Interfacial Adhesion of Viscoelastic Coatings on Medical Stents
A Quantitative Energy-Based Approach for Interfacial Fracture Toughness Determination

Introduction
The interfacial adhesion of film/substrate systems is of paramount importance to medical stent product performance and reliability. The newest generation of stents, the drug eluting stents, utilize a soft polymeric coating that contains a pharmacologic agent that helps prevent restenosis (reblocking) and thrombosis (clotting) within the artery. These polymeric coatings are typically only a few micrometers in thickness and geometrically complex scaffolding structure. These strict design constraints make typical micro and macro scale interfacial adhesion testing techniques impossible to perform on the actual product and requires the use of indirect measurement techniques. This application note will introduce a new method to quantitatively determine the interfacial fracture toughness of similar film on substrate systems based upon a scratch induced delamination energy approach, where only the interfacial pretreatment conditions differ.

Experimental Method & Results
Generic design stents laser cut from 304 stainless steel tubes (130 µm wall thickness) were coated with ~2 µm of parylene C using a vacuum deposition method at room temperature. An organosilane surface pretreatment was applied to the bare stent prior to coating deposition to enhance the interfacial adhesion. Scratch tests were performed using a TriboIndenter® nanomechanical testing system equipped with a 3D OmniProbe™ head and a 5 µm conospherical scratch probe.

The scratch load function consisted of applying various constant normal loads ranging from 20-35 mN over a lateral displacement of 500 µm. The normal force, lateral force, normal displacement, and lateral displacement were continuously recorded as a function of time. The chosen scratch function produced a periodic delamination pattern that can be seen in both the lateral force (LF) vs. lateral displacement (LD) data and the optical micrograph in Figure 2. As can be seen in Figure 2, there is a clear correlation between the measured force and the metrology of the delamination pattern. Energy values were calculated from the first slope change in the LF-LD data, corresponding to the onset of delamination, until the maximum lateral force is obtained and the probe raises over the coating pile-up and immediately begins a new delamination cycle. Energy values were numerically calculated by integrating portions of the lateral force vs. lateral displacement curve corresponding to each delaminated region via Equation 1, where \( F_{\text{max}} \) is the local minimum lateral force corresponding to the start of interfacial failure, \( F_i \) is the lateral force at any given displacement, and \( x_i \) is the corresponding lateral displacement. This integration of the lateral force vs. lateral displacement plot can ultimately be used to determine the shear energy required to remove a unit area of coating.

Figure 1: Optical micrograph of a medical stent coated with ~2 µm of parylene C.

Figure 2: Lateral force data corresponding to a cyclic film delamination and the corresponding optical micrograph of the delamination pattern.
The energy per unit area is simply obtained from dividing the energy required to delaminate one whole region by the area of that region, where the area of delamination was determined using an optical microscope equipped with an area measurement feature.

Previously performed in-house research has shown that scratch speeds ranging from 1.7 µm/sec to 25 µm/sec and probe geometries ranging from a 5-20 µm radius of curvature have no effect on the calculated interfacial fracture toughness values. However, the chosen normal loads have been shown to impact calculated adhesion values due to energy lost to deforming the substrate. Figure 3 shows optical micrographs or cyclic delamination patterns resulting from 20-35 mN constant force scratches. Figure 4 shows the raw calculated energy per unit area data as a function of applied normal load.

There is a clear increasing relationship between the size of the produced delaminated area and the calculated interfacial fracture toughness as a function of increasing normal load. Inspection of the scratch track after testing shows varying degrees of substrate deformation, which needs to be isolated from the energy required to deform and delaminate the coating. Figure 5 shows an optical DIC image of one delamination region with substantial substrate deformation. The degree of substrate deformation decreases during the course of each delamination cycle due to the probe being increasingly supported by the accumulating coating as the scratch process progresses.

The energy lost to substrate deformation can be accounted for by performing a series of ramped force scratches on an uncoated region of substrate material and correlating the measured energy to the width of the surface scratch and normalizing by the length of the residual scratch impression. Subtracting the substrate deformation energy from the total measured energy produces similar interfacial fracture toughness values, regardless of utilized load and can be seen in Figure 6.

Conclusion

A new energy-based method has been proposed to quantitatively assess the interfacial adhesion of soft films on compliant substrates with complex geometries. The method utilizes a scratching technique to determine energy required to delaminate a unit of area of coating while taking into account energy lost to substrate deformation.