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# Peel Tests on Thin Films of Segmented Poly(urethane ureas) and Dynamics of Interface Broadening by Neutron Reflection

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ABSTRACT: The rate of self-adhesion and interface width development between optical smoothness thin films of segmented poly(urethane urea) (PUU) has been investigated. The advantage of smooth solvent cast films for peel tests is that measurements can be made at early times when the interface strengths are very low. Viscoelastic dissipation contributions to the peel forces are also reduced because of the nondissipative nature of PUU, relative to other adhesives. The interfaces between self-adhering PUU thin films were found to remain relatively narrow by neutron reflection even after long annealing times, because the interpenetration of the mobile soft segments is strongly limited by the hard segment physical cross-links, although very strong interfaces eventually developed after aging at room temperature for a day or more or at elevated temperatures after shorter times. The time dependence of the peel strength for self-adhesion between very thin films of PUU follows a $t^{1/2}$ dependence, as has been predicted and experimentally verified for interdiffusion of linear polymers, suggesting that diffusion of mobile soft segments is the limiting process, even though center of mass motion of entire PUU chains is prohibited. The interface width reaches a limiting value of about 70 Å after about 2 days at 22 °C, while the interface strength measured by peel tests continues to increase up to remarkably longer times of more than 40 days. A tentative molecular mechanism is proposed related to hydrogen bonding of interdiffused segments.

## Introduction

This paper addresses two topics. One is related to the molecular mechanism for interface strength development with time, investigated with peel tests and neutron reflection (NR) studies of interface widths. The other regards the question of what we can learn about the very complicated contribution of the real interface strength to the measured peel forces, with thin self-adhering films and very strong interfaces. We can provide interesting insight into this complicated area of research by the use of very smooth films of a "nondissipative", highly elastic material. The films are smooth and flat enough that one can obtain intimate contact between poly(urethane urea) (PUU) layers in a few seconds. The observation that peel forces are independent of the applied pressure during sample annealing is the strongest evidence that intimate contact is immediate, and the only driving forces for interdiffusion are osmotic ones. Because of interdiffusion and hydrogen bonding, we will also show that peel forces measured at relatively low peel rates for self-adhering thin (2−3 $\mu$m) PUU elastomer films are remarkably high compared to those reported previously for systems exhibiting adhesive failure or even cohesive failure.[1] The results are contrasted with the molecular studies of interfacial broadening by NR. As expected, the dynamics are quite different from that seen for interdiffusion of typical linear polymers, because the interface broadening is limited in physically cross-linked PUU due to completely restricted center of mass motions. The time dependence of interfacial broadening will also be shown to be considerably different from the time dependence of the peel forces at longer aging times.

It is generally accepted that chain entanglement, chemical bonding, or some other strong bonding, are necessary for strong self-adhesion of high molecular weight polymers, when they are debonded in their solid or glassy states.[2−6] This is *not* the case for adhesives debonded well above their glass transitions because of the huge macroscopic dissipation contributions to the fracture energies[1,6−12] in some materials and some test geometries. Peel forces or related interface fracture energies per unit area ($W$) measured for elastomer adhesives above their glass transitions can be very high due to viscoelastic losses in the adhesive layer, even for bonding to rigid substrates where interdiffusion is not possible, and where no chemical or other strong bonds exist across the interface. Variations of several decades in peel force are routinely measured for elastomer adhesives by changing the peel rate and/or temperature, even though the "intrinsic interface strength" remains approximately constant.[1,7−12] One such example is adhesion to inert fluoropolymer and related substrates.[8] In these systems characterized by weak intrinsic interfaces, the high values of $W$ are only seen at high effective peel rates due to viscoelastic losses in the adhesive layer. The classic equation for adhesive failure is[6,8]

$$W = I(\text{const})[1 + f(\text{peel rate}, T)] \qquad (1)$$

Here $I$(const) is the intrinsic failure energy per unit area,[8] also known as the fracture energy at zero rate[12] or "threshhold toughness" [6] for the particular interface. In the following we will refer to it as simply $I$. In eq 1, $f$ describes the dissipation contribution from the bulk adhesive where the rate and temperature dependence of the bulk viscoelastic properties are approximately interchangeable,[1,4,8,11,13] at least in the empirical WLF formalism over limited frequency ranges. The important consequences of eq 1 are that a stronger interface allows higher stress transfer to the adhesive, causing enhanced energy dissipation in the adhesive layer,[4,6,8] suggesting the multiplicative effect, or simple "factorization", described by eq 1 where a series of parallel curves are seen in a log−log plot of $W$ vs reduced rate.[8,14,15] In other

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cases parallel curves are approximately seen only at low reduced rates,[9] and these limitations of eq 1 will be discussed below. At high rates the peel forces were almost independent of the real "interface strength".[9] A further complication is seen if variations in peel rate (and/or temperature) cause a change in state (liquid to rubber, rubber to glass), which can cause a significant change in the level of energy dissipation, or even cause a change in failure mode which can be detected by peel or fracture tests.[1,7]

Gent and co-workers[9,14,15] made the important connection of elastomer adhesion studies with the theory of Lake and Thomas,[16] which gives a physical basis for the tear strengths of elastomers. Because not all the energy can be concentrated on the growing crack at higher rates, bulk tear strengths of elastomers are dependent on tear rate.[16] Similarly, the amount of energy concentrated on the growing crack in a peel test is also rate dependent, as Gent and co-workers have discussed for a variety of systems.[9,14,15] The theory of Lake and Thomas[16] shows that materials with higher effective cross-link densities have lower tear strengths because the dense network dissipates less energy. The results exactly parallel the trend in the magnitude of $W$ with cross-link density, where higher cross-link density elastomers give lower values of $W$ for related reasons.[9,14,15] Thus, the rate dependence and magnitude of $W$ for different elastomeric materials can be understood. We will return to a discussion of the dissipation contributions in PUU at the end of this section.

For interfaces governed by purely dispersive (van der Waals) forces, $I$ is the reversible work of adhesion,[8,17] equal to two times the surface energy ($I_o = 2\gamma = \sim 0.1$ J/m$^2$ for organic polymers). This important limit where only dispersive interactions exist across the interface was first proved in a study where $I$ was shown to be essentially equal to $2\gamma$ for a model adhesive on different "inert" polymeric film substrates.[8] This was done by measuring $W$ for a variety of reduced rates for the same adhesive on different model substrates. By replacing $f$ in eq 1 by adhesive bulk fracture energies, normalized by the minimum tearing (fracture) energy, Andrews and Kinloch[8] effectively normalized out the huge contribution of viscoelastic dissipation in the adhesive, leaving only the inherent interface strength term ($I = I_o = 2\gamma = \sim 0.07$ J/m$^2$). Such limits have also been measured directly at very low fracture rates by peel methods for self-adhesion of highly cross-linked silicone rubber adhesives[15] interacting only by dispersive forces, and also by JKR[18] methods at ultralow rates for similar siloxane systems.[19]

The other extreme is the case of chemical bonding across an interface, where the values of $I$ at low reduced rates becomes much higher than $2\gamma$. Systematic studies covering 15 decades in reduced peel rates for systems ranging from no chemical coupling to "complete" chemical coupling have shown some agreement with eq 1 at lower reduced rates,[9] as did the studies on "inert" substrates.[8] Deviations from the simple factorization (eq 1) at high effective peel rates were seen,[9] but at the highest peel rates, the very strong peel forces are dominated by plastic deformation of the solid adhesive,[9] which is below its effective $T_g$, so one may expect the values to be entirely dominated by this, and $f$ may not contribute in an entirely linear fashion. They have also shown very high values of $I$ relative to $2\gamma$ at the low rate limit for bulk cross-linked polybutadiene physically adhered to bare glass,[9] presumably because of specific interactions.

Because of the possible complexities in a somewhat polar material like PUU, we now consider the many situations where $I$ could deviate from the simple dependence indicated by eq 1. As was discussed above, we would expect that specific bonding like polar or hydrogen bonding in some systems would contribute to values of $I$ somewhat greater than $2\gamma$. In practice, it is difficult to predict whether specific interactions are contributing to an increase in $I$ above $2\gamma$ simply by examining the composition of adhesive and substrate. In systems such as hot melt bonded Kraton (styrene−butadiene−styrene) on Mylar,[1] or a variety of other slightly polar adhesives or substrates such as cross-linked polybutadiene on glass,[8] $I$ is probably higher than $2\gamma$, because of specific interactions acting across the interface. Also, it may not always be appropriate to obtain $I$ by extrapolating to zero reduced rate by increasing the temperature, because this could also change $I$, e.g., weaken the strength of ionic bonding, hydrogen bonding, acid−base interactions, or other polar bonding because of their temperature dependencies. Further problems with eq 1 are expected in the case of interdiffusion and entanglements. Entanglements would act like chemical coupling across the interface at high enough rates, but at lower reduced rates, they would contribute much less to reinforcement of the interface, explaining discrepancies from eq 1 for interdiffused systems,[11] as is also reviewed by Brown.[6] This is still a controversial area,[6] but it is clear that for both polar and entanglement interactions, that $I$ should depend on rate and/or temperature. Thus, the simple factorization described by eq 1 is not complete, and one should consider that $I$ could also depend on rate and temperature in certain cases.

$$W = I(\text{peel rate}, T)[1 + f(\text{peel rate}, T)] \qquad (2)$$

If one could obtain $f$(peel rate, $T$) from fracture experiments on a system where $I$ is a constant, then one could extract the rate and or temperature dependence of $I$ using peel measurements on a different substrate governed by specific interactions or entanglements, assuming $f$(peel rate, $T$) is independent of the substrate. To our knowledge, this has not been accomplished.

In eq 2, rate and temperature may not be equivalent for the description of $I$, as they are for $f$,[1,4,8,11,13] because the dependence of $I$ may not be purely governed by viscoelastic properties. For example, in cases such as hydrogen bonding or acid−base interactions across the interface, one would also expect to a first approximation that $I$ would depend more on temperature than rate. This statement is based on our knowledge of the strong temperature dependence of the strength of polar or hydrogen bonds. These features are important in the design of experiments to understand self-adhesion of PUU where hydrogen bonding is important. High-temperature peel tests could be strongly affected by any temperature dependence of $I$ in addition to the temperature dependence of $f$, making the standard interpretation inaccurate. This is an area that should be addressed in the future, and others have recognized the limitations of eq 1 and have incorporated system specific modifications of eq 1.[20,21]

Much of the discussion given above is presented in order to contrast the extensive literature with the system of interest in this paper, PUU, and its low

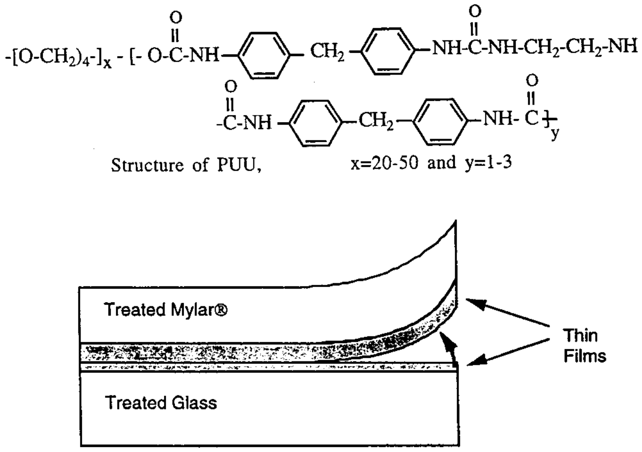

**Figure 1.** Structure of PUU and schematic of peel test for self-adhesion where the top PUU film has a 0.045 mm thick corona treated Mylar backing film, which is used as the inextensionable peel arm in the 90° peel tests.

**Table 1. Selected Fitted Parameters for NR Experiments on *d*-PUU/*h*-PUU Interfaces (Dimensions in Å)**

| | | | *h*-PUU | | *d*-PUU | |
|---|---|---|---|---|---|---|
| | geometry | width | *l* | *b*/*V* (cm$^{-2}$) | *l* | *b*/*V* (cm$^{-2}$) |
| A | front | 38 | ... | 0.5 | 336 | 6.4 |
| | ([*d*-PUU(60k)/*h*-PUU(50k)], ~12 h, 22 °C) | | | | | |
| A1 | back | 37.5 | ... | 0.4 | 333 | 6.4 |
| | ([*d*-PUU(60k)/*h*-PUU(50k)], ~16 h, 22 °C) | | | | | |
| A2 | back | 59 | ... | 0.5 | 352 | 6.3 |
| | ([*d*-PUU(60k)/*h*-PUU(50k)], ~30 s, 180 °C) | | | | | |
| B | back | 11 | ... | 0.5 | 366 | 6.9 |
| | ([*d*-PUU(60k)/*h*-PU-ester(50k)], ~24 h, 22 °C) | | | | | |
| C | back | 20 | ... | 0.5 | 290 | 6.5 |
| | ([*d*-PUU(60k)/*h*-PUU(150k)], ~12 h, 22 °C) | | | | | |
| A1 | back | 59 | ... | 0.5 | 352 | |

dissipative properties. Although the thinness of the PUU layers used in the present study contribute to some reduction in the dissipative contribution to *W*,[1] the more important contribution that contributes to the low *f* is the high effective cross-link density in PUU, in the context of the theory of Lake and Thomas[16] discussed above. This explains the very low values of *W* for adhesion to Mylar, with the values orders of magnitude lower than those for typical adhesives discussed below. Furthermore, PUU is a system different from others because it may be one of the few nonchemically coupled systems where *W* can become quite large, even though *f*(peel rate, *T*) is rather low. This allows one to better study intrinsic interface strength development as opposed to viscoelastic contributions of the adhesive.

The PUU system has not been studied by methods such as the JKR technique[18,19] where ultraslow fracture rates can be attained. With this method, very low elastomer fracture toughnesses were measured on model elastomer interfaces reinforced by copolymers,[22] and correcting for the rate dependence, these values were approximately consistent with peel test data on the same systems.[23] The peel test values of *W* for these model elastomers are still orders of magnitude lower than those for PUU self-adhesion under similar conditions.

## Experimental Section

The PUU studied here is a segmented block copolymer consisting of 85 vol % poly(tetramethylene oxide) (PTMeO, $T_g = -70$ °C) soft segments and 15% aromatic urethane−urea linked hard segments (Figure 1). The PUU samples are microphase separated, which is typical of this type of segmented poly(urethane−urea),[24−26] and below about 150 °C, these high melting hard segment physical cross-links effectively inhibit flow or creep over short times, making these materials reversible elastic "solids". The overall number average $M_n$ for the control hydrogenated PUU(*h*-PUU) measured by light scattering is about 50 000, with a dispersity of about 2, and for the higher MW sample, $M_n = 150\,000$. For neutron reflectivity and related studies, a deuterium-labeled material (*d*-PUU) was prepared by substituting perdeuterated (*d*-PTMeO) for PTMeO. The *d*-PUU sample also had a $M_n$ of about 60 000.

**Neutron Reflectivity.** Neutron reflectivity (NR) experiments were performed using the POSY-II spectrometer at the Intense Pulsed Neutron Source of Argonne National Laboratory. This technique affords very high resolution for concentration profiles normal to the plane of the interface. The interface widths reported here are full widths defined in terms of a linear gradient profile. For example, a 50 Å full width[27,28] would be equivalent to a 25 Å error function "half-width". The NR data were fitted using a weighted nonlinear regression program supplied by Argonne.

Films for specular reflectivity must be optically flat and any losses by scattering of neutrons reduces or prohibits one from obtaining good quality data. With many phase separated or semicrystalline polymers, it is difficult to obtain the high quality thin films needed, and substantial effort was devoted to developing sample preparation conditions for these microphase-separated polymers.[28] Studies of microphase-separated systems by NR are rare,[29,30] and the high quality of the data for PUU were somewhat unexpected. The best control proving that the sample quality is sufficient to allow precise interfacial width determination is to use NR to determine the surface roughness of the simplest system, a single spin-coated layer of deuterated PUU. This was found to behave exactly like a spin-coated single layer of a standard amorphous glassy polymer, *d*-polystyrene, with very low surface roughness on the order of 10 Å, verifying that the films are sufficiently homogeneous in the bulk and also very smooth on the surface. No significant bulk scattering losses were detected, even though there is presumably some neutron contrast between hard and soft segment domains because of the microphase-separated morphology, characterized by small-angle X-ray scattering[31] and atomic force microscopy.[32] AFM data showed that the hard domains were on the order of 5 nm in dimension.

Another test of how close these samples approximate a homogeneous system, can be seen in the observed values of the average neutron refractive index (*b*/*V*) for these copolymers. Assuming that the hard and soft segments are homogeneously mixed, the average *b*/*V* for *d*-PUU is calculated[28] to be $5.8 \times 10^{-10}$, knowing that there is 85% *d*-PTMeG, and 15% nondeuterated urea hard segment. This is in reasonable agreement with the approximate value of $(6.2 \pm 0.2) \times 10^{-10}$ cm$^{-2}$ determined from fitting many reflectivity profiles for thick *d*-PUU films,[28] and about $6.5 \times 10^{-10}$ cm$^{-2}$ for the very thin films (Table 1). Recall that for *d*-PUU, only the soft segment is deuterated which comprises 85% of the total chain. The critical angle is sensitive to *b*/*V* of the deuterated layer, so this value of *b*/*V* is relatively precise. Again, assuming homogeneous mixing of hard and soft segments, the calculated *b*/*V* for *h*-PUU is $0.45 \times 10^{-10}$ cm$^{-2}$, which compares reasonably well with experimentally determined values (Table 1), which are much less precise.

The following conditions were found to give films and bilayers of acceptable quality. Individual *d*-PUU films were spin coated at 45 °C onto 2 in. diameter Si-wafers from ca. 7 wt % solutions in DMAC. They were 250−7000 Å thick by ellipsometry or NR. The *h*-PUU films (ca. 1−2 μm thick) were prepared by solution coating at $T > 45$ °C onto poly(ethylene terephthalate) (PET, Mylar film) because of its known low adhesion to PUU. Bilayers of the two were produced by

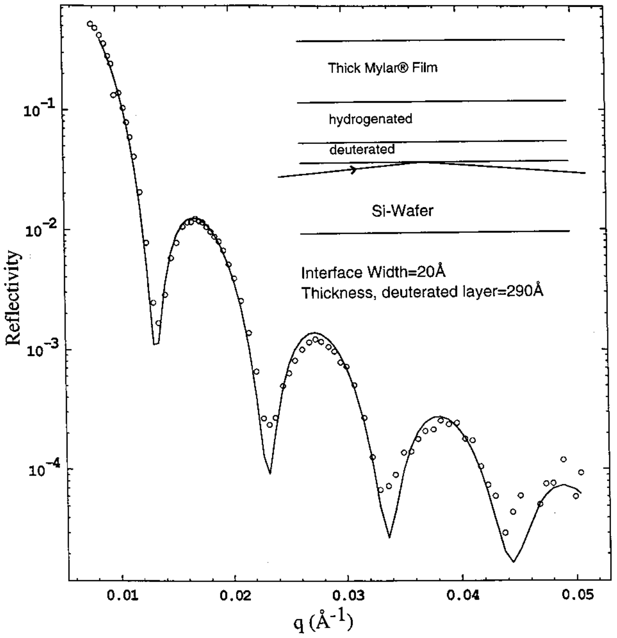

**Figure 2.** Reflected intensity vs neutron momentum transfer ($q$) for a typical diffusion couple in the backside geometry. From top to bottom the layers are air/Mylar/$h$-PUU/$d$-PUU/Si. The beats in the reflectivity profile are governed by the $d$-PUU layer thickness of 290 Å. The inset is a schematic of the experimental "back-side" geometry.

pressing the $h$-PUU film onto the $d$-PUU film and running a blunt wedge across the Mylar surface to remove air bubbles. If self-adhesion is high enough (>~50 J/m$^2$), then the Mylar can be removed, leaving the two layers ($h$-PUU/$d$-PUU) on the Si substrate. Thus, "top-side" neutron reflection could be performed, where the beam was directed at a grazing angle of about one degree through the top $h$-PUU layer, to the $h$-PUU/$d$-PUU interface. For top-side reflection, the various layers arranged from top to bottom are: air/$h$-PUU/$d$-PUU/Si.[28] Without removing the Mylar, top-side reflection from (air/Mylar/$h$-PUU/$d$-PUU/Si) was found to be impossible because of attenuation of the neutron beam in the 100 $\mu$m thick Mylar layer (distance = 2 × 100 $\mu$m/sin $\theta$ = ~12 000 $\mu$m for $\theta$ = 1°). Apparently the density fluctuations due to crystallinity in Mylar cause too much scattering in addition to the normal attenuation from adsorption in the Mylar.

To study the narrow (weak) interfaces at early times we had to flip the sample over and perform so-called "back-side" reflection where the beam was directed through the Si wafer, which has very low loss (inset, Figure 2). For this the $d$-PUU layer had to be slightly thinner than the 2000−7000 Å thick layers used in the top-side reflection studies. We used ~250−1000 Å thick $d$-PUU layers in order to attain sufficient intensity of the evanescent field at the $d$-PUU/$h$-PUU interface, since transmitted intensity becomes very low at distances larger than 1500 Å in this geometry because of the strong subcritical reflection from the Si/$d$-PUU interface (inset, Figure 2).

**Peel Tests.** Peel tests were done by peeling the top Mylar-backed PUU layer at a 90° peel angle (Figure 1). The common test of self-adhesion between two $h$-PUU films is depicted in the figure. For this experiment PUU films were cast on Mylar and glass microscope slides from solution, and dried at $T$ > 45 °C before pressing them together to make a PUU/PUU junction (Figure 1). Study of strong PUU/PUU interfaces requires good adhesion to the substrates. For this purpose, the Mylar was corona treated, and the glass was treated with triethoxy(aminopropyl)silane (APS). Solvent-cast PUU films adhered strongly to both of these treated substrates. The APS coating was cured at 110 °C before application of the PUU solution. For the thin (0.003 mm) PUU self-adhering films, the air bubbles had to be squeezed out with a blunt edge. Good contact could not be obtained with these thin films against solid substrate surfaces such as glass or Mylar because of low elastic deformation, but for self-adhesion, intimate contact was rapidly attained. For the thicker (0.2 mm) films, intimate contact was quite easy to obtain because of higher elastic distortion.[23] One could view the meniscus as intimate contact developed between these thicker films, somewhat like a meniscus for wetting films of a fluid between substrates.

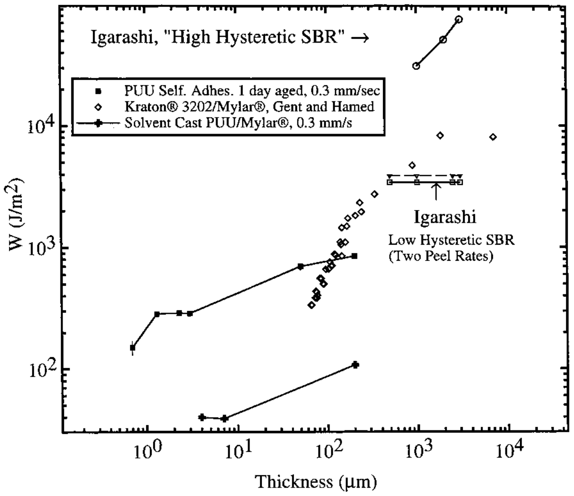

**Figure 3.** Peel test detachment energies ($W$) vs adhesive layer thicknesses for PUU self-adhesion and selected literature. Igarashi's[33] SBR materials were bonded to a nylon substrate, and "high hysteretic and low hysteretic" refer to the amount of hysteresis in the stress−strain curve for each respective rubber. Data from Gent and Hamed[1] for Kraton 3202/Mylar adhesion are also shown (see text).

Strips 2 cm wide by 10 cm long were peeled using an Instron tensile tester at a rate of 0.3 mm/s unless otherwise specified. The PUU films were 0.003 ± 0.001 mm thick unless otherwise indicated. For peel tests it is important to use a rigid Mylar backing sheet to minimize stretching (Figure 1).[1] The work of detachment per unit area of interface ($W$) was calculated from the peel force (P) measured using the standard equation[1]

$$\begin{aligned} W &= P(1 - \cos\theta)/w \\ &= P/w \quad (\text{for } \theta = 90°) \end{aligned} \tag{3}$$

where $w$ is the width of the peel strip. Our choice of 90° peel angles and relatively thick Mylar films minimize dissipation due to plastic deformation of the Mylar backing,[1] except at the highest values of $W$ (above ~400 J/m$^2$). Plastic deformation in Mylar is detected by permanently curled peel specimens after fracture. The unique and low dissipative contributions of the adhesive (PUU) layers are more subtle and will be discussed below.

## Results

**Adhesive Layer Thickness Dependence.** The values of $W$ for PUU self-adhesion are roughly independent of thickness in the range 0.002−0.005 mm (Figure 3), but for film thicknesses below 0.001 mm (=1 $\mu$m) the values of $W$ were found to decrease slightly, presumably due to modification of the deformation zone at the crack tip or other effects which are not well understood. Contact problems also become more severe as the films became thinner than 0.0005 mm (0.5 $\mu$m), even for self-adhesion. For the 0.002 mm films annealed for only 1 day, the values of $W$ are found to be substantially higher than those estimated by extrapolation to low adhesive layer thicknesses for Gent and Hamed's[1] SBR (Kraton 3202) data (Figure 3).

**Table 2. Selected Fracture Energies ($W$) from Peel Tests at Two Different Peel Rates**

| | $W$, 0.01 mm/s | $W$, 0.3 mm/s |
|---|---|---|
| PUU self-adhesion | | |
| as-prepared, ~2 $\mu$m thick PUU films | 3 | 7 |
| 1 day aged, 22 °C, ~2 $\mu$m thick | 120 | 180 |
| 1 day aged, 22 °C, ~0.7 $\mu$m thick | ... | 125 |
| 40 day aged, 22 °C, ~2 $\mu$m thick | ... | 700 |
| PUU/Mylar, solution coated, 2 $\mu$m thick PUU | 23 | 40 ± 10 |
| PUU/Mylar, solution coated, 200 $\mu$m thick PUU | 59 ± 5 | 110 ± 5 |
| PUU/corona[e] Mylar, solution coated, 2 $\mu$m | | 500 ± 300 |
| PUU/glass, solution coated, 2 $\mu$m | | 60 ± 30 |
| PUU/APS[a] treated glass, solution coated, 2 $\mu$m | | 700[a] |
| PUU/glass, pressed,[b] 200 $\mu$m thick | 5 | 11 |
| PUU/Mylar, pressed,[b,c] ~200 $\mu$m | 3.7 | 6.5 |
| PUU/Mylar, pressed,[b,d] ~200 $\mu$m | 1.0 | 2.3 |
| PUU/corona[e] Mylar, pressed,[b] 200 $\mu$m | 8 | 28 |

[a] APS is triethoxy(aminopropyl)silane which was applied to the glass surface from 2%APS in 5% ethanol/95% water. These high strengths were quite scattered. It is likely that APS simply reduces the amount of water at the PUU/glass interface but does not chemically "couple" with the PUU for 50 °C solvent-cast films. [b] Pressed at 25 °C. Thicker (0.2 mm) PUU layers were needed to get good contact. See also Figures 4 and 6 for $W$ vs time for PUU/Mylar. [c] Clean Mylar. [d] "Dirty" Mylar was solvent washed but contains a high $T_g$ hydrophobic silane "slip additive", which covers a small fraction of the surface. [e] Corona treated on a high speed line in air. No significant surface roughening is induced by this mild corona treatment. The corona surface is more polar as is indicated by advancing and receding angles before and after corona, which are 75 and 55° before and 70 and 15° after corona, respectively.

After solvent casting and drying off the DMAc at ~50 °C, the bonds to Mylar and glass are considerably higher than those obtained by breaking the initial interface between solvent cast PUU and Mylar and then re-adhering by pressing (e.g., compare with results for pressed samples in Table 2). These stronger interfaces must be due to better bonding sites; possibly the hard segments can interact with the solid surfaces by hydrogen bonding when they are applied in a highly mobile state out of solution. The air/PUU surface is dominated by soft segment,[36] so this may be a kinetic barrier for attaining these strong interactions when the junctions are formed by re-pressing "solid" PUU against glass or Mylar. Since PUU does not flow or creep, this seems to be an effectively permanent barrier.

The dependence of $W$ on adhesive thickness is apparently not resolved for thinner layers, nor is the situation completely clear for thicker layers. Igarashi[33] and Gent and Hamed[1] have proposed the following modified form of eq 1, which has been applied to explain the thickness dependence for intermediate thicknesses (Figure 3).

$$W = I[1 + f(\text{peel rate}, T)] + l_a U' \qquad (4)$$

Equation 4 is modified slightly for our 90° peel geometry as opposed to their equation[1] for $T$-peel (180°) tests, $l_a$ is the thickness of the adhesive, and $U'$ is the energy dissipated per unit volume of the adhesive determined from the integrated area of the hysteresis loop in the stress−strain curve. One interesting case is a low hysteretic SBR (low $U'$) adhesive melt bonded to Nylon film studied by Igarashi[33] and reproduced in Figure 3 for his rather thick SBR films between 0.5 and 3 mm. The values of $W$ are independent of thickness, while in another case,[33] a "high hysteretic" SBR adhesive showed a large thickness dependence (Figure 3), consistent with large values of $U'$ measured by independent methods for that adhesive. PUU has small $U'$, and for our studies using thin layers, we should be safe in ignoring the $U'$ contribution. This would also explain the independence of $W$ on thickness for the lower thickness range (Figure 3), while a slight dependence on thickness is seen in our prelilminary data for larger thicknesses.

For Igarishi's[33] low hysteretic SBR, the values of $W$ were still very high (4000 J/m$^2$), independent of thickness for a limited range, emphasizing the importance of the $If$(peel rate, $T$) term in eq 4 (or eq 1). Evidently, more work is needed to understand whether different materials behave differently in terms of the thickness dependence of $W$. It should also be noted that the $l_a U'$ contribution to $W$ is not expected to be valid for extremely thick films because the adhesive becomes so thick that the entire volume is no longer stressed during fracture, explaining[1] the plateau at high thicknesses in Gent and Hamed's Kraton 3202 data (Figure 3). This also illustrates one other problem with the analysis by eq 4; for weak interfaces the volume which is stressed also may become considerably smaller than the film thickness, making eq 4 inapplicable for typical thicknesses. The $l_a U'$ contribution in eq 4 must also be inapplicable for very thin adhesive films, because the deformation zone is modified by the substrate(s) if the layer becomes too thin. This is a topic for future study. Because the $l_a U'$ contribution is negligible for PUU, for the rest of the discussion we ignore this term in the analysis.

**Macroscopic Viscoelastic Dissipation Contributions to $W$.** The low bulk dissipation in the highly elastic PUU is substantially more important than the low thicknesses in the study interface strength variations, and contributes to our ability to separate them from viscoelastic effects. Table 2 and Figure 3 show that $W$ only varies by a factor of 2 for solution cast PUU/Mylar junctions for thickness variations of a factor of 100. Independent of thickness, the high effective cross-link density in PUU contributes to the low dissipation (small $f$ in eq 1) in the spirit of the theory of Lake and Thomas.[16] For PUU, the cross-links are the physical cross-links associated with the urea hard segment domains. This immediately explains the very low values of $W$ for PUU/Mylar adhesion (Figures 4−6 and Table 2) relative to more dissipative adhesives. Because $f$ is small, the increase in $W$ from very small to very large values for PUU self-adhesion in Figure 4 must be due to interdiffusion. We will discuss this in detail below. Contact area is not an issue because PUU/Mylar interface strengths were independent of time (Figure 4), and all the aging results were independent of pressure. The higher contribution of energy dissipation in adhesives such as "PIB" [11] and SBR[33] is not unexpected (Figure 4). "PIB" [11] contains linear poly(isobutylene) chains for which the cross-link density is close to zero, and one would expect that viscoelastic dissipation would be very high according to the Lake and Thomas theory. This explains the high values of $W$ in Figure 4 at early times, even though the "PIB" interfaces must be relatively weak. Note, that the "PIB" system is a lightly cross-linked butyl rubber impregnated by 50% high MW linear chains of poly(isobutylene) (PIB) ($T_g = -60$ °C). The slabs of "PIB" are molded against smooth steel and fabric reinforced on the back to reduce stretching of the peel arm during the peel test.

To explain the large value of $W$ for SBR data taken from the literature[33] (Figure 4), the authors have noted

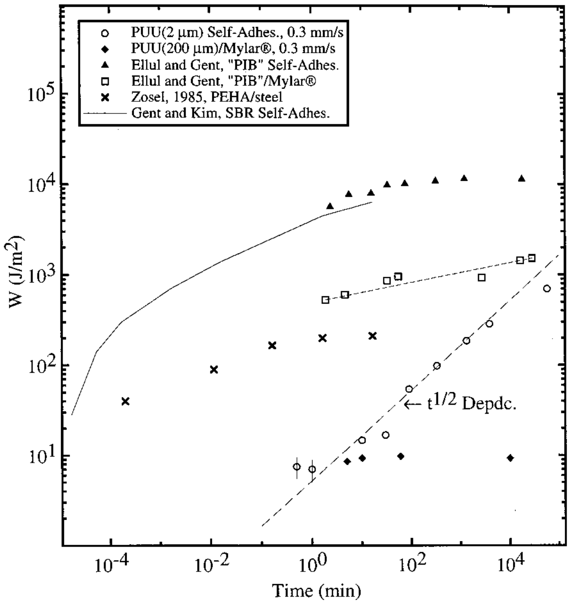

**Figure 4.** Comparison of literature data with peel tests of PUU self-adhesion. Detachment energies (*W*) are shown vs aging time at 22 °C. For PUU self-adhesion the peel rates were 0.3 mm/s, film thickness = 0.003 mm, peel temperature was 25 °C, and aging pressure was 0 MPa. For PUU/Mylar, peel rates = 0.3 mm/s, film thicknesses = 0.2 mm, peel temperature was 25 °C, and aging pressure was 0 MPa. Peel tests of self-adhesion[11] of butyl rubber with 50% linear high MW PIB, and adhesion of same material to Mylar[11](peel rate 0.4 mm/s, PIB film thicknesses 1.5 mm, peel temperature 25 °C, and aging pressure 1 MPa [1 MPa = $10^6$ N/m$^2$]). For SBR,[33] thickness = 1 mm, rate = 500 mm/s, and aging temperature = 25 °C. Interface fracture results[12] for poly(ethyl hexylacrylate) (PEHA)/steel "joints" (fracture rate ~2 mm/s, PEHA film thickness 0.05 mm, fracture temperature 25 °C, aging pressure 0.2 MPa).

that plastic deformation of the polystyrene domains dissipates energy[1] as would be expected even at small deformations in SBR, while the hard segment domains in the more reversible elastic PUU film do not undergo significant plastic deformation. Studies of materials such as PUU are apparently rare. At room-temperature PUU is not a good pressure sensitive adhesive because of its lack of flow and low energy dissipation compared to PIB and SBR adhesive materials.

It is important to address the classical question of whether the low rate limit of *W* (eq 1) agrees with the reversible work of adhesion, $2\gamma$. This is considerably easier with PUU because of the low values of *f*, and because *f* is less rate dependent because of the highly elastic nature of PUU. Self-adhesion data for PUU are shown in Figure 5 as a function of rate and are compared with data for systems with weaker interfaces. For the PUU systems adhering to different solid substrates, the curves are relatively parallel, in rough agreement with eq 1. Extrapolation to lower rates for PUU/"dirty" Mylar, indicates that the value is roughly consistent with $W = 2\gamma = \sim 0.1$ J/m$^2$. For self-adhered PUU, the low rate limit is larger because of interdiffusion, as is the case for PUU on corona treated Mylar, presumably because of polar interactions. The solid curves in Figure 5 were generated using an empirical expression consistent with simple factorization, e.g., eq 1 where the functional form of *f* was empirically chosen to fit the slope of the data for PUU and different values of *I* were chosen for the vertical shifts.

$$W = I(1 + f) = I(1 + 3\ln(660 \times \text{rate}^{0.7})) \qquad (5)$$

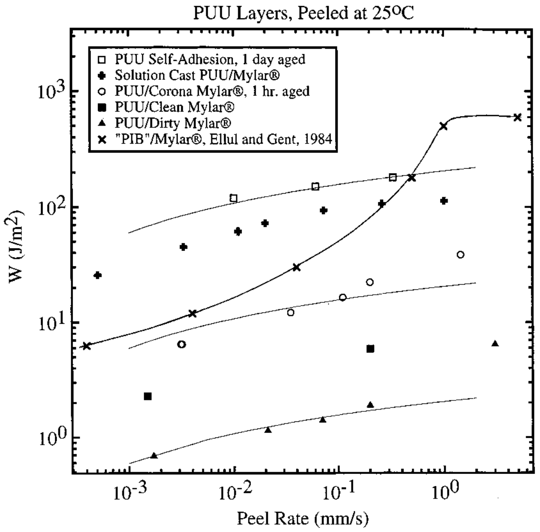

**Figure 5.** Detachment energy per unit area of interface (*W*) vs peel rate for self-adhered PUU(0.002 mm thick) aged at 22 °C for 24 h and thicker (0.2 mm) PUU films pressed against Mylar with different surface pretreatments, aged for about an hour with no applied pressure before peeling. Also shown are data for solution-cast PUU on Mylar. See the text for discussion of why the initial solution cast bonds are stronger than those for "pressed" PUU layers which were also initially cast from solution. Literature data[11] for 17% PIB in a cross-linked rubber network bonded to Mylar are also indicated (peel rate 0.4 mm/s, adhesive thicknesses 1.5 mm, peel temperature 25 °C, aging pressure 1 MPa [1 MPa = $10^6$ N/m$^2$), aging temperature 60 °C, and aging time 14 h.).

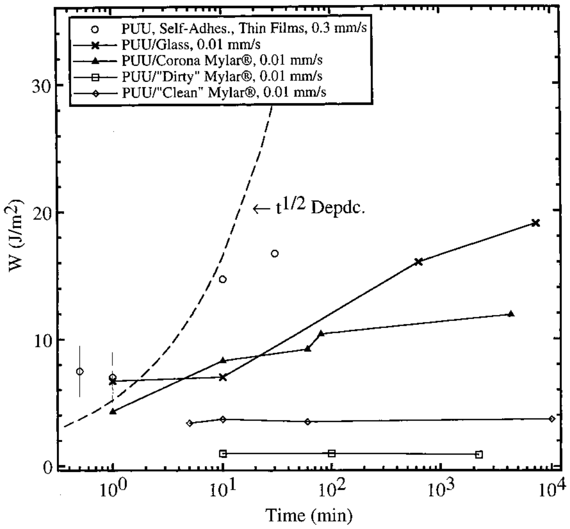

**Figure 6.** Time dependence of *W* for self-adhesion of PUU and PUU adhered to the indicated solid substrates. The dashed curve indicates the $t^{1/2}$ curve which fits the PUU self-adhesion data as indicated in Figure 4. Little or no increase is seen in *W* with time for glass, Mylar, and corona-treated Mylar solid substrates, compared to the sharp increase of *W* with time for self-adhering PUU (see text).

where rate is the peel rate in mm/s. For the three solid curves from top to bottom in Figure 5, *I* was chosen to be 10, 1, and 0.11 J/m$^2$, and these would be very qualitatively the zero rate limits of *I*.

For the "PIB"/Mylar system,[11] a higher rate sensitivity is seen for 25 °C peel test data (Figure 5), even though it has a glass transition similar to that of PUU. This is a general trend, where it is always found that the more dissipative materials (e.g., those with larger *f*), also exhibit a higher rate sensitivity. In this case, the interface can support more load at higher rates even though the "interface" is weak, because of the highly dissipative network due to the low cross-link density of "PIB".[16] This is directly seen by comparison with the rate dependence of the *tear* strengths of the bulk adhesive,[11] and in both cases the growing crack supports more load at higher rates, because less energy is concentrated on the growing crack and more energy is dissipated in the adhesive.

Coming to the time dependence of PUU adhering "weakly" to solids, very low time-independent values of $W$ are seen for our thicker (0.2 mm) PUU films adhered to Mylar, normalized to peel rates of 0.01 mm/s (Figures 4 and 6). Figure 6 shows a similar trend is seen with PUU/corona Mylar and PUU/glass, and the results were independent of contact pressure (not shown). A slight increase over a period of several hours is seen for PUU/corona Mylar and PUU/glass, presumably due to enhanced interactions with "polar" binding sites. Presumably, the slow but steady increase in $W$ for "PIB"/Mylar in Figure 4 is also due to PIB chains finding better binding sites on the Mylar, or improved contact area with time, multiplied by the huge dissipative contributions discussed above.[11] PIB is easily oxidized and polar impurities could lead to the stronger binding sites. Note that chains obviously cannot "interdiffuse" because the Mylar interface is impenetrable.

Finally, Figure 4 compares the PUU results with a system where the increase in contact area with aging time dominates the time dependence of $W$, such as the case of pressure-sensitive adhesives. The increase in $W$ for poly(ethylhexyl acrylate) (PEHA) bonding to steel under "low pressure" conditions[12] illustrates the effect of a rapid increase in contact area, as can be proved by examining the change in rate of the increase in $W$ as it is affected by pressure and polymer viscosity. In the pressure sensitive adhesive application, PEHA was shown to behave in a manner similar to linear poly(iso butylene).[12] PEHA is a low $T_g$ ( $= -47$ °C) "fluid" with a low (~zero) effective cross-link density, so dissipation ($f$ in eq 1) should again be high compared to a more elastic material like PUU, even though the intrinsic "bonding" ($I$) to the surface is relatively weak. The expected strong dependence of $W$ with fracture rate is seen, where the maximum values of $W$ fall from about $W = 200$ J/m$^2$ at a peel speed of 2 mm/s to about 50 J/m$^2$ at 0.1 mm/s for room-temperature fracture tests.[12]

**Microscopic Interpretation of Interface Strengths.** The advantage of having smooth thin films for the time-dependent studies is that the results are independent of contact area affects, as is proved by the pressure independence of the results and also supported by the temperature dependence of the rate of increase of $W$ discussed below. Early time data can be obtained before any significant bond strength develops allowing one to routinely cover a rather large dynamic range of about 2 decades in $W$ for PUU self-adhesion. The lower limit of the value of $W$ is somewhat independent of time at lower times, and seems to reach a minimum value of $7 \pm 2$ J/m$^2$ for any times shorter than about a minute (Figure 4) for the 2 $\mu$m thick films, although very short times cannot be accessed. This value of 7 J/m$^2$ is somewhat elevated over $2\gamma$ (~=0.1 J/m$^2$) because of the polarity of PUU and also because of viscoelastic contributions at this peel rate (0.3 mm/s).

Contrasting the early time data for PUU with that for "PIB", Figure 4 shows that large interface strengths in "PIB" have developed after a minute, times far shorter than the time needed for interdiffusion for the high MW PIB chains. This is again because of the dominant contribution of $f$ to the measured values of $W$ for the thicker "PIB" layers. The approximate half decade increase in self-adhesion of "PIB" over a period of several hours (Figure 4) is partly due to interdiffusion and entanglement of the very high MW chains, consistent with a time constant for interdiffusion estimated from creep data to be about 12 h.[11] A plateau is reached at long times in "PIB" self-adhesion, as must be the case in every system. In the case of PUU (Figure 4), we could not reach the plateau because the peel strength approaches the cohesive tear strength of the thin elastomer films at the highest values of $W$ in Figure 4.

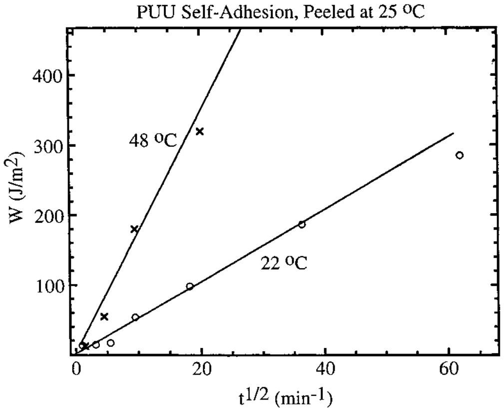

**Figure 7.** Detachment energy per unit area of interface ($W$) vs $t^{1/2}$ (min$^{1/2}$) for PUU aging at the two different temperatures indicated. All peel tests were done after cooling to room temperature.

The strong nonlinear dependence in Figure 4 agrees with the $t^{1/2}$ power law, especially at intermediate values of $W$. At larger values of $W$ around $500 \pm 200$ J/m$^2$ and higher, the data become less accurate because of cohesive tearing of the thin PUU layers and/or debonding at the treated glass or Mylar interfaces. The $t^{1/2}$ dependence has been predicted for an interdiffusion process of high MW polymers,[2,3,34] in approximate agreement with experiments on polymer glasses above $T_g$.[2,3] A smaller exponent of $n = {}^1/_4$ would be predicted for samples where chain end excesses are not present at the original interface.[34] Surface analysis by X-ray photoelectron spectroscopy and secondary ion mass spectrometry (SIMS) on PUU[35] and other segmented polyurethanes[36] shows that the surface of solvent cast films is dominated by polyether soft segment, proving that chain ends of PUU would be initially present, and this may explain the $n = {}^1/_2$ vs $n = {}^1/_4$ power law dependence. In PUU the "mobile" species consist of both soft segment blocks between physical cross-links (hard segments), and chain ends fixed at one end by a physical cross-link. Both center and end blocks consist of PTMeG blocks with MW = ~4000 equivalent to a degree of polymerization of about 50. The physical meaning of the scaling exponent for PUU is not clear because center of mass diffusion of the entire chain is prohibited, as will be shown below by NR. We can speculate that diffusion rates of these mobile units are still important in interface strength development, and this is why we observe a power law dependence similar to that for linear polymers.

Now, for temperature dependence, the values of $W$ for PUU self-adhesion in Figure 7 exhibit a pronounced

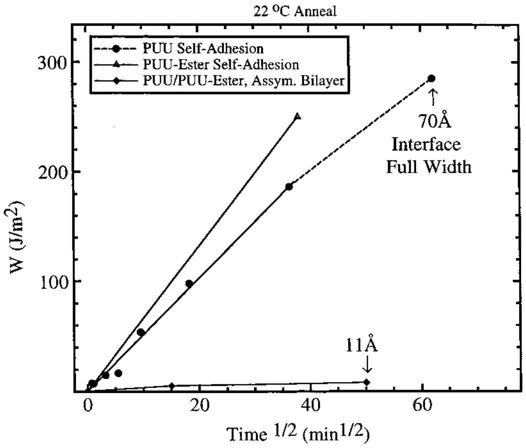

**Figure 8.** Detachment energy (*W*) from peel tests vs the square root of aging time for two symmetric bilayers (PUU/PUU and PU−ester/PU−ester) and an asymmetric bilayer (PU−ester/PUU) of two "incompatible" materials. The interface widths were measured at the times indicated by the arrows.

nonlinear dependence with time that can be approximately described by the $t^{1/2}$ dependence at both aging temperatures. All peel tests were performed after quenching to 22 °C, a substantial increase in the rate of increase in *W* is seen at the higher aging temperature, and this trend is seen in many other experiments of PUU self-adhesion performed at aging temperatures between 22 and 100 °C. No distinct thermal events occur between 22 and 50 °C in PUU, and the values of dynamic modulus and loss measured by dynamic mechanical experiments (not shown) are constant within a few percent over this range. Thus, the increase in rate (Figure 3) must be related to an increased rate of interdiffusion with temperature. In other recent self-adhesion and adhesion studies,[33] samples were peeled at the same temperature that they were aged at, and competing effects lead to approximate independence of rate of self-adhesion increase at the two different temperatures studied. These two competing effects were the viscoelastic barrier for forming intimate contact, and the inherent resistance to fracture,[33] both of which are dependent on temperature.

**Interface Width Studies.** Typical "back-side" NR data are shown in Figure 2 for system characterized by a narrow interface (full width = 20 Å) between the high MW(154k) PUU sample and a thin layer of deuterated (50k) PUU. The inset gives the sample geometry that was used and the important fitting parameters, which are also listed in Table 1 for the sample designated as "C". For stronger interfaces, the Mylar could be removed, and top-side reflection could be performed using the normal geometry, air/*h*-PUU (∼2 $\mu$m)/*d*-PUU(∼0.5 $\mu$m)/Si. Table 1 shows that the fitted parameters are essentially the same for backside and top-side reflection on the same sample, where the Mylar was removed for both measurements (compare samples "A" and "A1").

As a control to verify our sample preparation methods and ensure that we can make sufficiently smooth surfaces, the interface width for a *d*-PUU layer in contact with an incompatible low $T_g$ elastomer, which we refer to as PU−ester, was measured by NR(Table 1, Figure 8). A width of 11 Å was measured by backside reflection after about 2 days ($t^{1/2}$ = 50 min$^{1/2}$) of annealing, demonstrating that interdiffusion is necessary for the development of interface strength in PUU. This interface is very narrow, and is about the same as the *air*/*d*-PUU interface width of 12 ± 5 Å,[28] or a typical air/polymer interface width of a spin-coated amorphous polymer film like *d*-polystyrene on a Si wafer. Consistent with this, the interface strengths (*W*) for the incompatible pair do not change significantly from the initial time of contact. In fact, they are so low they remain at essentially at the level of wetting forces, e.g., a value of about 7 J/m² at peel rates of 0.3 mm/s, which is what we measure at the earliest possible times for PUU self-adhesion (Figure 4). We can conclude that interdiffusion is almost completely inhibited by incompatibility of the polymers. There is no observable interdiffusion, and the width is considerably smaller than the value that was measured at the shortest times possible with the NR technique for *d*-PUU/*h*-PUU which was about 40 min (Figure 9).

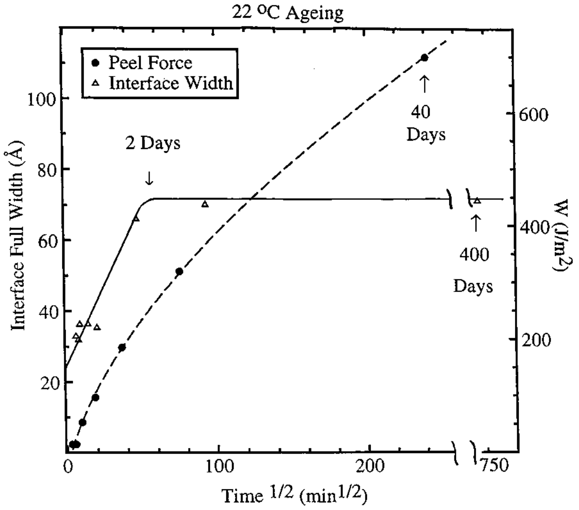

**Figure 9.** Interface width (Å) and detachment energy per unit area of interface (*W*) vs $t^{1/2}$ for self-adhesion of PUU. All aging was at 22 °C. The value for the interface width reaches a constant value much earlier than the value of *W* determined from peel tests (see text).

Using backside reflection we could also study early time interface development in *d*-PUU/*h*-PUU. NR data acquisition takes at least 30 min, so data at earlier times could not be acquired. We found that the interface width increased significantly at aging temperatures of 22 °C during the first 24 h (Figure 9). After about 2 days, the values level off at about 70 Å and remain at this value for times up to more than a year (Figure 9). It was shown earlier by NR[28] that the measured interfacial full width of *h*-PUU/*d*-PUU maximizes at about 65 ± 5 Å for high (120 °C) temperature treatments, consistent with these results. The relatively narrow dimensions even after long times are consistent with the hard segment domains strongly limiting the motion of the mobile soft segments, as is expected for a physically cross-linked system like PUU. The interface half-width is slightly larger than the radius of gyration ($R_g$) of the PTMeO soft segment block, which is estimated to be about 28 Å for a 4000 g/mol soft segment block length. The very strong interfaces which develop (Figure 9) were quite unexpected because the interfaces are quite sharp, not too much broader than those for immiscible PS and PMMA with interface full widths of 40 ± 5 Å.[37−39] For PS/PMMA, the interface strengths only reach about *W* = 10 J/m$^{2,40}$ while those for PUU/PUU reach levels of several hundred J/m² (Figure 9), although the fracture conditions may be different because of the different moduli and the different techniques applied to the two different systems. The hydrogen-bonding mechanism discussed below would explain why the peel forces are so high, even though the interfaces are quite narrow in the case of PUU self-adhesion.

Figure 9 also shows the interesting feature that while the interface width plateaus after about 2 days or less, the interface strength continues to grow stronger for substantially longer times over a period greater than 40 days. The interface strengths increase with some small deviations from a $t^{1/2}$ dependence which are likely due to problems with film cohesive tearing for the very strong interfaces. We do not believe that the number of segments crossing the interface increases significantly after the 2 day period, because we would expect that this would contribute to a change in the interface profile. This was not detected even though NR should have sufficient sensitivity. The 4000 g/mol mobile chain segments in PUU are short and should not require days to entangle. We propose that hydrogen bonding of the polar MDI group at the end of the soft segment blocks lead to the slow development of strength at essentially constant interface width, as the already interdiffused segments attempt to find better anchoring sites across the interface by hydrogen bonding. Presumably, the very slow increase in $W$ for "PIB"/Mylar in Figure 4 is also due to the PIB chains finding better anchoring sites, although in that case "inter-diffusion" is completely inhibited because Mylar is a impenetrable solid. A hydrogen bonding type of mechanism would also explain why the peel forces are so high, even though the interfaces are quite narrow in the case of PUU self-adhesion. Chemical reactions across the interface at room temperature are tentatively ruled out because the interface can be broken at any time, and then re-formed with strength development increases the same as a fresh interface.

The molecular mechanism also should consider end group effects. It is likely that the MW = 4000 PTMeG chain end blocks would have a significantly greater ability to interpenetrate, and this would also explain how the interface broadens to distances slightly greater than the random coil radii of gyration, e.g., the interface half width is equal to 35 Å and $R_g = 28$ Å. The "stretching" to such large dimensions of chain center PTMeG blocks pinned at both ends by hard segments, is unlikely. Chain end PTMeG blocks comprise a significant fraction of the total chain, roughly 10−15 vol % of each PUU chain, relative to the chain centers and could contribute to a sufficient density of chains coupling across the interface to explain strong interfaces. Similar effects have also been seen in thick film peel tests of cross-linked elastomers,[11] which show large values of self-adhesion, even though center of mass diffusion is prohibited by the (chemical) cross-links. The strong interfaces are presumably due to interdiffusion of dangling chain segments.[11]

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