn using the equation generated from the PMA (unfilled, 38 kDalton) data in Figure 2. The uncertainties of the PMA (41 kD)-silica measurements (less than 7% error) were found to be larger than those of the unfilled PMA (38 kD). Once again,

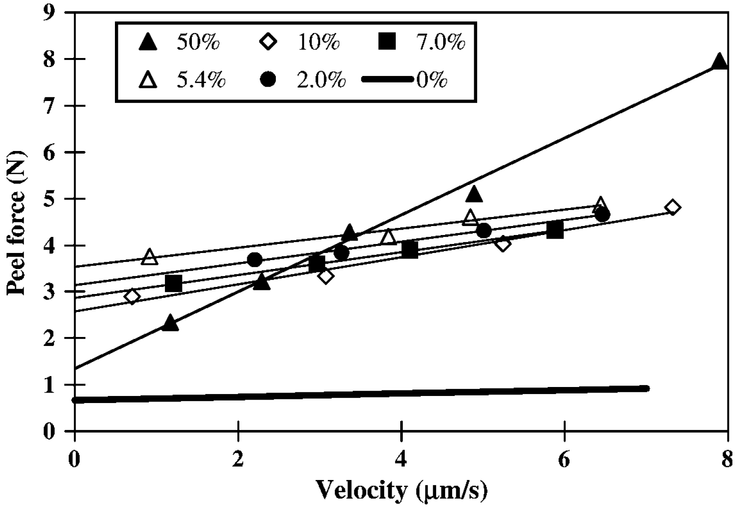


FIGURE 3 Peel force *vs.* peel velocity for various silica content (w/w) in PMA (41 kD) films. For comparison the extrapolation of the data for the unfilled PMA (38 kD) is shown.

the relationship between the peel force and velocity was observed to be linear, as it was for the PMA and PMMA films. For PMA-silica films the force required to separate two surfaces was greater (roughly varying from 2 to 5 times) than that observed for unfilled PMA films (shown in Figure 3 as the line without data points). In addition, the slopes of the force *vs.* velocity curves were much larger than those for the unfilled PMA films. For samples with 2–10% silica the slopes were quite similar (roughly 7 to 10 times that for the unfilled samples). The behavior of the 50% silica sample had a slope almost 30 times those of the unfilled samples. Ultimately, the extrapolated peel force at zero velocity is much lower for this filled amount than those for the other filled samples.

The fracture energies for the silica-containing films initially increased with silica content until a critical amount was reached and then these energies decreased. A small amount of silica dramatically increased the force required to separate the surfaces, but beyond a critical concentration an increase in silica content decreased the force required to separate the two surfaces. The G_c values are shown in Table 4 and plotted in Figure 4 as a function of silica fraction in the polymer layer. The highest value of fracture energy was for the film with 5.4% silica and was found to be around 181.9 (±5.37) J/m^2.

Peel experiments were also performed with tape and bare glass. The results of these studies showed that adhesion strength was around 20 times ($1169 \pm 26\,J/m^2$) as great as that observed for experiments with 50-nm thick PMA coated (55.6 ± 1.1) glass slides. The reproducibility of these experiments with bare glass was much worse than for the coated slides. Presumably this greater uncertainty was due to the greater adhesion and the nature of our peel test. In particular, the impurities on the bare glass may play a significant role in the reproducibility.

TABLE 4 Force-Velocity Analysis and Fracture Energies (at Zero Velocity) for PMA-Silica

Silica% (w/w)	Slope*	Intercept*	G_c (v = 0) (J/m^2)*
0	0.035 (+/−0.0012)	0.67 (+/−0.036)	35.28 (+/−1.5)
2.0	0.235 (+/−0.012)	3.132 (+/−0.055)	164.8 (+/−2.9)
5.4	0.206 (+/−0.022)	3.53 (+/−0.100)	185.9 (+/−5.3)
7.0	0.248 (+/−0.0026)	2.86 (+/−0.010)	150.6 (+/−0.5)
10	0.293 (+/−0.026)	2.58 (+/−0.12)	135.5 (+/−6.6)
50	0.825 (+/−0.026)	1.35 (+/−0.15)	71.0 (+/−7.8)
Bare glass			1169 (+/−26)

*Uncertainties given as +/−1 S.D.

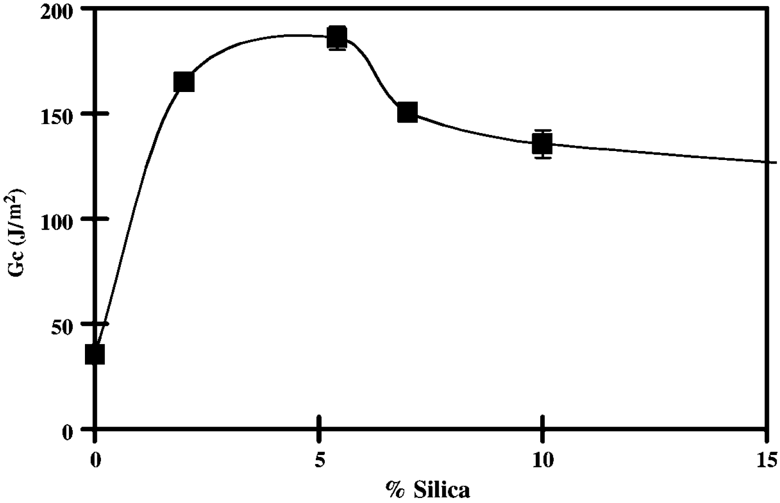
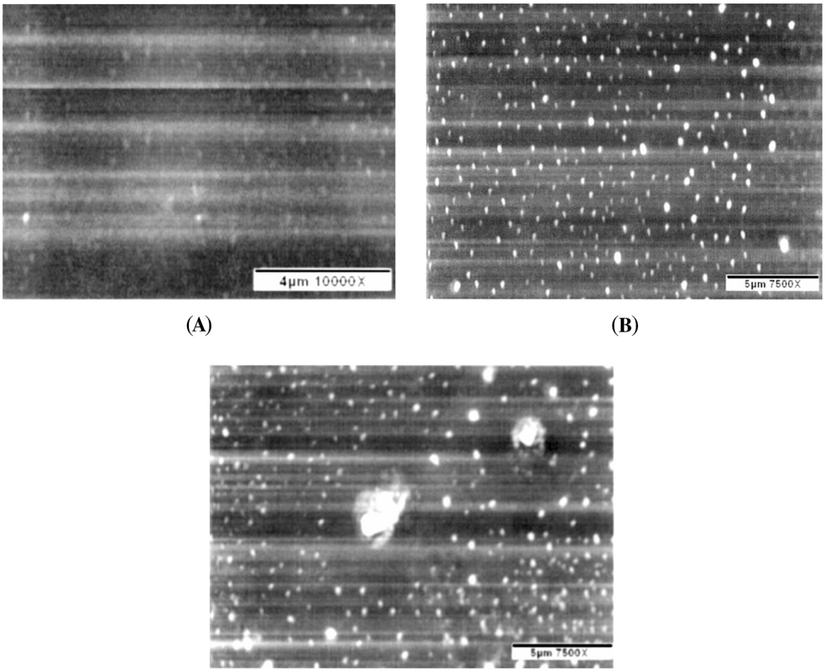


FIGURE 4 Variations in fracture energy with variations in silica concentrations in PMA-silica films.

SEM micrographs of the silica-filled thin films are shown in Figure 5. For the 2% silica sample the light spots due to the filler seem to be uniformly dispersed and also buried (for the most part) below the surface. For the 5.4% sample the silica still seems uniformly dispersed, but the spots are much brighter suggesting that there are many more near the surface of the composite film. At 10% filler large areas of heterogeneity are found which appear to be from the aggregation of the silica. The aggregation of the silica and its segregation at the surface both increase with the amount of silica.

To verify that the fractures occurred at the interface (adhesive fracture), rather than through one of the polymer layers (cohesive failure), tapping mode AFM was used to study the surface of the polymer samples before and after the peel experiments. The results were similar to those reported previously [6] and need not be repeated here. They showed that the thicknesses before and after the peel tests were within the experimental error. In addition, the peeled slides showed no evidence of significant amounts of chain pullout or pinholes; although, the roughnesses of the surfaces of the peeled samples were greater than those before peeling. The surface roughness (rms) of the unpeeled substrates was typically 30 nm compared with 60 nm for the peeled samples. This compares with about 20 nm for the bare glass slide and 75 nm for the tape.



(A) (B)

(C)

FIGURE 5 SEM pictures of (A) 2.0%, (B) 5.4%, and (C) 10% silica-filled PMA thin films. The scale bars are 4 µm in (A) and 5 µm in (B) and (C).

DISCUSSION

Fractures are considered cohesive, if they occur in the bulk of the material, or adhesive, if they occur at the interface; these have been probed for soft adhesives [16]. The AFM micrographs did not indicate chain pullout, cavitation, significant changes in film thickness upon peeling, or other effects. The absence of these effects in this case suggests that the failure was adhesive. The work required to initiate a crack at an interface is related to the fracture energy. According to the Griffith energy balance criteria [17], the fracture energy is defined as the amount of energy applied to a system per unit extension of crack area when a fracture takes place, or

$$G_c = \left(\frac{P_0}{b}\right)^2 \left(\frac{1}{2Eh}\right) + \left(\frac{P_0}{b}\right)(1 - \cos\theta) \qquad (1)$$

where b is the width of the interface, E is Young's modulus of film, θ is the peel angle, and h is the thickness of the film. The first term in Equation (1) gives the amount of recoverable strain energy. In the present case the peel angle was close to 90°, around which the lateral stress on the film was expected to be negligible. This reduces the lateral elongation of the film. For peel angles around 90° the first term of Equation (1) should be insignificant. In that case the fracture energy is given as [5,18],

$$G_c = \left(\frac{P_0}{b}\right) \tag{2}$$

Fractures at the interface are often rate-dependent quantities due to chain pullout, chemical reactions, or viscoelastic processes at the interface [19–23]. For our data a linear extrapolation to zero velocity was appropriate and accurate. The force, determined from the zero velocity load, P_0, gives the fracture energy, using Equation (1).

The results for the 384 kD PMA as a function of film thickness were quite consistent with those in previous work from this laboratory for a different molecular mass sample [6]. This is as expected because both samples were in the high molecular mass range. Nevertheless, it is useful to know that the results are reproducible and that they can serve as a basis for comparison with the other studies reported here. As in our previous study, we found that the data, extrapolated to zero velocity, yielded fracture energies that decayed exponentially and were given by:

$$G_c = A\exp(-h/\tau_c) + G_{c,\infty} \tag{3}$$

where the fitted parameters were found to be: $A = 52.7$ (± 1.4) J/m^2, $G_{c,\infty} = 20.3$ (± 0.6), and $\tau_c = 125$ (± 6) nm. A plot of G_c as a function of thickness is shown in Figure 6 with the best fit and the data from our previous work. The values reported are those yielding a minimum least-squares error (predicted—experimental)^2 from Equation (3). The uncertainties are given as the values representative of 1 s.d. of the squares of the residuals.

We ascribe the differences in fracture energies and thickness dependence between the PMA and PMMA systems to the effect of segmental dynamics on the adhesion of these tape systems. PMA and PMMA have similar surface energies [24–25], as expected due to the similarity of their functional groups. Therefore, the proposed mechanism is that the interactions between the different polymers across the interface come and go at a rate dependent on the local segmental mobility of the polymer chains. For a glassy polymer, such as PMMA,

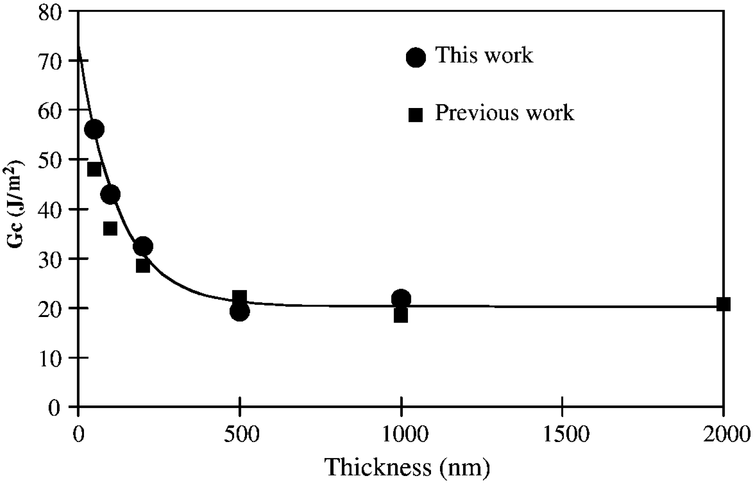


FIGURE 6 Fracture energies for 384 kD PMA as a function of thickness showing an exponential fit to Equation 3. For comparison the data from the previous work are also given [6].

the PMMA groups at the interface are fairly rigid and so their contribution to adhesion is greater than that for PMA, which has mobile segments. In PMA the mobility of the segments causes more frequent breaking of interfacial interactions. In some respects this is similar to changes in physical (especially rheological) properties over the glass transition region. The absence of a thickness dependence for PMMA can also be understood because its surface is rigid regardless of how thick the film is. In contrast, the PMA at the adhesive interface is influenced by the thickness of the PMA layer (or the proximity of the segments to the glass slide). The thicker the PMA layer, the lower the mobility in the PMA film, and the greater the adhesion in the PMA-tape system. This effect can also be applied to the adhesion for bare glass, which is about a factor of 6 stronger than that for PMMA [6]; although, in this case, the interactions are clearly not the same.

A number of studies of the rheological properties of polymer thin films have been performed and these all show that the rheological properties of thin films vary from those of the bulk polymers [26–29]. The length scale of the decay of the G_c values reported here is on the order of other measurements made using the surface forces apparatus. The shear modulus for thin films of *cis*-polyisoprene showed measurable differences from bulk behavior at around 30 nm and shorter with small effects evident at around 100 nm [29].

A somewhat shorter, but comparable, distance scale is found for the shear modulus of thin polybutadiene films [28]. Clearly, the present results and their interrelationships with rheological properties are worthy of additional study.

The dependence of peel data on molecular mass appears to be minimal. There may be a slight dependence of adhesion on molecular mass with the lower masses having slightly larger fracture energies. However, it is possible that the low molecular mass samples have the capability of interpenetration, whereas the higher molecular mass samples would not. We do not see evidence of chain pullout [20].

With as little as 2% silica there was a substantial increase in the fracture energies compared with unfilled thin films. The maximum value occurred with 5.4% silica. The increase in the adhesion in the filled samples was clearly due to the presence of the silica. We believe that a combination of two effects may account for the increase in fracture energies. First, the silica itself has a stronger adhesion with the tape and, second, the dispersed silica modifies the dynamics of PMA. If the silica segregates to the surface, it may increase the adhesion. The electron micrograph for the 2% filled sample suggests that not many particles are at the surface, so, at least for this sample, we believe that the second mechanism is dominant. At large silica amounts, the fracture energy decreases. One possible explanation for this decrease, based on the SEMs in Figure 5, is that larger silica clumps segregate to the surface of the film at increased silica contents. These larger aggregates of silica possibly reduce the contact between the two surfaces. This effect is especially obvious in the adhesion data for the 50% silica data. From the peel force velocity data this sample is clearly in a different regime, possible dominated by the presence of asperities.

The second mechanism is that the dispersed silica modifies the dynamics of the PMA. It is well established that the interaction of silica with PMA significantly reduces the mobility of the PMA [11–12]. These studies also identified the presence of a gradient in mobility with respect to the proximity to the surface. Just as the interaction of the PMA and the glass slides affected the fracture energies, so did the interaction with the particles. The presence of well-dispersed particles reduced the mobility of the polymer film and increased the adhesion. One can envision a change from a two-dimensional effect on dynamics (due to adsorption on the glass slide) to a three-dimensional effect (due to polymers adsorbed on random particles). This change in dimension could qualitatively change the magnitude of the effect and may account for the large change with added particles. In addition, we expect the adsorption effect to be greater than that due to geometric confinement as (even for the less-polar cis-polyisoprene) the adsorption effect dominates [30]. If one uses the larger aggregates in Figure 5B to estimate an aggregate radius size of about 0.2 µm, a simple cubic lattice calculation would suggest that the particles at a 5% loading are about 1 µm apart. Thus, most of the polymer should be within about 0.5 µm, or less, of a particle. This likely represents an upper limit as it is based on the larger particles, but the distance is clearly within the range of distances where the particles increase the adhesion by reducing the mobility of the polymer.

The effects due to the silica particles seem similar to those observed by others with respect to the effect of dynamics and related viscoelasticity on adhesion. Newby *et al.* [5,21,31] noted the differences in adhesion and related these to differences in polymer dynamics. Slippage at the interface due to faster dynamics was attributed to lower adhesion. Amouroux *et al.* [7] studied the effects of a filler resin on the adhesion behavior of polydimethylsiloxane on glass. The filler resin, with its stronger interaction (anchoring sites) with the substrate, accounted for the reduction in slip mechanisms. A similar effect can also be achieved with a chemical modification of the polymer [9,32] or with physical changes such as solvent exposure [33].

CONCLUSIONS

The effect of the dynamics of the polymer layer has been shown by simple peel tests to affect the adhesion in PMA-tape systems. The linear extrapolation of the force velocity data yielded fracture energies which were exponential with PMA layer thickness. The effects of the molecular mass of the PMA did not seem to affect the adhesion very much. In contrast, the presence of small amounts of silica substantially increased the fracture energy. A maximum fracture energy was found with 5.4% silica.

The results for the glass slide-PMA-tape system, with and without filler, may be explained on the basis of the mobility of polymer segments. In the case of the silica-filled systems the larger values of fracture energy were due to the interaction of the polymer with the filler. The proximity of the polymer segments to the silica particles (to which some of them were hydrogen bonded) reduced the mobility of the polymer, resulting in higher adhesion. The maximum in the fracture energy (as a function of the amount of silica) is worthy of further study; although, this may be the result of the competition between the reinforcing behavior of the silica and its segregation at the surface.

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