Combinatorial adhesion measurements: Factorial design concepts for data collection and library evaluation

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INTRODUCTION

Polymeric adhesive formulations often include multicomponent blends of viscous polymers and tackifiers. These mixtures are designed to allow proper substrate wetting, maintain the necessary adhesive strength, and, if required, release from the surface while leaving as little residue as possible. Most often in industry, determination of the optimal adhesive formulation for a given application is based on an inefficient process that combines empirical knowledge and experimental trial and error. A more efficient method of discovering the optimal adhesive formulation for a specific application would greatly enhance the time and effort required for a new adhesive formulation to transition from idea to product. A potential methodology lies in the application of *combinatorial methods* to design assays that encompass a large combination of possible formulations across one sample. The specimen assay or *library* is scanned with a high throughput analysis method to search for mapping regions of optimal adhesion.

Recently, NIST has successfully applied combinatorial techniques for knowledge discovery in material science. In this research, gradients in sample thickness, composition, surface energy, or elastic modulus, which encompasses a large parameter space, are combined to create the specimen library. For example, combinatorial techniques have been successful in creating a complete polystyrene-poly(vinylmethyl ether) composition-temperature phase diagram in a single experiment [1]. An instrument developed at NIST to measure adhesion across a library in a high throughput fashion is the multi-lens combinatorial adhesion test (MCAT) [2]. This instrument utilizes an array of microlenses to conduct adhesion measurements across a sample. The fabrication of adhesion libraries has previously been demonstrated by Crosby et al. [2]. For adhesives development, a combinatorial approach might employ orthogonal gradients of formulation composition and sample thickness to quickly determine the most promising combination of these factors for a specific application. Here, the challenge lies not in creating the combinatorial library, but in analyzing many thousands of possible experiments included in the sample. In this study, we examine a methodology that utilizes NIST-developed instrumentation and statistical analysis to determine the best possible route to measure adhesion across a gradient library.

THEORETICAL

The Johnson-Kendall-Roberts (JKR) theory modifies the Hertzian equations of contact to account for the adhesive surface forces between two spherical bodies brought into contact. If the bodies are held together by a specific load *P*, then the contact radius (*a*) is related to the radii of curvature (*R*), the energy release rate (*G*), and the modulus of the deformable material (*E*) [3]:

$$a^3 = \frac{9R}{16E}\left(P + 3\pi GR + \left[6GRP + (3\pi GR)^2\right]^{\frac{1}{2}}\right) \qquad \textbf{E.1}$$

Equation E.1 shows that measuring the load and contact area allows the energy release rate, or adhesion energy to be calculated. Gent and Maugis [4,5] have shown that this equation is equivalent to the fracture mechanics relationship for the driving force for propagating an interfacial crack between two contacting bodies. For linear elastic solids, a relationship which relates the contact area and applied displacement to *G*:

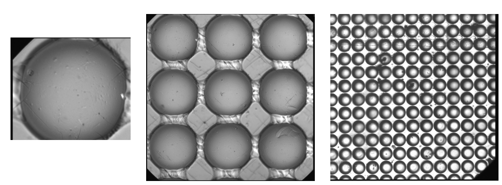
$$G = \frac{2E(\delta' - \delta)^2}{3\pi a} \qquad \textbf{E.2}$$

where $\delta' = a^2/R$ is the displacement required to establish a contact radius of *a* without the presence of surface or adhesion forces [6]. If finite size or viscous effects influence the adhesion between two surfaces, then E.2 may be modified using the appropriate correction factors [7]. Equation E.2 is essential to combinatorial adhesion tests because displacement and contact area are the relevant measurements recorded during an MCAT adhesion test. Since displacement and contact area may be measured for each microlens in contact with the substrate, the instrument is uniquely suited to both qualitatively and quantitatively measuring adhesion over a large parameter space.

DISCUSSION

The multi-lens JKR technique has been described elsewhere [2]. Briefly, the technique utilizes a symmetric array of spherical lenses mounted onto a Burleigh Instruments inchworm drive [8] actuator arm to drive the lens array into contact with the normal plane of a flat substrate. The contact area between the array and substrate is visualized with a Leica DM IRE2 inverted microscope and measured with Image Pro software. Labview software is used to record the actuator position and load data during an experiment. Since the microscope and data acquisition are computer controlled, a large number of lenses may be tracked during a loading and unloading experiment [8]. This technique has been proven effective in measuring the dependence of polystyrene self-adhesion on thickness and temperature [2]. One potential drawback of this technique is the volume of data generated during an adhesion test. Multi-lens arrays may be fabricated to contain anywhere from 100 up to 1000 or even 8100 individual lenses over an area of 1 cm^2. Each lens represents an individual JKR test and it is difficult to efficiently analyze the contact area and displacement data generated, for each lens, from one loading and unloading experiment. Second, the gradients generated to form a library typically span distances over hundreds of centimeters. Due to this difference in length scales between the library and the micro-lens array, complete characterization of the gradient surface is accomplished by sampling smaller areas. Figure 1, A and B, illustrates the potential workload inherent in the different JKR techniques. For the figure on the left (A), the lower surface density of lenses reduces the amount of data analysis. This array geometry is conducive to investigating samples with shallow gradients. On the contrary, the figure on the right would require a much more intensive analysis to determine the adhesion forces over the same area as in (A). One solution to this problem currently under investigation is to utilize a statistical analysis technique (factorial design) to determine the best method of analyzing the combinatorial library with a multi-lens array [9]. Depending on the complexity of the gradient library, the number and location of sample points required to create a

Figure 1. The MCAT can utilize any of the three lens scenarios presented here. (A) a single microlens. The multi-lens array in the middle (B) contains fewer microlenses per area than the lens on the right (C). This figure printed with permission from Crosby et al. [2].



A B C

representative map of adhesion across the library may not be apparent. With factorial design, the *main effect* of any single experimental parameter, which defines the library, on the experimental results may be tested. The main effect is calculated by the difference between adhesion energy when one variable, for example thickness, is at its highest and lowest value, while all other variables are constant. This technique allows for determining whether two experimental parameters *interact* to influence the experimental results. Therefore, the combined effect of any two *interacting* experimental parameters on the results is quantified.

For example, a combinatorial library is designed with a polymer film possessing a thickness gradient orthogonal to a surface energy gradient. We wish to measure how these parameters influence adhesion with the multi-lens array. A multi-lens JKR experiment is performed to measure adhesion in either random areas or near the sample boundaries depending on the complexity of the gradient. The purpose of this initial testing is two-fold: If the gradient is steep enough to produce different adhesion behavior across the width of an array; then the multi-lens test will measure adhesion contour lines in the parameter space. If the gradient is shallow, then the multi-lens test will produce an excellent statistical adhesion measurement across the multi-lens array. In either case, factorial design is employed to determine the whether thickness or surface energy have a greater effect on the measured adhesion or whether these two parameters interact. Let us assume that our factorial design indicates that surface energy has a greater effect on adhesion than thickness. Experimental efficiency would be greatly increased by focusing adhesion measurements across the steepest gradient in surface energy. Figure 2 is a pictorial example of how this technique might be beneficial. After the gradient library is created, factorial design methods are utilized to determine if one experimental variable is more influential in the experimental outcome.

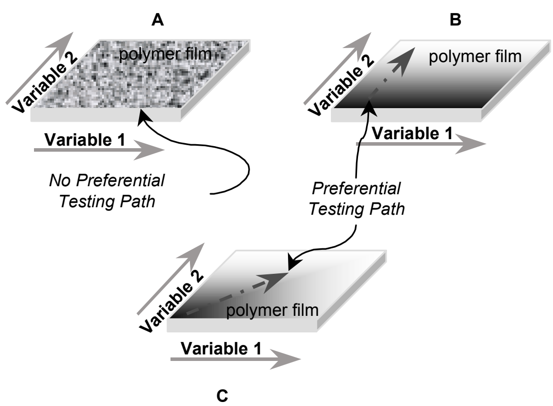


Figure 2. Different scenarios possible when creating a gradient library for adhesion studies. A) Variable 2 is dominant. B) Variables 1 and 2 interact with each other to influence the outcome. C) There is no preferential path, both variables influence the experimental outcome equally.

From this analysis, adhesion measurements would be conducted along the path demonstrated to have the largest effect on the experimental outcome. This example is extremely simple, but the technique is easily extended to analyze a more complex parameter space. As a demonstration of the combinatorial adhesion tests and statistical analysis approach, we present a series of multi-lens and macrolens JKR tests conducted on gradient libraries of polymer and elastic thin films. Initial adhesion measurements will be conducted to provide the necessary statistics to conduct the factorial design analysis. This statistical analysis will define the most efficient sampling pathway to create a representative adhesion map across the library. The multi-lens tests will be used to produce a qualitative adhesion map and the macrolens test will measure the work of adhesion across the gradient library. The representative map is compared to a complete adhesion map, i.e. characterization of the entire library, to determine whether statistical analysis was beneficial to the analysis of the library.

CONCLUSIONS

Discovering and evaluating new polymer adhesives can be an inefficient process due to a traditional reliance on empirical knowledge and experimental trial and error. The MCAT instrument developed at NIST can improve the efficiency of this process by utilizing combinatorial methods to create sample libraries that encompass a large parameter space. One drawback of this technique is the volume of data collected during each evaluation of a new sample library. Statistical analysis may reduce this volume by directing experimental testing to sample areas that contain the most useful information. This work seeks to combine statistical analysis with MCAT measurements to reduce the time and effort necessary to formulate new adhesives.

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