

HIGH THROUGHPUT SCREENING OF INTERFACIAL ADHESION STRENGTH IN COMPOSITIONAL LIBRARIES OF EPOXY FILMS*

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Introduction

Adhesion between multi-component materials and a substrate is an important characteristic that affects service life, durability and overall performance in many applications. Interfacial adhesion strength is known to depend on a host of factors such as surface chemistry, roughness, material properties, cure conditions, and even relative humidity. To successfully survey such a large and diverse parameter space, it would be very attractive to perform simultaneous measurements of interfacial adhesion on samples or libraries having discrete or continuous changes in two or more of these controlling factors.¹

Due to the success of the combinatorial approach for polymer coatings development²⁻⁴, we have championed a combinatorial approach to the edge lift-off test.⁵ In demonstrating the potential of this test method, we have quantified the interfacial adhesion of various coating systems as a function of polymer thickness, surface energy of the substrate and test temperature⁶. Further, the ability to rapidly discover optimum performance space for new materials and formulations is critical to success with reduced technology cycle times and increased performance to cost pressures in a variety of industrially relevant areas⁷⁻¹¹. Therefore, we propose an extension of this body of work where we characterize the interfacial adhesion between multi-component materials and a substrate as a function of composition. Our initial demonstrations focused on the deposition system and its performance.^{12,13} Here, we discuss in more detail the results on measuring the interfacial adhesion strength in epoxy coatings.

Experimental¹⁴

2.1 Materials. The model epoxy system studied in this work consisted of 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate (epoxy resin), hexahydro-4-methylphthalic anhydride (curing agent), and cobalt (III)

acetylacetonate (catalyst). These chemicals were purchased from Aldrich and used as received. The epoxy resin used in this study was pre-mixed with a catalyst at 150 °C for 1 h and the catalyst pre-mixed epoxy will simply be referred as “the epoxy resin” hereafter.

Silicon wafers (8.9 mm diameter, 3 mm thick) were immersed in an acetone bath, and then rinsed by toluene, ethanol, and acetone and dried with nitrogen. After the cleaning process, the wafers were placed into a UV-ozone cleaner for 25 min for further cleaning of the surface. The borosilicate glass (100 mm x 100 mm x 5 mm) was also prepared by the same surface treatment as the silicon wafers.

2.2 Library fabrication. Compositional gradients of epoxy resin were generated using a custom-built meter / mix / dispense system described previously.^{7,8} Before depositing the epoxy library on the substrate, Kapton adhesive tape (130 μ m thick, 6 mm wide) was placed on the substrate as a spacer, and then the designated compositions of epoxy mixtures were deposited on the substrate. A poly(dimethyl siloxane) (PDMS) block was placed on top of the epoxy mixtures in order to squeeze out excess epoxy from between the Kapton spacers. Finally, the epoxy was cured at 170 °C for 2 h. After curing, the PDMS blocks and Kapton spacers were removed from specimens and compositional library was diced into 5 mm squares using an automated dicing machine.

2.3. Testing. The epoxy libraries were placed on a cryogenic temperature stage to drive the debonding process. The temperature of the cryogenic stage was controlled by the flow rate of liquid nitrogen through the stage. With decreasing temperature, debonding events and corresponding temperatures were recorded by a digital camera.

Results and Discussion

Fig.1 shows the experimental results from the combinatorial edge delamination test after sequentially exposing the samples to cryogenic temperatures from 0 °C to -180 °C.

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Upon cooling the epoxy libraries from 0 °C to -180 °C, delamination occurs in the epoxy rich films first (higher temperatures) and then progressed down to the 1:1 mixtures (lower temperatures). Fig. 1 presents failure events of the epoxy films as a function of temperature based on the digital images acquired during quenching. The epoxy film that was fabricated in the higher epoxy pumping ratio (2.42:1) show the first failure around -50 °C and saturates around -120 °C. The failure evolution of the films 12, 11 and 10 shows similar shapes and only shifts toward lower temperature.

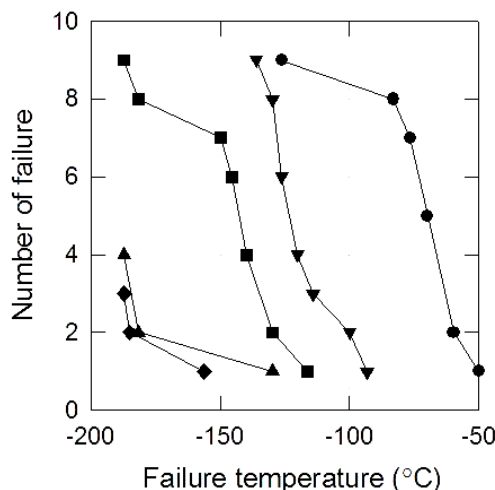


Figure 1. Failure events of the epoxy films during the test and compositions of the epoxy films on silicon substrate vary from 1 to 12. The lines are drawn to guide the eye. (●: Film12, ▼: Film11, ■: Film10, ▲: Film8, ◆: Film3)

Using eq. 1, we can estimate the stress (σ_0) at which delamination occurs. In this equation, α is the coefficient of thermal expansion, E is the Young's modulus, ν is the Poisson's ratio, and T_r is a reference temperature (taken as the glass transition temperature of the epoxy film). The subscripts f and s denote the film and substrate, respectively. From the digital images, we can determine the temperature at which the film delaminates (T_1).

$$\sigma_0 = \frac{(\alpha_f - \alpha_s)(T_1 - T_r)E_f}{1 - \nu_f} \quad (1)$$

Once we establish the critical stress of debonding, we can then determine fracture toughness of the interface by the following equation:

$$K_{IC} = \sigma_0 \sqrt{\frac{h_f}{2}} \quad (2)$$

where h_f represents the epoxy film thickness. In our calculations, we used $\alpha_f = 77 \times 10^{-6} / \text{K}$, $\alpha_s = 3.2 \times 10^{-6} / \text{K}$ and $\nu_f = 0.3$.

Fig. 2 presents the K_{IC} values of the representative epoxy films. For calculating K_{IC} , the biaxial stress was determined by the first delamination event on each composition of the epoxy films. The K_{IC} decreased with increasing epoxy mixing ratio and the lowest interfacial strength occurred at a mixing ratio of 2.42.

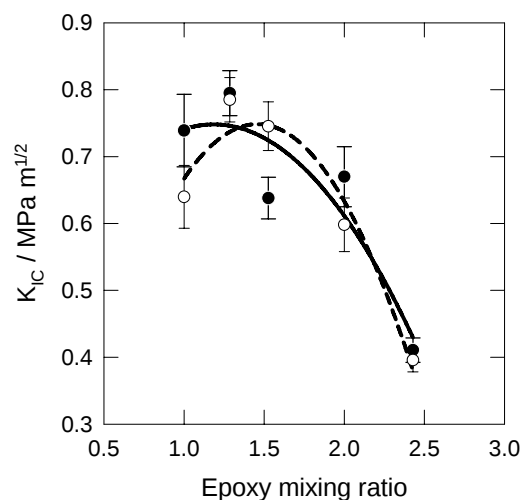


Figure 2. K_{IC} of the epoxy/silicon (●) and glass (○) vs. epoxy mixing ratio. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

Conclusions

We have developed the framework of a combinatorial approach for mapping the interfacial reliability of polymer coatings based on the edge lift-off test geometry. Combinatorial libraries of composition in epoxy films qualitatively provided the rapid screening capability for assessing interface strength, which clearly showed a transition in the film failure mode with changing composition. Based on the experimental results in this study, we successfully show that this methodology is capable of providing rapid and valid assessment of adhesion.

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14. Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply the materials are necessarily the best available for the purpose.