

HIGH-THROUGHPUT APPROACH TO STUDY THE EFFECTS OF POLYMER ANNEALING TEMPERATURE AND TIME ON ADHESION

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Introduction

In many engineering applications, such as composite manufacturing and durability, coatings, biomedical devices and implants, and packaging for microelectronics components, the challenge of understanding the mechanisms of polymer adhesion is of primary importance. Current (traditional) approaches to the characterization of adhesion have focused on attempts to isolate a single adhesion-controlling parameter and monitor the changes in adhesion with changes in that single parameter. However, this methodology is time consuming, discrete, and does not allow interplay between variables to be investigated. Stimulated by the initial success in the high-throughput (combinatorial) approach to some fields of polymer characterization [1-5], we extend the approach to polymer adhesion through peel tests to explore the effects of polymer annealing temperature and time on adhesion development for different substrates. Also, the relationship between the annealing time, annealing temperature, and surface energy to the film adhesion has been examined using the combinatorial approach. Poly (methyl methacrylate) (PMMA) has been selected as the subject polymer. Silicon, aluminum, chromium, copper and gold have been used as the substrate. The ultimate goals of this research are to develop techniques for processing and analyzing multi-variables of the interface and to map the dependence of adhesion on these adhesion-controlling parameters rapidly, practically, and efficiently.

Experimental¹

The PMMA sample (from Polysciences, Inc, Warrington, PA, USA) used in this study has a molar mass and polydispersity of 100,000 g/mol and 2.26, respectively. Preliminary test indicated that it has a glass transition temperature (T_g) of ca. 105 °C (probed by Differential Scanning Calorimeter (DSC) with a heating rate of 20 °C/min).

In this study, PMMA films (ca. 100 nm in thickness) were placed on silicon wafers (Polishing Corporation of American, CA) as well as on silicon wafers coated with thin metal layers of Au, Al, Cr, and Co, to mimic different substrates such that their effects on the adhesion can be

investigated. These metal layers were deposited on the silicon wafer using a thermal evaporator (Granville-Phillips Company, Boulder, CO) at a pressure of less than 0.2 Pa. It should be noted that in the thermal evaporation technique, the average energy of vapor atoms reaching the substrate is generally low (order of kT , i.e., tenths of eV). This can seriously affect the morphology of the metal layer and often results in a porous and weak adherent layer. In addition, we deposited PMMA films on silicon substrates having an alkylsilane self-assembled monolayer (SAM), and the surfaces of these SAM-coated substrates were UV-modified to introduce different surface energy levels. The PMMA film thickness was measured after solidification using a UV reflectance interferometer F20 (Filmetrics, San Diego, CA) with a 0.5 mm diameter spot size, and corroborated by a Dektak 8 stylus profiler (Veeco Co, Santa Barbara, CA).

Results and Discussion

In order to examine the role of heat diffusion in the development of polymer adhesion to a substrate, samples of the PMMA/Al system annealed with a temperature gradient were subjected to peel tests to characterize the adhesion behavior. Three annealing temperature gradients (ranging from 83 °C to 170 °C, 88 °C to 180 °C, and 93 °C to 193 °C) were applied to samples annealed for various time ranging from 10 min to 12 h. Peel tests were conducted at a constant load and rate for the samples with the same annealing temperature gradient (Fig. 1). During the loading, the PMMA film would be peeled from the substrate to a certain position, and the remaining bonded length of the film, l_o , was recorded for a specific annealing time. Afterwards, a critical temperature, T_c , is determined based on the l_o , the original bonded length and the temperature gradient that the sample has been subjected to.

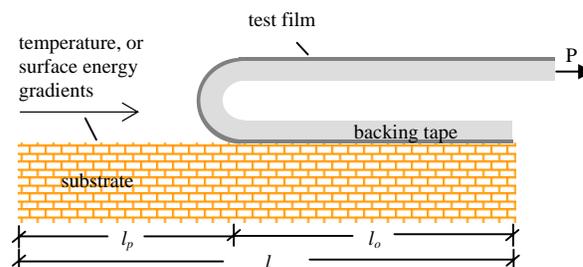


Fig. 1 Schematic of peel test for peeling a commercial tape (as a backing tape) adhered to a test film at 180° peel angle. l is the original sample (bonded) length. l_p is the peeled length. l_o is the bonded length after peeling.

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Fig. 2 shows typical variations of the l_o and T_c as a function of annealing time for an annealing temperature gradient from 93 °C to 193 °C. Within the temperature gradients studied, all the results on the development of PMMA adhesion to Al exhibit similar trends and can achieve at relatively low temperatures. Also, the results in the figure qualitatively express the significance of time-temperature dependence on the adhesion development.

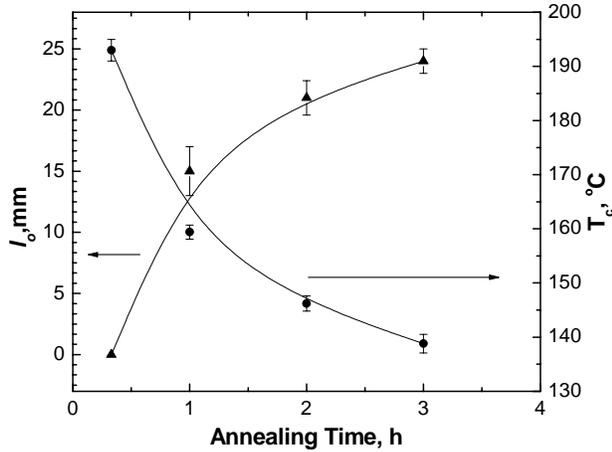


Fig. 2 Typical variations of the unbroken length, l_o (\blacktriangle , mm) and critical temperature, T_c (\bullet , °C) as a function of annealing time (h) for an annealing temperature gradient of 93 °C –193 °C.

Fig. 3 gives the variation of T_c with annealing time for PMMA films with different metal substrates subjected to a temperature gradient from 85 °C to 180 °C. For these film/metal systems, the loads and loading rates adopted in the peel tests remained constant. The results in the figure suggest that the aforementioned time-temperature relationship is a common feature for any metal substrates (*i.e.*, Cr, Cu and Au) employed with PMMA. Also, the adhesion behavior of PMMA to the substrate displays a profound dependence on the metal layer. The region above each curve in the figure can be regarded as a *bonded* area while the region below the curve revealed as a *debonded* area. Each curve represents a distribution of failure (failure map) as a function of annealing temperature and time for the PMMA film peeled at 180° from the corresponding substrate. Although more research is needed, these results suggest that the PMMA forms the strongest adhesion to the Cu and the weakest adhesion to the Au coated substrate. This dependence of the adhesion of PMMA on the metallic nature of the substrate could be partially attributed to the differences in wettability and roughness of the substrates, which are beyond the scope of this study.

As the surface wettability (surface energy) of the substrate usually affects the solid/liquid adhesion, it is worthwhile to use a combinatorial approach to study the effect of the contact angle, annealing time and annealing

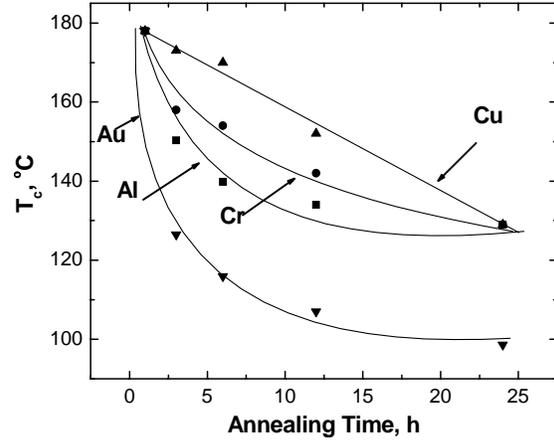


Fig. 3 Variation of critical temperature, T_c , as a function of annealing time for different metal substrates. The annealing temperature gradient is from 85 °C to 180 °C.

temperature on the peel strength. Fig. 4a displays the variation of the critical contact angle (θ_c , which will be defined later) with the annealing time for different constant annealing temperatures. In this case, a sample of a PMMA film, deposited on a silicon substrate having a contact angle gradient, was annealed at a specific temperature for a specific time period. Then, a constant peel force was applied to the sample starting from the sample end having a largest contact angle. Consequently, the PMMA film would be partially peeled from the substrate, and a contact angle corresponding to the bonded length (l_o) is obtained. This contact angle is defined as θ_c . One can note from the results in Fig. 4a that the dependence of θ_c on the annealing time becomes less obvious when the annealing time increases. Also, with the increase in the annealing time, the l_o becomes larger (*i.e.*, a larger l_o corresponds to a higher contact angle --- more hydrophobic part was left on the substrate). In other words, the PMMA tends to adhere to a surface area with lower contact angles (more hydrophilic area) [6]. This argument is reasonable since the polar species of PMMA prefers to interact with the polar groups of the surface. Therefore, the surface chemistry of the substrate plays a critical role in the adhesion of PMMA to a substrate.

If the relationship between the annealing time-temperature and the adhesion observed in Fig. 4a can be treated with the time-temperature superposition principle for the modulus of a viscoelastic material, one may apply this equivalence principle to the annealing time-temperature, such that a correspondent time (t_c) for a certain annealing time (t_a) is:

$$t_c = a_T t_a \quad (1)$$

where a_T is the shift factor, and a_T can be related to temperature (T) through the WLF equation [7]:

$$\log a_T = \frac{-C_1 (T - T_g)}{C_2 + T - T_g} \quad (2)$$

where C_1 and C_2 are constants and vary rather slightly from polymer to polymer. If taking $C_1 = 17.4$ and $C_2 = 51.6$ (universal constants) and applying the data in Fig. 4a to Eqs. 1 and 2, one can construct a master curve that illustrates the dependence of the critical contact angle (for the film peeled at 180° from the substrate) on the arbitrary choice of annealing time and temperature (Fig. 4b). Assuming that the WLF equation is applicable [8], the results in the figure also provide a failure map as a function of contact angle and annealing temperature and time. This failure map provides designing engineers and manufacturers a tool to determine materials (or the critical surface energy) needed for practical considerations of the adhesive bond of interest.

Conclusions

Using high-throughput peel tests of PMMA films from various metallic substrates, this study has demonstrated that the proposed combinatorial approach has the potential to characterize the interrelationship among the adhesion-controlling parameters rapidly, practically, and efficiently. The approach is expected to provide accurate results because of its large sampling space. In addition, using the proposed combinatorial peel test in conjunction with WLF equation, we have developed the annealing time-temperature superposition for determining the dependence of the critical contact angle to peel a film from a substrate (with a specific peel angle) on any arbitrary annealing time and temperature. Consequently, a master curve (a failure map) that relates the critical contact angle and the annealing time and temperature of the film/substrate system can be constructed. Furthermore, the proposed combinatorial peel test can be extended to construct master curves for other parameters relevant to peel adhesion (*e.g.*, the dependence of peel force on any choice of temperatures and peeling rates).

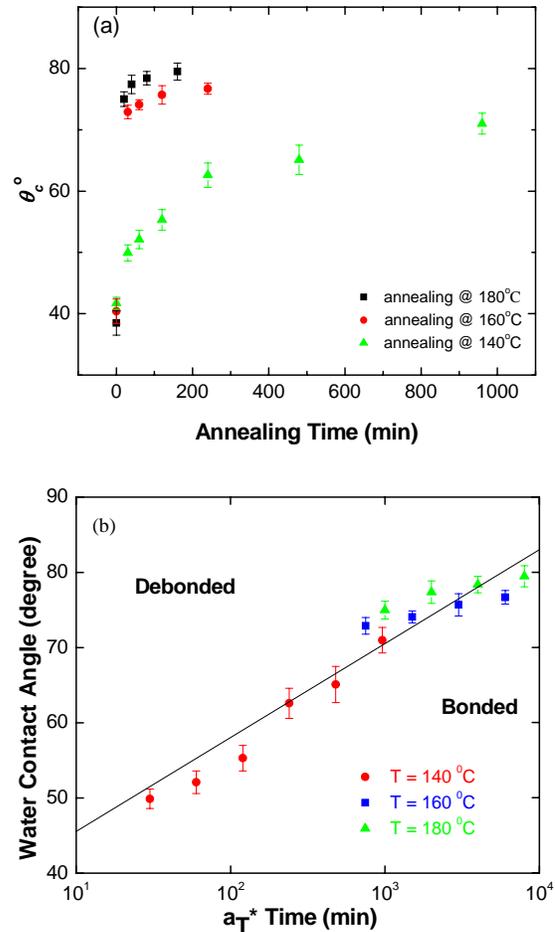


Fig. 4 The critical contact angle gradient, θ_c , as a function of annealing time for various annealing temperatures (a), the master curve of peel force as function of annealing time and temperature for PMMA films peeled at 180° from silicon substrates (b).

References

1. M.Y.M. Chiang, W. Wu, J.M. He, E.J. Amis, *Thin Solid Films* 2003, **437**, 197-203.
2. A.J. Crosby, *J. Material Science*, 2003, **38**, 1-11.
3. C.M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. Amis, M. R. Vanlandingham, H.-C. Kim, W. Volksen, R. D. Miller, and E. Simonyi, *Nature Materials*, 2004, **3**, 545-550.
4. E.J. Amis, *Nature Materials* 2004, **3**, 83-85.
5. M.Y.M. Chiang, R. Song, A.J. Crosby, A. Karim, C.K. Chiang, E.J. Amis, *Thin Solid Film*, in press, 2004.
6. A. Pfau A, R. Sander R, S. Kirsch, *Langmuir* 2002, **18**, 2880-2888.
7. Williams ML, Landel RF, Ferry JD. *J. Am. Chem. Soc.* 1955; **77**: 3701.
8. M.Y.M. Chiang, G.B. McKenna, J. Yuan, *Polymer Engineering and Science* 1994, **34**, 1815-1822.