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EFFECT OF POLYMER-SURFACE MOBILITY ON ADHESION IN POLY (METHYL ACRYLATE)-TAPE SYSTEM

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Introduction

The interaction between two polymer layers, especially adhesion between them, plays an important role in polymer processing and other applications. Detailed knowledge of the molecular structure and dynamics of polymer interfaces, and how they relate to macroscopic mechanical properties, should help designers construct more functional systems. Unfortunately, there have been few studies where both molecular and macroscopic studies have been performed on similar systems. In previous studies from our group, we have probed the dynamics[1] of poly(methyl acrylate) (PMA) and thermal behavior[2] of poly(methyl methacrylate) (PMMA) on silica. These studies helped us paint a picture for strongly bound molecules on silica, where a motional gradient perpendicular to the surface was observed. More mobile, lower T_g, material was found at the air-polymer interface, while less mobile, higher T_g material was found at the polymer-substrate interface.

A previous study[2] from our group showed that the glass-transition temperature of PMMA changes with the thickness of the polymer layer on silica. By examining the thermal behavior of the polymer with modulated differential scanning calorimetry (MDSC), it was observed that the glass-transition temperature increases as the thickness of the polymer layer decreases. Blum and Lin[1] have also used the deuterium NMR to probe the dynamics of bulk and silica-absorbed poly(methyl acrylate)-d_3 (PMA-d_3). It was found that, an increase in the absorbed amount of polymer increased the mobility of polymer at the air–polymer interface and a decrease in the absorbed amount of polymer, decreased the polymer mobility. It is not known how this change in mobility relates to the mechanical properties of polymers, especially adhesion between two polymer layers.

Of the various methods available for measuring adhesion-related properties, peeling is considered to be the most convenient.[5] Current theories consider peeling to be the principal mode of separation of an adhesive from the substrate. It is proposed that adhesion strength is proportional to the surface free energy.[3,4] Research has been done to find the adhesion strength between films and substrates, but there are some questions which remain unanswered like: Does adhesion strength depend on the thickness of the polymer layer? Does adhesion strength relate to the mobility of polymer segments on the surface?

In the present report, we summarize some of our macroscopic studies, namely peel tests, on systems similar to those previously studied. We find that the mobility of the polymer chains at the interface play an important role in determining the peel strength between the two polymer layers. We decided to use a 90° peel angle method. At this high angle, the lateral stress in the film is very negligible, thereby reducing the lateral elongation of the film. In addition, at this angle, there is no slip at the interface. Our studies show that as the polymer film thickness decreases, the force required to initiate fracture between two polymer surfaces increases and the fracture energy also increases proportionately. We have also observed how fracture energy changes with a change in film thickness.

Experimental

Poly(methyl acrylate) PMA 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 CaH_2 (calcium hydride) and then vacuum distilled. 25 ml of methyl acrylate was mixed with 0.03 gm of AIBN and reaction was carried out at 60° C for 5 h. The properties measured for PMA are given in Table 1. The polymer was dissolved in toluene and precipitated with methanol. Glass slides (Corning Micro Slides 2948, single frosted) were used as the substrate for the experiments. PMA solutions in toluene were prepared to coat the glass slides. Glass slides were washed with methanol to remove impurities before coating with a PMA solution. Slides were then air-dried and later vacuum dried. The

glass slides were coated with the PMA solution using a spin coater. The samples were washed with a solvent (toluene) to remove the excess polymer from the substrate and then air-dried. The samples were annealed for 10 hrs in a vacuum oven. Scotch tape (Scotch Magic Tape 810) was applied to the samples after they cooled down. The samples were kept in desiccators for 2 days to allow the polymer to relax before the mechanical studies. We used AFM and varied the sample preparation conditions to find appropriate concentrations of polymer solutions required to get continuous films on the glass slides.[6] Solutions of different concentrations of PMA in toluene were prepared. We observed that, to have continuous film on the glass surface, the appropriate concentration of the polymer solution was greater than 1%(w/w). Below 1%(w/w) polymer concentration, we observed discontinuities in the film.

Scotch tape was peeled at a 90° angle with a string, which ran over pulleys. Peel velocities were controlled by hanging different dead loads on the free end of the string. At each load, peel velocities were averaged from at least four data sets. Experiments were conducted at room temperature. The thickness of the polymer layer before and after the peeling experiments was measured using tapping mode AFM.

Table 1. Characterization of PMA

Polymer	T_g °C	Mw	Polydispersity
PMA	10	342,000	2.01

Results and Discussion

Peel force vs. peel velocity data for various film thicknesses are tabulated in Table 2. From the data, it can be seen that peel velocities increases as the amount of force used in separating two surfaces increases. Figure 1 shows the trend of peel force versus the peel velocity. A linear relationship between peel force and peel velocity is observed. The x intercepts give the amount of force required for initial crack formation in the system. At higher forces, the excess energy is used for the propagation of crack.
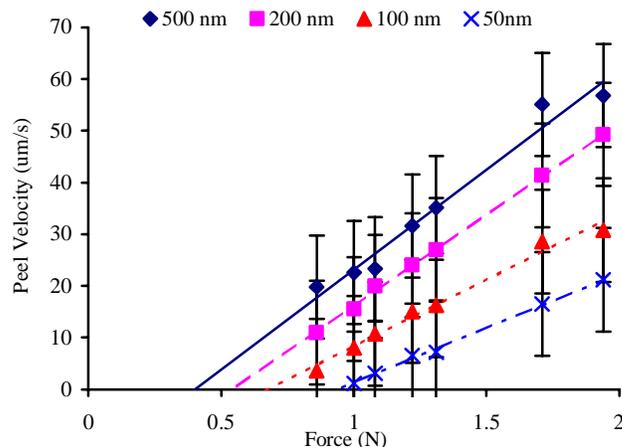

Figure 1. Force (N) vs velocity (μm/s) for various film thicknesses. The experiments were conducted at a 90° peel angle.

It was observed that the force required to separate the two polymer layers increases as the film thickness decreases. We believe that this phenomenon is related to the polymer mobility at the polymer-polymer interface and at the polymer–substrate interface. It is observed that in the vicinity of an interface, the dynamics of a polymer chain may be altered. The mobility of polymer is greater at the air-polymer interface because of the free volume available at that interface.[7] In addition, for strongly bound polymers, such as those observed here,[7] the polymer mobility is decreased at the substrate-polymer interface, where polymer sticks to the surface. Increasing the amount of polymer coated on the substrate, i.e. changing from thin films to thick films, the polymer mobility increases at the air-polymer interface. Blum and Lin[8] studied the mobility of polymer segments at the polymer-polymer interface using deuterium NMR. These results show that mobility of polymer at the polymer-polymer interface decreases compared to the air-polymer interface because of the interaction between the two polymer layers. At the polymer-polymer interface, the mobility of polymer attached to the substrate

decreases with reduction in the absorbed amount of polymer on the substrate. The increase in the force required for initiating the cracks at different film thicknesses suggest that the mobility of the polymer on the substrate plays a role in the adhesion strength.

Table 2.

Thickness		500nm	200 nm	100 nm	50~75 nm
Force (N)	Fracture Energy (J/m²)	Velocity (μm/s)	Velocity (μm/s)	Velocity (μm/s)	Velocity (μm/s)
0.86	43	19.8	11.0	3.60	-
1.00	50	22.6	15.5	8.06	1.17
1.08	54	23.3	19.9	10.7	3.11
1.22	61	31.6	24.0	15.1	6.56
1.31	66	35.1	27.0	16.3	7.20
1.71	86	55.1	41.4	28.6	16.5
1.94	97	56.8	49.3	30.8	21.2

Fracture energy is defined as the energy applied to the system per unit extension of the crack area when fracture takes place in the system. The fracture energy was calculated using the Griffith energy balance criterion. According to the Griffith energy balance the fracture energy is a rate dependent quantity. Fracture energies were calculated using equation 1.[9] In equation 1, P is peel force per unit width of film, E is Young's modulus of film, θ is peel angle and h is the thickness of the film. The first term in equation 1 gives the amount of recoverable strain energy. For high peel angles (e.g. 90°) the first term of the equation, which represents the elastic strain energy term, is insignificant and so for our case the fracture energy is given by eq. 2.[9,10,11]

$$G_c = (P^2 / 2Eh) + P (1-\cos\theta) \qquad (1)$$
$$G_c = P (1-\cos\theta) \qquad (2)$$

In our case, the peel angle is 90°. So the fracture energy (G_c) is equal to the peel force per unit width of the film (P). The fracture energy for different peel velocities is tabulated in Table 2. From the data, it is observed that the fracture energy also increases as the film thickness decreases. The intercept of the peel force vs peel velocities in Figure 1 gives the value of energy required to start cracking process between polymer layers. This energy is equal to the work required to start crack initiation in the interface.
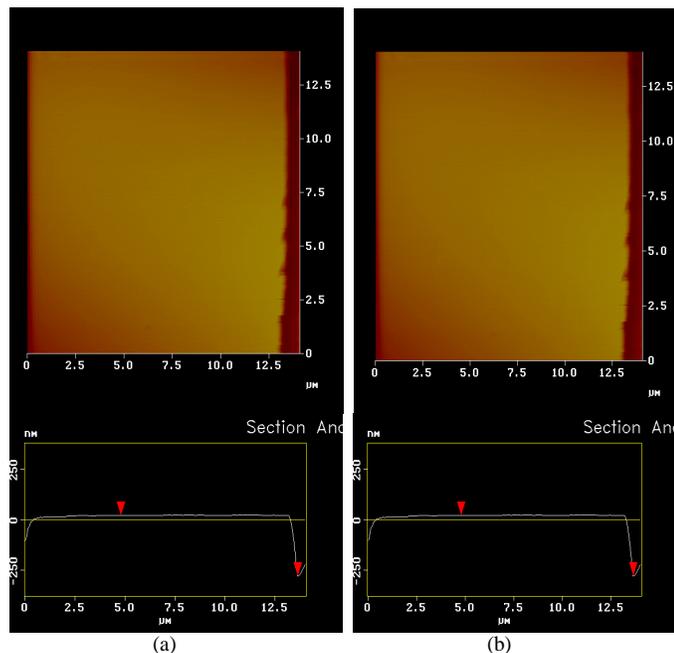

Figure 2. AFM image of PMA (200 nm) (a) before and (b) after the peel experiment.

Fractures can be of the cohesive or adhesive type. To ensure that the fracture is taking place at the interface (adhesive fracture), AFM studies of the samples were conducted before and after the peeling experiments. Tapping mode AFM was used to study the surface of the polymer. Figure 2 (a) shows PMA coated on the glass plate initially (before the peeling experiment) and Figure 2 (b) shows the PMA surface after the peeling experiment. No significant change in thickness of polymer layers was observed. No chain pull out appeared to occur.

Figure 3 shows the film thicknesses vs. fracture energy plot for different velocities. It is observed that the graph has the same trend for all the film thicknesses. The data is fit to power law dependence. The present treatment does not allow for a complete discussion of this fitting.
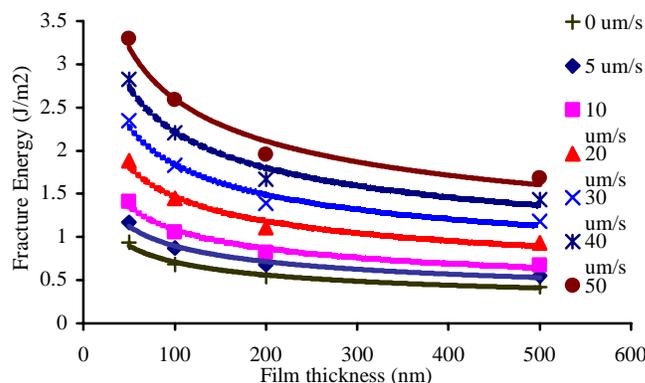

Figure 3. Variation in fracture energy with the film thickness for different velocities.

Conclusions

From the experimental data, we conclude that fracture energy depends on the film thickness. The mobility of the polymer is also a function of film thickness, and we believe that this means that the fracture energy depends on the mobility of polymer, since the amount of energy required to initiate fracture between two polymer layers increases as the polymer thickness decreases. The fracture energy also behaves in a manner similar to the peel force with changes in thickness. We have worked with PMA (rubbery polymer) and further research is likely to be with PMMA (glassy polymer).

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