

# MANIPULATION OF ADHESION VIA SUB-SURFACE PATTERNING

John A. Howarter, Peter M. Johnson, Jun Young Chung, and Christopher M. Stafford  
Polymers Division, National Institute of Standards and Technology,  
Gaithersburg, MD 20899, USA  
john.howarter@nist.gov

## Introduction

The delamination characteristics of patterned and hierarchical interfaces are of great interest due to the advanced adhesion capabilities found with many biological surfaces. Using nature-inspired design principles, micro- and nanostructured surfaces have been shown to significantly alter the adhesive performance of a given material.<sup>1</sup> In-plane patterning, whether chemical or physical is a simple method of creating a heterogeneous interface, thus disrupting or altering the adhesion and delamination events during separation. However, nature is considerably more complex, often relying on hierarchical structures and gradients in mechanical properties. We synthesized model surfaces which have discrete modulus variation in-plane and through depth to investigate the effect of sub-surface texture on the adhesive performance. We use a modified cantilever peel adhesion test to correlate the energy to fracture with the morphology of the advancing crack front.

## Experimental

The cantilever peel test, similar in many ways to a traditional tape test, employs a rigid cantilever fixed to the adhesive interface to be measured. By knowing the cantilever stiffness and measuring the load required to peel the cantilever, typical load-displacement curves are generated. The geometry of the cantilever peel test differs from the 90° tape test, as the delamination occurs at a very shallow angle ( $\approx 1^\circ$ ) and the rigid cantilever is only deformed elastically, as compared to the mechanical loss due to bending and plastic deformation of the peeling tape. A custom cantilever peel apparatus was built based on the descriptions of experimental procedures by Chaudhury and coworkers.<sup>2</sup>

The cantilever peel testing apparatus is shown schematically in Figure 1. The adhesion specimen is an elastic film which is strongly bonded to a rigid substrate. Dynamic delamination experiments were performed at a constant displacement rate where the flexible plate is raised at a controlled speed. An optical microscope with video recording capability was used for visual characterization of the delamination event, including the morphology of the crack front upon initiation and during crack growth.

**Materials.** Poly(ethylene glycol) dimethacrylate (molar mass = 890 g/mol, PEGDMA), poly(ethylene glycol) methyl ether methacrylate (molar mass = 420 g/mol, PEGMA), and adhesion promoter tetraethylarrium disulfide (TED) were obtained from Aldrich.<sup>3</sup> The photoinitiator

2,2-dimethoxyphenyl acetophenone (DMPA) was purchased from Ciba. All chemicals were used as supplied.

**Variable Moduli Substrates.** To create polymer networks with variations in moduli, the ratio of the crosslinking dimethacrylate (PEGDMA) and linear methacrylate (PEGMA) was varied. The high modulus PEG methacrylate network contained 50/50 % PEGMA/PEGDMA by mass, while the low modulus network contains 80/20 % PEGMA/PEGDMA by mass. DMPA (0.5 % by mass) and TED (0.5 % by mass) were added to each formulation prior to polymerization. To create a sample with buried high modulus features, the high modulus formulation was filled between two glass substrates with a spacer ranging between 150  $\mu\text{m}$  to 900  $\mu\text{m}$ . A lithographic mask was placed on top of the sample and photocured to polymerize selected regions of the sample to the glass substrate. Regions which were not polymerized remained uncrosslinked (monomer) and could be removed with hexanes. The cleaned substrate was then capped with a second sacrificial substrate using a 1 mm spacer. The created void space was filled with the low modulus monomer formulation and photopolymerized. In all cases, photopolymerization was conducted using a Novacure 2000 ultraviolet mercury arc lamp (EXFO, Mississauga, ON) at a light intensity of 10.0  $\text{mW}/\text{cm}^2$  for 600 s. Once polymerized, the polymer film was delaminated from the sacrificial substrate, presenting a continuous low modulus PEG surface to which the cantilever was affixed.

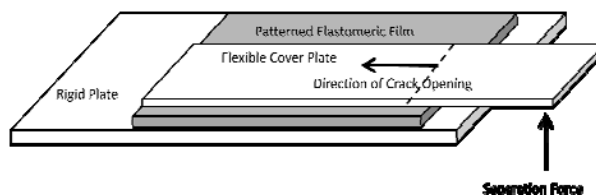


Figure 1. Schematic of the cantilever plate experiment.

## Results and Discussion

Elastomer specimens comprised of high modulus patterned chip encased in a low modulus matrix material were measured with cantilever peel test. The depth at which the patterned surfaces were buried in the low modulus matrix was varied between 0  $\mu\text{m}$  and 900  $\mu\text{m}$ . At 900  $\mu\text{m}$  the high modulus pattern exhibited no measurable effect on the adhesion performance of the elastomer and the material behaved equivalently to the neat low-modulus elastomer surfaces. Patterns buried at shallower depths showed similar characteristics to simple patterned surfaces with dis-

rupted initiation-propagation events, thereby creating stick-slip behavior. However, the regions of low modulus elastomer that were the most confined (i.e. buried at the most shallow depth) exhibited the greatest deviation in fracture energy required to separate the cantilever. Homogenous elastomer surfaces were used as a reference for adhesive performance along with an unburied patterned surface.

Previously we have applied the cantilever peel test to patterned surfaces to characterize initiation and propagation events during delamination. It has been observed that the crack front is affected by the material in the immediate neighborhood beyond the actual crack. This is most clearly demonstrated in the fracture behavior of asymmetrical or directionally textured surfaces where the energy to fracture is greatly affected by the area in front of the fracture contact line and the length of contact line alone does not necessarily predict fracture behavior.

Similarly theoretical models have been applied to demonstrate the effect of spatially varied modulus on peeling fracture.<sup>4</sup> Again, there is evidence that the fracture events are affected by the properties of a neighborhood of material larger than the fracture contact line. Here, we experimentally demonstrate that this material effect is extended through the depth of the film and not confined to in-plane patterns or features.

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### **References**

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2. A. Ghatak, and M.K. Chaudhury, *Langmuir*, 2003. **19**: p. 2621.
3. 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.
4. A. Ghatak, *Physical Review E*, 2010, **81**, pp. 021603.