Nanoscopic Adhesion Test for Polymers by A Light-lever System

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Abstract. Polymer nano-adhesion between a cantilever tip coated with polymer and a flat polymer film was studied by a light-lever system using an atomic force microscope. The polymer interface was adhered at a temperature above the surface glass transition temperature for a given time. Nano-adhesion force ($F_{\text{nano}}$), at which the tip was detached from the surface, was estimated from the deflection of the lever with a known spring constant. Nano-adhesion strength ($G_N$) was simply obtained dividing $F_{\text{nano}}$ by the contact area, which was estimated on the basis of Johnson-Kendall-Roberts theory. The time evolution of the interfacial thickness was independently examined by dynamic secondary ion mass spectrometry. Interestingly, $G_N$ increased with increasing interfacial thickness. However, it can be hardly judged whether $G_N$ is proportional to the interfacial thickness with the exponent of 1 or 2. Then, temperature dependence of $G_N$ was examined. Above the bulk glass transition temperature, the relation between temperature and $G_N$ was well expressed by a Williams-Landel-Ferry type equation. This means that the nano-adhesion strength is governed by friction between segments. Once this is accepted, $G_N$ should be proportional to the interfacial thickness with the exponent of 2.

1. Introduction

Recently, various kinds of organic thin-film devices such as solar cells and electro luminescence devices have been widely studied due to their flexibility, shock-resistant properties and processibility [1]. Buried interfaces between organic layers in these devices play crucial roles in their performances. Thus, it should be discussed how the interfaces are formed as well as how their structure and physical properties differ from those in the internal state. Besides, the other research trend for organic thin-film devices is a size effect [2]. The device performance might be a function of its size; the smaller would be the better because macroscopic and microscopic defects should be reduced with decreasing size. In that sense, to design and construct ultimate-functionalized devices, their size should be as tiny as possible based on either a top-down or bottom up method.

When the size of materials becomes smaller and smaller, usual methods to assemble pieces of materials, such as glue, adhesives, and so forth, cannot be used. This is because it’s technically difficult to paste such viscous liquids homogeneously onto nano-spaces. So far, segmental dynamics at polymer surfaces has been widely studied by many researchers using a wide variety of experimental techniques. One of the main conclusions emerged thus far is that the surface glass-transition temperature ($T_{g,s}$) is lower than the corresponding bulk value [3]. In other words, the chain mobility at the surface is more enhanced than that in the internal phase. This leads to a demonstration that (polystyrene (PS)/PS) bilayer interface can be evolved in terms of the thickness even at a temperature...
being well below the bulk glass-transition temperatures \( T_g^b \). Then, this knowledge was applied to adhesion between PS films with macroscopic area. Even if the adhesion temperature \( T_{ad} \) was lower than the \( T_g^b \), adhesion strength for the PS bilayers increased with annealing time on account of the segmental interdiffusion within 10 nanometers [4]. This behavior could be simply explained in terms of the enhanced mobility for chains in the interfacial region, which was originally the film surface. Based on these results, it seems reasonable to infer that tiny pieces of polymer materials can be assembled for one another without using usual adhesives if only the surface mobility is activated. However, the lateral area should be adhered was macroscopic for the previous experiment. Hence, it is necessary to discuss what happens with the adhesion if the adhered area also decreased to be nanometer scale. The objective of this study is to give a direct answer to this question, nano-adhesion measurement.

2. Experimental

As a polymer, monodisperse PS (\( M_n = 26,000, M_w/M_n = 1.06 \)) was used. The \( T_g^b \) value for PS was evaluated to be 372 K by differential scanning calorimetry (DSC). Figure 1 shows the schematic illustration for nano-adhesion measurement conducted by a light-lever system of an atomic force microscope (AFM). A tip was gently dipped into a dilute solution of PS with the aid of a micrometer and then took out from the solution right away. Then, the tip was dried and well annealed to relax the preparation history. Also, a film of PS was spin-coated onto silicon wafers and was also annealed to reach a quasi-equilibrium state. The tip coated with PS was attached to the film under a gentle pressure in the AFM vacuum chamber. The interface was allowed to be developed at a temperature above the \( T_g^s \). After a given time \( t_{ad} \), nano-adhesion force \( F_{nano} \), at which the tip was detached from the film surface, was evaluated on the basis of the deflection of the lever with a known spring constant. Nano-adhesion strength \( G_N \) was finally obtained dividing \( F_{nano} \) by the contact area \( \pi a^2 \) where \( a \) is radius of contact area.

\[
G_N = \frac{F_{nano}}{\pi a^2} \tag{1}
\]

Contact area made upon the adhesion process is not always the same, depending on original tip shape, adhesion time, temperature, and so forth. Hence, the adhered area for each run was calculated on the basis of a traditional contact mechanics proposed by Johnson-Kendall-Roberts [5], as shown in Figure 2. According to this framework, the \( a \) value is given by

\[
a^3 = \left[ \frac{(R/K)(F_N + 2F_{ad} + (4F_{ad}F_N + (2F_{ad})^2)^{1/2})}{-2} \right] \tag{2}
\]

where \( R, K, F_N \) and \( F_{ad} \) are radius of the curvature for the tip, reduced elastic modulus, normal force applied and adhesion force, respectively.
3. Results and Discussion

3.1. Time evolution of nano-adhesion strength. Figure 3 shows the time evolution of $G_N$ for (PS/PS) interfaces adhered at 365 K. The $T_g$ for the PS used was 303 K [3]. That is, the adhesion temperature ($T_{ad}$) was between the values of $T_g^s$ and $T_g^b$. When $t_{ad}$ was shorter than $10^3$ s, the $G_N$ remained almost constant. This time independence implies that the adhesion strength in this region may be generated by a static factor such as van der Waals force rather than a dynamic one. Once $t_{ad}$ went beyond $10^3$ s, the $G_N$ first increased with increasing $t_{ad}$, and then, reached a constant value of about 5 MPa after $10^5$ s. The solid and dotted lines, which are both the guide of the eye, possess the slopes of 1/2 and 1/4 to the $G_N$-$t_{ad}$ relation. The physical meaning of this exponent is later discussed.

We also examined the time evolution of interfacial thickness ($d$) at 365 K by dynamic-secondary ion mass spectrometry (DSIMS) [6]. In this case, the interface became thicker with increasing time until a given time, and then reached a constant. As segments reach in the depth region in which relatively large scale molecular motion, such as segmental motion, is frozen, the interdiffusion ceases. The slope for the $t_{ad}$ vs. $d$ relation was 1/4. According to a dynamic picture of polymer chains by Doi and Edwards [7], this exponent indicates that not chains but segments interdiffused across to the interface. Since the interface is originally formed by two surfaces, a half of the interface corresponds to a region where segments can be moved. The half thickness of the interface being in a quasi-equilibrium state was evaluated to be approximately 4 nm, as shown in Figure 3, and was smaller than the spatial dimension of a PS chain used here. Taking into account these, it seems reasonable to claim that the adhesion strength is generated by the interdiffusion of segments.

3.2. Relation of nano-adhesion strength to interfacial thickness. We now come to a direct comparison between $d$ and $G_N$ at a given $t_{ad}$. Figure 4 shows the result for the (PS/PS) interface adhered at 365 K. When the $t_{ad}$ was shorter than $10^3$ s, the interface could not be experimentally obtained because the interfacial broadness was comparable to the detection limit of DSIMS. Thus, in this $t_{ad}$ region, the $d$ value was assumed to be 0. The $G_N$ value simply increased with $d$. The solid and dotted curves are drawn for the guide of the eye. The former and latter denote the relations of $G_N \sim d^2$ and $\sim d$, respectively.

Figure 3. Time evolution of $G_N$ for (PS/PS) interfaces adhered at 365 K.

Figure 4. Relationship between $d$ and $G_N$ for (PS/PS) interfaces adhered at 365 K.

Figure 5. $T_{ad}$ dependence of $G_N$ for (PS/PS) interfaces adhered at temperatures above $T_g^b$. 

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While the relation of $G_N$ to $d$ seems to be reasonable for glassy polymers [5], this may not be the case for rubbery chains. Schnell and co-workers have proposed that adhesion strength between rubbery polymers results from the resistance force based on monomer friction [8]. In this model, so-called chain pull-out model, $G_N$ is expressed by the following,

$$G_N = \sum f_{\text{mono}} d^2 (2C_{C-C} l_0) A_{f_{\text{mono}}} d^2$$  \hspace{1cm} (3)

where $\Sigma$, $f_{\text{mono}}$, $C_{C-C}$, $l_0$ and $A$ are areal density of chains, monomeric friction coefficient, characteristic ratio and C-C bond length, constant, respectively. That is, the $G_N$ value is proportional to the square of $d$. It can be hardly judged only from Figure 4 whether which model is appropriate to explain our current experimental results.

### 3.3. Temperature dependence of nano-adhesion strength.

According to the chain pull-out model, the $G_N$ value for the (PS/PS) interfaces being in a quasi-equilibrium state should be dominated by the monomeric friction. Since the friction coefficient is a function of temperature, we next examined the $T_{\text{ad}}$ dependence of $G_N$. In this case, $T_{\text{ad}}$ was long enough to reach a constant in $G_N$ to reach in a quasi-equilibrium state. Figure 5 shows $T_{\text{ad}}$ dependence of $G_N$ for (PS/PS) interfaces adhered at temperatures above $T_g^b$. The abscissa is expressed by $(T_{\text{ad}}-T_g^b)$. The $G_N$ value for the (PS/PS) interfaces decreased with increasing $T_{\text{ad}}$. Lodge and co-workers have reported the temperature dependence of $f_{\text{mono}}$ for monodisperse PS, which follows the Williams-Landel-Ferry (WLF) equation above $T_g^b$ [9].

$$\log\left(\frac{f_{\text{mono}}}{f_{\text{ref}}}\right) = -C_1(T-T_{\text{ref}})/\{C_2 + (T-T_{\text{ref}})\}$$  \hspace{1cm} (4)

where $C_x$ ($x = 1, 2$) is fitting parameters, and $f_{\text{ref}}$ is monomeric friction coefficient at reference temperature ($T_{\text{ref}}$). The experimental data was well fitted by eq. (4) with $C_1$ of 0.866 and $C_2$ of 59.5, as shown in Figure 5. This makes it clear that the $G_N$ value under the current condition is controlled by $d^2$. Once we accept this, the slope for the $G_N-T_{\text{ad}}$ relation shown in Figure 3 is plausible to be 1/2 rather than 1/4. More conclusive study will be reported in the near future.

### 4. Conclusions

Polymer nano-adhesion measurement was successfully carried out using an AFM. The adhesion strength for the (PS/PS) interfaces could be apparently expressed both by the interfacial width and its square. The $T_{\text{ad}}$ dependence of equilibrium $G_N$ followed the WLF type equation. Hence it can be concluded that the adhesion strength would be dominated by the frictional force between segments.

### References

[1] N. Sariciftci, L. Smilowitz, A. Heeger, and F. Wudl, *Science*, 258, 1474 (1992).
[2] H. Hoppe, T. Glatzel, M. Niggemann, W. Schwinger, F. Schaeffler, A. Hinsch, M. Ch. Lux-Steiner, and N. S. Sariciftci, *Thin Solid Films*, 511, 587 (2006).
[3] K. Tanaka, A. Takahara, and T. Kajiyma, *Macromolecules*, 33, 7588 (2000).
[4] K. Akabori, D. Baba, K. Kouguuchi, K. Tanaka, and T. Nagamura, *J. Polym. Sci. Part B*, 44, 3598 (2006).
[5] K. L. Johnson, K. Kendall, and A. D. Roberts, *Proc. R. Soc. Lond. Ser. A*, 324, 301 (1971).
[6] D. Kawaguchi, K. Tanaka, T. Kajiyma, A. Takahara, and S. Tasaki, *Macromolecules*, 36, 1235 (2003).
[7] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford University Press, pp. 213 (1986).
[8] R. Schnell and M. Stamm, *Macromolecules*, 32, 3420 (1999).
[9] J. M. Milhaupt, T. P. Lodge, S. D. Smith, and M. W. Hamersky, *Macromolecules*, 34, 5561 (2001).