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Adhesion and cohesion in structures containing suspended microscopic polymeric films

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ABSTRACT

This paper presents a novel technique for the characterization of adhesion and cohesion in suspended micro-scale polymeric films. The technique involves push-out testing with probes that are fabricated using focused ion beam techniques. The underlying stresses associated with different probe tip sizes were computed using a finite element model. The critical force for failure of the film substrate interface is used to evaluate adhesion, while the critical force for penetration of the film determines cohesion. When testing a standard material, polycarbonate, a shear strength of approximately 70 MPa was calculated using the Mohr–Coulomb theory. This value was shown to be in agreement with the results in the literature. The technique was also applied to the measurement of adhesion and cohesion in a model drug-eluting stent (the Nevo™ Sirolimus Eluting Coronary Stent) containing suspended microscopic polymeric films in metallic Co–Cr alloy reservoirs. The cohesive strength of the formulation was found to be comparable with that of plastics such as those produced by reaction injection molding and high-density polyethylene.

1. Introduction

In the rapidly expanding fields of medical devices and microelectronics thin polymeric films have enhanced the properties of the systems they coat [1]. For example, the results obtained from prior work suggest that in cases where formulations of drugs and polymers have been applied to stents the resulting drug-eluting stents result in reduced restenosis, the re-narrowing of treated arteries, over their metallic counterparts [1]. The adhesion of such films to their substrates has been the subject of several studies [2–9].

Nano-mechanical tests have been developed to gain an insight into the adhesion and the fundamental mechanical properties of thin films [2–6]. In these tests a stylus first comes into contact with a sample, which is then indented to shallow nano-scale depths. In the nanoindentation test a normal force is applied to the tip and its displacement is recorded [2]. A stress is induced in the film surrounding the indenter that can initiate and propagate interfacial cracks.

Single/multiple indents (as in ISO method 14577) have also been used to measure hardness, the Young's modulus, and interfacial fracture toughness of thin films, thick coatings and bulk materials [3–6]. The indentation interfacial toughness, a direct measure of adhesion, can be estimated by analyzing the indented area. For example, a nanoindentation method was used to evaluate the adhesion strength of poly(N-isopropylacrylamide) co-polymers on nitinol wires [5]. The interfacial fracture toughness G varied from 0.1 to 0.3 J m^{-2}, depending on the surface roughness of the film.

The nanoscratch test consists of application of vertical and lateral forces to the tip [3,4]. Using either constant or progressive forces the critical load that provokes coating detachment can be measured. This measurement is then used to evaluate scratch hardness and scratch adhesion of the thin films. For example, to evaluate the relative adhesion of the coatings of three commercial drug-eluting stents to their corresponding substrates the forces to induce delamination between the coating and the stent were measured by a nanoscratch method and were found to be comparable [6].

In previous works [7–9] we have used a combination of models and experiments to study the adhesion between soft films and hard substrates. Atomic force microscopy (AFM) [7] and interfacial fracture mechanics techniques [8,9] were used to measure the adhesion between different interfaces within and between the coated substrates. A combination of adhesion theory and interfacial fracture mechanics models was then used to obtain adhesion

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energy measurements for a wide range of interfaces between hard and soft materials with different chemistries [7].

An orthogonal interfacial fracture mechanics method [8,9] has also been used to corroborate the AFM measurements of adhesion. In this method layers of the film were independently applied to metallic disks. These disks were sandwiched to form Brazil nut sandwich specimens that mimic the chemistries of the films on the stents. These specimens were deformed continuously until interfacial failure was induced from notches that were oriented at different angles to induce mixed modes between pure mode I and pure mode II. Hence, using the Cypher® Sirolimus Eluting Coronary Stent as an example [9], the adhesion energy of every interface of the coating, consisting of a Parylene C primer layer and a drug-eluting layer of sirolimus, poly(*n*-butyl methacrylate) and poly(ethylene-co-vinyl acetate) on 316L stainless steel was quantified and verified.

Although the above methods provide ways of measuring the adhesion between thin films and conforming substrates, there are currently no methods for measuring the adhesion of a film that has limited contact with the substrate, i.e. a suspended film. For example, in the case of the Nevo™ Sirolimus Eluting Coronary Stent (NSES) the formulation is suspended within several hundred reservoirs (length 120 μm × width 80 μm × depth 100 μm) that are filled with a formulation of sirolimus and the degradable polymer *poly(lactic-co-glycolic acid)* (PLGA) (Fig. 1). A mixture of sirolimus and PLGA is dissolved in solvent. The formulation is introduced into the reservoirs by a nanojet spraying method. After solvent evaporation the film remains suspended in the reservoir. The stent is fabricated from an L605 (Co–Cr) alloy. Hence, unlike stents with conformal coatings, the NSES contains formulation inlays within the stent reservoirs. AFM and nanoscratch styli cannot normally measure adhesion to the steep walls or overhangs. There is, therefore, a need to develop a novel technique for the measurement of adhesion between the formulation and the L605 alloy substrates and/or cohesive failure within the formulation layer.

The objective of this paper is to present a new method to measure the adhesive and cohesive strengths of suspended polymeric films. Inspired by ASTM Standard Test Method D732 [10], the technique involves the use of a micron-scale probe in the application of loads to suspended polymeric films that are mounted within a customized micro-tester. After the measurement of critical loads on a standard reference material, polycarbonate, the shear strength of the standard material is then calculated and compared with prior measurements of the mechanical properties of thin films. When used to evaluate NSES probes with small cross-sectional areas, relative to the cross-sections of the suspended polymeric films, are shown to result in cohesive failure, while probes with larger cross-sectional areas result in adhesive failure between the formulation films and the Co–Cr substrate. The measured adhesive and cohesive strengths are compared with measurements obtained in control experiments.

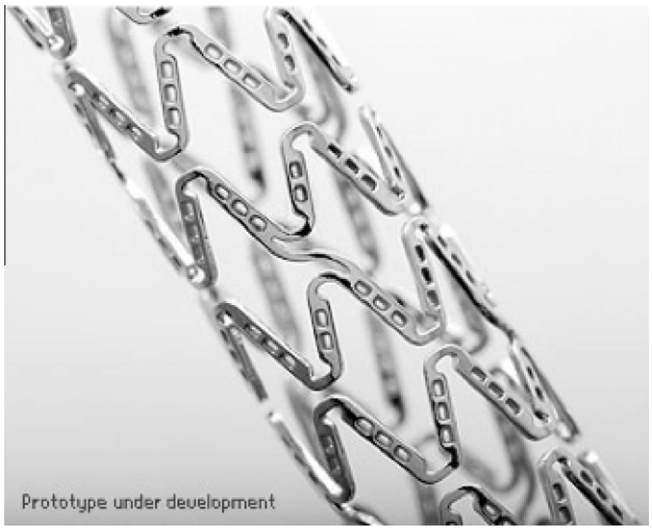

Fig. 1. Optical microscopy image of the NSES.

2. Experimental methods

2.1. Polymeric film adhesion and cohesion strengths testing

A schematic of the suspended film adhesion and cohesion strengths testing system is presented in Fig. 2. It consists of an actuator that is driven electronically by a wave generator to apply loads to the formulation film in the stent system (Fig. 1). The sample was clamped to a mechanical stage that was mounted on an anti-vibration table. A wave generator was used to generate the desired waveforms to input in a piezo-transducer (PZT) controller. The signals were amplified and used to drive the PZT. The loads from the PZT controller were applied in series to a tungsten probe (Fig. 2) (AutoProbe™ 300, Omniprobe, Dallas, TX) with a tip geometry that was micro-machined using an FEI Strata 235 dual beam focused ion beam (FIB) workstation. The loads were transduced through a 50 g load cell (Model 530, Coopers Instruments, Warrenton, VA) that was connected directly to a computer. In this way load data were acquired continuously throughout the measurements.

In an effort to immobilize the samples during testing these were clamped to a specially designed and machined fixture that was mounted on an *x*–*y* mechanical stage, as shown in Fig. 2. The clamping fixture system consisted of four layers. The bottom layer was a poly(methyl methacrylate) (PMMA) substrate, while the middle two layers were stainless steel sheets with identical grooved geometries. The top layer consisted of a thicker stainless steel sheet with a rectangular hole of the same size as the groove area of the middle two. The sample was sandwiched between the middle two layers. All four sheets were clamped with four cap screws and bolts along the length and width of the substrate.

To facilitate in situ imaging two digital Proscope HR™ (Bodelin Technologies, Lake Oswego, OR) microscopes were oriented perpendicularly to each other. The positioning of the probe (relative to the inlay) was achieved by aligning the *x*–*y* mechanical stage during in situ imaging. A photograph of the digital microscopes and the loading/mounting fixtures is presented in Fig. 2. These were used to obtain videos during push-out testing of the suspended polymeric films. The local curvatures of the films around the probe tip upon application of penetration forces were estimated from the video recordings.

The suspended film adhesion and cohesion strengths tests were conducted on NSES samples (Fig. 1) provided by Cordis Corporation. The specimens were first expanded to separate the stent from its delivery catheter. They were then cut, flattened, and inserted into the test fixture immediately after opening the package. The flattened specimens were then subjected to testing in air within 3 h of exposure to the laboratory environment. The laboratory air had a relative humidity of 38–55% and a temperature of 20–25 °C. The loading was carried out under displacement control at a constant rate of 40 μm s^{-1}.

NSES samples that were subjected to the adhesion/cohesion tests were analyzed in a Zeiss EVO scanning electron microscope (Carl Zeiss SMT Inc., Peabody, MA). Scanning electron microscopy (SEM) micrographs were obtained for both adhesive failure and cohesive failure, while energy dispersive spectroscopy (EDS)