Effects of He^{++} ion irradiation on Adhesion of Polymer Micro-structure Based Dry Adhesives

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June 21, 2010

Abstract

Irradiation of polymer based gecko-like synthetic adhesives (GSAs) using an accelerated beam of He^{++} ions has been performed. This irradiation simulates large α radiation doses that the GSAs may experience if deployed on a robotic platform in some radiological environments. After irradiation, the adhesive samples were tested for adhesion on a three-axis adhesion testing stage and were examined via scanning electron microscope. The GSA samples showed significant changes in surface morphology at high radiation doses. Additionally, radiation doses larger then 750kGy resulted in a significant deterioration of the adhesive performance. Eventually, the adhesive samples lost all ability to generate frictional adhesion. Such results allow us to make quantitative statements about the applicability of GSAs for robotic applications in nuclear environments.

1 Introduction

Biologically inspired directional dry adhesives have become a topic of significant interest in the robotics community. These adhesives have proven to be effective on a growing variety of surfaces, including those with surface roughnesses on widely ranging length scales. Many adhesives consist of sheets of elastomeric polymers with micro-scale surface features formed via molding processes [1], [2]. Others have utilized single- and multi-walled carbon nano-tubes produced on silicon wafers using additive methods such as chemical vapor deposition [3]. The adhesives discussed in this paper consist of a silicone elastomer with asymmetric micro-features and are considered *directional* adhesives, i.e. they generate maximum adhesion when loaded in a preferred shear direction. Additionally, they can be considered *controllable* adhesives because they produce virtually no adhesion in the absence of a shear load [1].

The Los Alamos National Laboratory has shown recent interest in utilizing these adhesives in robotic applications in nuclear environments such as gloveboxes. These airtight stainless steel boxes protect workers from contamination while allowing them to manipulate nuclear material by reaching through ports in the box containing sealed rubber gloves. Glove ports allow workers to access most of the glovebox without undue effort. However, some areas are extremely difficult, if not impossible, to reach. This characteristic makes a number of common tasks such as cleaning and leak testing very difficult. Climbing robots represent a potential solution to this problem. A small, climbing robotic platform would be able to reach and perform maintenance tasks in areas where workers cannot. Robotically assisted maintenance has a number of advantages over current practices including reduced ergonomic stress on workers due

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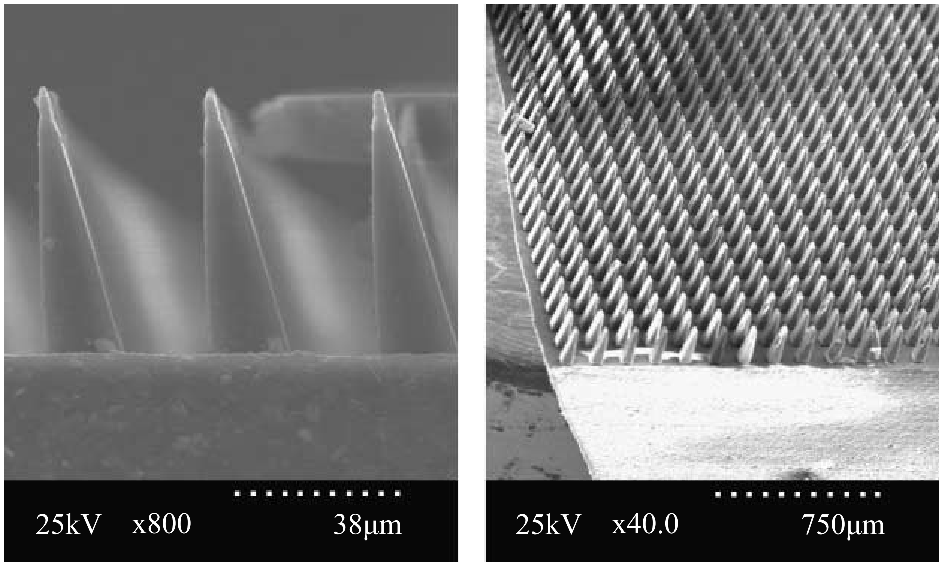

Figure 1: SEM Images of the micro-structure adhesive. *Left:* A side view of the micro-structure. *Right:* A larger view of the patterning of the micro-structures on the surface.

to excessive reaching, reduced radiation dose taken by workers, and reduced operational cost.

Ideally, an adhesive for such a platform would have excellent resistance to alpha and gamma radiation. Having stable adhesive performance at doses in the many tens or hundreds of kGy would allow for very long lifetimes given the radiation levels seen in nuclear facilities. Unfortunately, there is limited information available on how these adhesives will react in the presence of radiation doses. Radiation induced molecular and mechanical effects [4],[5], and volatile evolution [6], [7], [8], of the bulk silicone have been discussed in the literature. While knowledge of the changes in the chemical and mechanical properties of these materials may enable us to make general predictions about how the adhesives will perform, further experimentation is necessary in order to determine the precise functional relationship between adhesion and radiation dose.

In this paper, we focus solely on simulated α radiation (in the form of accelerated He^{++} ions) and its effect on the durability of polydimethlysiloxane (PDMS) elastomer based adhesives. The effect of varying radiation dose on the adhesive performance, surface morphology, and surface energy are discussed. Of particular interest is the simulated α dose after which the adhesives can no longer generate directional adhesion.

2 Experiments

2.1 Material Preparation

PDMS adhesive pads were prepared using a Dow Corning Sylgard 170 elastomer kit and a mold patterned via photolithography methods. A detailed discussion of the mold preparation can be found in [1]. The Sylgard 170 A and B components were mixed vigorously, vacuum degassed for 1-2 minutes, and poured under vacuum onto the mold which was then spun to produce a thin film of the bulk, uncured elastomer. The elastomer and mold were then placed in an oven at 85°C for 15 minutes. The adhesive was then manually peeled from the mold and cut into 1 cm^2 squares for testing. Figure 1 is a SEM of the micro-patterned surface of the adhesive.

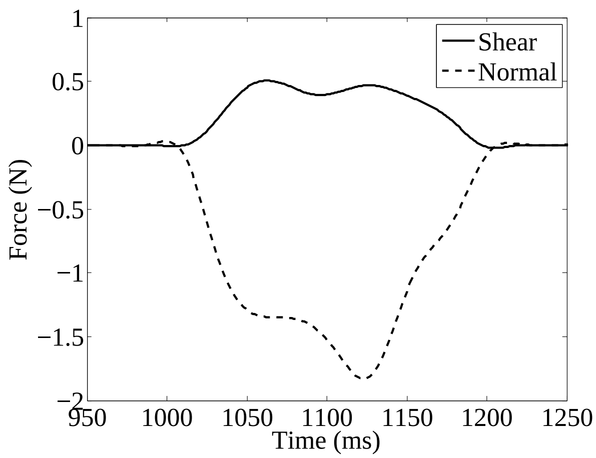

Figure 2: Load-Pull Data from a single run of an un-irradiated adhesive sample. Preload is generated by approaching the substrate at 45° to a depth of 80μm, and can be seen as the small positive normal force (dashed line) at approximately 1s. The sample is then loaded in shear (solid line) and the adhesion generated by the sample is represented by the negative normal force.

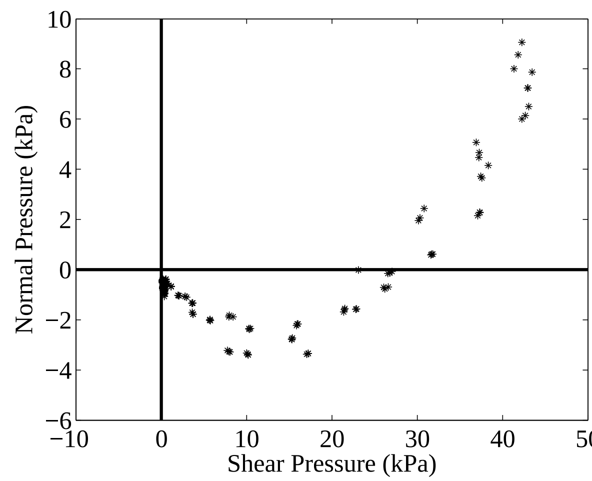

Figure 3: Limit curve from a single battery of LP tests on an un-irradiated adhesive sample. Maximum adhesive pressure achieved is approximately 3.7kPa. Each point indicates adhesive failure through slipping or detachment from the surface. Note the adherence to Autumn's frictional adhesion model in which adhesion is generated only in the presence of shear loading.

2.2 Radiation

The irradiation took place in the Ion Beam Materials Laboratory at the Los Alamos National Laboratory. The samples were attached to a sample fixture with carbon tape and placed on a sample goniometer inside the irradiation chamber which was evacuated to approximately 10^{-6} Torr. He^{++} beam at 2.5MeV was produced by an NEC Alphatross source on the 3MV Tandem accelerator to simulate intermediate energy alpha particles emitted from a purified plutonium source and associated daughter products. The beam current on target was 20-30nA and dosage was calculated by integrating the current on the sample using a 1000C Brookhaven Instruments Corporation current integrator. The sample and sample holder were biased to +150V to allow accurate current integration throughout the irradiations. A homogeneous dose across the entire sample surface was performed by rastering the He^{++} beam. The irradiation time took between 1-20 minutes of exposure, depending on dose.

2.3 Adhesion Testing

Data were collected on an experimental setup capable of moving the adhesive samples into contact with a glass substrate along a specified trajectory and loading the adhesive in normal and tangential directions. The experimental setup consists of a three-axis positioning gantry (Velmex, MAXY4009W2-S4 and MA2506B-S2.5) capable of 10μm positioning resolution in the tangential direction and 1μm positioning resolution in the normal direction. The gantry is responsible for moving the substrate in and out of contact with the adhesive, which is mounted on a stationary, six-axis force/torque transducer (ATI Industrial Automation, Gamma Transducer SI-32-2.5). The transducer is mounted on a two-axis (roll and tilt) goniometer (Newport, GON40U/L) to allow the adhesive and substrate to be precisely aligned. Tests were preformed by bringing the adhesive into contact with the substrate along a 45° angled trajectory to a certain pre-load depth, defined as the distance past which the tips of the micro-structure initially make

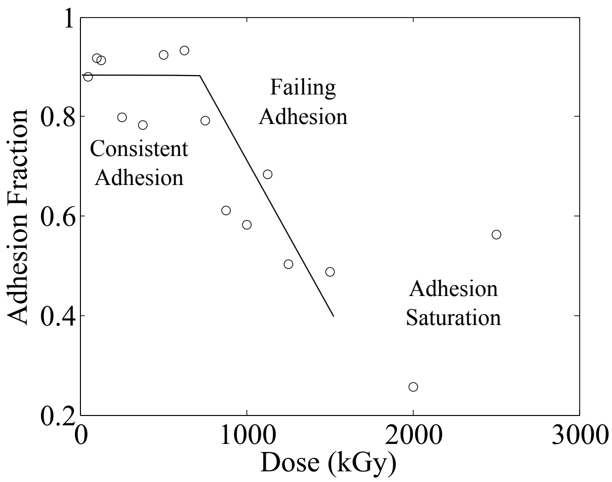

Figure 4: The maximum adhesive pressure of samples with doses ranging from 0-2500kGy as a fraction of their un-irradiated performance.

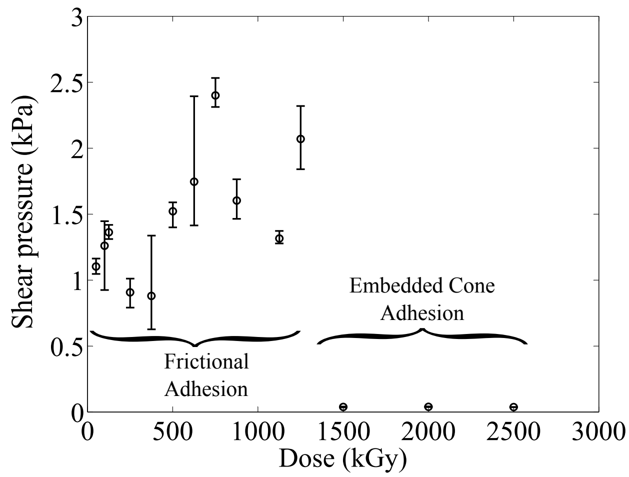

Figure 5: The shear pressure at which samples produce maximum adhesion pressure for various doses shows the transition between adhesion models. Data points are average values with error bars denoting the minimum and maximum measured values. It can be seen that at doses below 1500kGy the samples produce maximum adhesion in the presence of a significant shear load, similar to the the Autumn frictional adhesion model. At and above a dose of 1500kGy, the samples very consistently produce their maximum adhesion in the presence of virtually no shear loading.

contact with the substrate. Once the sample was at the appropriate pre-load depth it was loaded in shear and then pulled away at a specified angle. Force data were recorded and filtered by a low-pass, third-order Butterworth filter with $f_c = 20$Hz. Such tests are referred to as Load-Pull (LP) tests.

Figure 2 shows the results of a single LP test performed on an un-irradiated sample with a pre-load depth of 80μm and a pull off angle of 10°. The normal force (dashed line) can be seen to have a small positive peak at approximately 1s. This is the pre-load phase of the trajectory. Subsequently, as shear load (solid line) is applied, the normal force drops below zero, indicating that it is producing adhesion. Note that the sample produces adhesion only in the presence of shear loading, behavior consistent with the frictional adhesive model proposed by Autumn, et. al [9]. To obtain the adhesion *limit curve* [10], a battery of LP tests are performed for pre-load depths ranging from 30-80μm in 10μm increments and pull-off angles ranging from 0-90° (with respect to the vertical) in 10° increments. This curve, which can be seen in Figure 3, shows the limit of the adhesive's performance for a given shear/adhesion load. If a load lies above the curve in force space, the adhesive will remain attached. Any load below the curve in force space will cause the adhesive to detach from the surface.

Because physical differences between individual samples as well as minute changes in sample alignment between batteries may cause variation in adhesive performance, an adhesion baseline was established with each sample prior to irradiation. Each sample was put through three separate batteries of LP tests to determine the maximum adhesive pressure it was capable of generating. Variation in adhesion generation due to misalignment from mounting and un-mounting of the sample over multiple runs was small (<5%) and results from the three batteries were averaged to produce a reasonable baseline for maximum adhesive pressure. After irradiation, samples are then put through the same adhesion testing procedure conducted prior to irradiation.

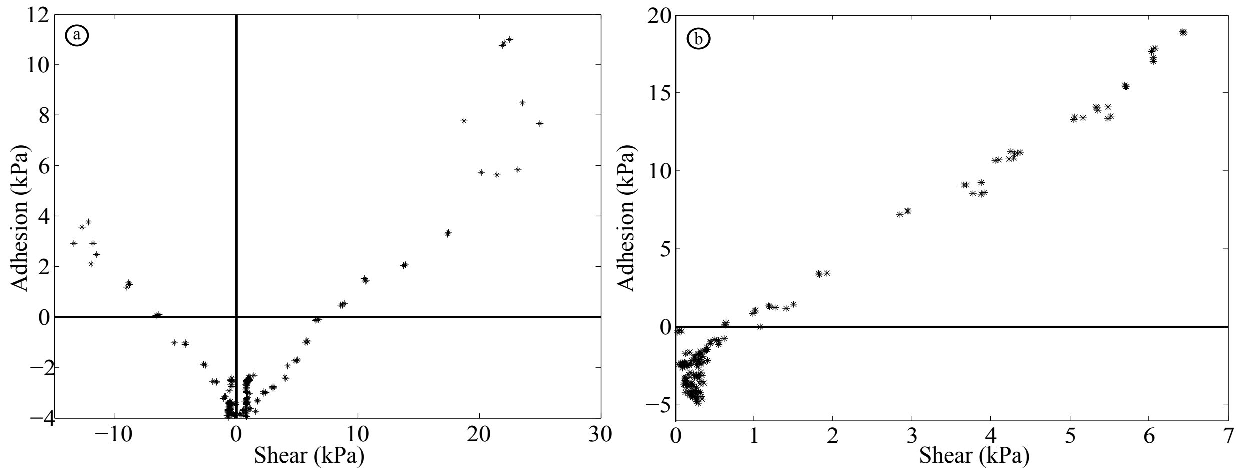

Figure 6: *Left:* The limit curve produced by a flat sample of PDMS. Note the resemblance to the JKR or embedded cone model. *Right:* A limit curve produced by a sample of directional adhesive irradiated with a dose of 2500kGy. At this dose, all ability to produce directional adhesion has been lost and the sample behaves like a flat piece of PDMS.

3 Results and Discussion

3.1 Adhesion

Post-irradiation testing focused on the ratio of post- to pre-irradiation maximum adhesion production and the results are summarized in Figure 4. Samples irradiated with 50-750kGy maintain the large majority (80-95%) of their adhesion generation capability. As radiation doses continue past 750kGy the samples begin to lose increasing amounts of adhesion, continuing until a dose of 1500kGy. At and above 1500kGy adhesion begins to saturate, i.e. the samples produce a constant amount of adhesion, approximately 1kPa, regardless of increased dose. In this region, ratios of the post-irradiation adhesion to pre-irradiation adhesion become less meaningful due to the fact that the post-irradiation adhesion values have saturated.

In the saturation region, samples begin to behave as flat elastomeric adhesives. Their limit curves resemble the JKR model described in [11] for a rounded elastomeric material contacting a flat surface or the simpler "embedded cone" extension of Coulomb friction originally proposed to account for the effects of adhesion in elastic materials with friction [12, 13].

The transition from frictional adhesion to embedded cone behavior can be seen when examining the shear pressure at which the maximum adhesion is generated. Figure 5 shows that the samples follow the frictional adhesion model, i.e. generating maximum adhesion under shear loading, up until a dose of 1250kGy. At 1500kGy and larger doses, maximum adhesion is produced in the presence of close to zero shear load, a characteristic of the JKR or embedded cone models.

In these models, adhesive capacity is greatest with zero shear load and decays as shear load is applied in either direction. A similar limit curve, produced by conducting the same adhesion testing on a flat piece of PDMS, can be seen in Figure 6a. As doses increase past 1250kGy, the limit curves produced by the samples tend increasingly toward the embedded cone shape. Figure 6b shows the limit curve from a sample irradiated with 2500kGy. The resemblance of this curve to the embedded cone model shows the extent of the radiation induced damage as the samples have lost all ability to generate directional adhesion, producing curves similar to that of flat PDMS.

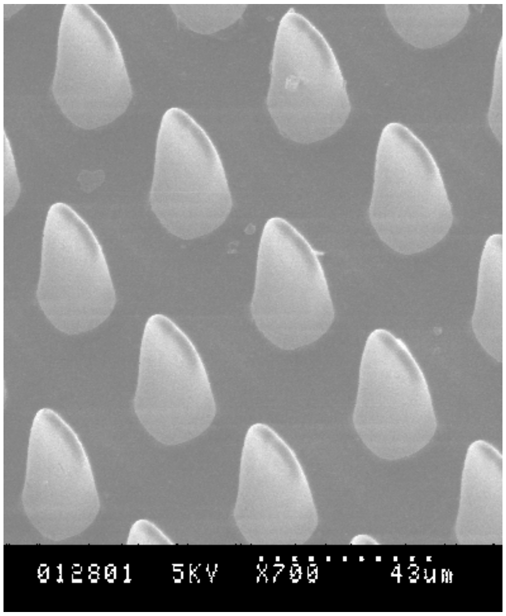

Figure 7: SEM of a sample irradiated with 1.125MGy. No obvious damage is visible in the wedges or the backing layer at this dose. Adhesion generation, however, is approximately 50 percent of the pre-irradiation value.

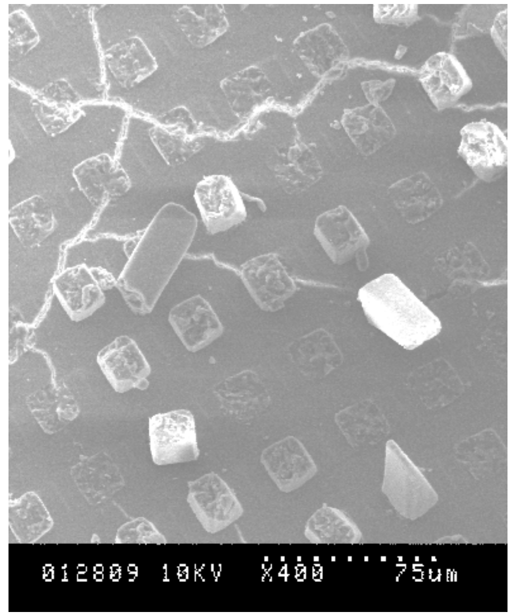

Figure 8: SEM of a sample irradiated with 2.5MGy. Widespread brittle cracking of the micro-structure is present along with significant cracking in the base layer of PDMS. Samples irradiated with this dose no longer conform to the frictional adhesion model and demonstrate embedded cone style adhesion when tested.

3.2 Surface Morphology and Surface Energy

Surface properties of the irradiated samples were examined via SEM. The surface morphology of the adhesive micro-structures for various doses is shown in Figures 7 and 8. Figure 7 shows the resulting surface morphology for doses up to 1250kGy. It can be seen that there is no obvious surface damage. However, further irradiation begins to produce more noticeable changes. At doses above 2MGy brittle cracking becomes evident in the backing layer of the adhesive. As doses increase, the cracking becomes more significant. Figure 8 is an SEM of a sample irradiated with a dose of 2.5MGy. The fractures are present across the entire sample, some of which are large enough to be seen with the naked eye. In addition, the embrittling effect of high radiation dose is evident given the widespread brittle cracking of the micro-structure.

To gain insight on possible changes in surface energy induced by the irradiation, water droplet experiments were performed. Samples of flat PDMS were irradiated at the same doses as the micro-structure adhesives. The samples were then tested with a Surface Electro Optics Phoenix 300 Contact angle analyzer to examine the contact angle of a droplet of water with the flat PDMS. To account for any possible localized irregularities, three experiments were conducted per sample on different areas of the sample. The averaged results for contact angle versus dose are shown in Figure 9.

Contact angles for un-irradiated PDMS samples begin at close to 94° and gradually increase with increasing radiation dose. The rate of increase begins to slow after 750kGy and the contact angle values begin to stabilize between 98°-99°. Increasing sample hydrophobicity indicates that the surface energy of the irradiated PDMS is decreasing. Assuming contact

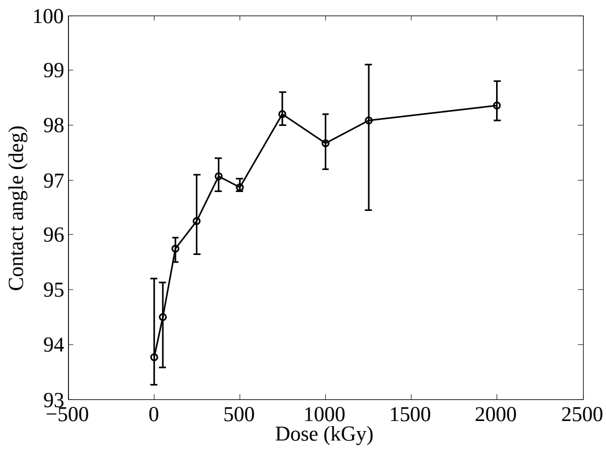

Figure 9: Water droplet contact angles for samples of flat PDMS irradiated with doses up to 2MGy. The increase in contact angle with increasing dose suggest a progressive decrease in the surface energy of the PDMS due to irradiation.

angle and surface energy are roughly correlated, this data is in agreement with the adhesion experiments. A decrease and subsequent stabilization of surface energy would result in a proportional decrease and stabilization of adhesion, much like the trend seen in the experimental adhesion results.

3.3 Discussion

Evaluating the appropriateness of the adhesive for radiological environments requires an understanding of the typical doses seen in these environments. A hypothetical and quite conservative usage scenario might involve deployment of the adhesives in a radiological environment until they have absorbed a dose of approximately 750kGy, the dose at which they first begin to deviate significantly from their un-irradiated behavior. The highest radiation environment defined by the Los Alamos National Laboratory and the DOE is a *very high radiation area*, an environment in which a dose of over 500 rad an hour would be absorbed. At a conversion rate of 1 rad to 10 mGy this dose rate is equivalent to 5Gy per hour. In the given usage scenario, we will assume a dose of 10Gy per hour for a more conservative estimate. At this rate, the adhesive would not need to be replaced for greater than eight and a half years. This factor, combined with the high re-usability of the adhesives shown in [1], make the adhesives an attractive option for radiological applications involving high α radiation levels.

4 Conclusions

Polymer based directional dry adhesive were irradiated with He^{++} ions to simulate the effects of high α radiation dose. The adhesives have proved to be robust in the presence of significant amounts of radiation, making them a competitive candidate for applications in nuclear and radiological environments. Samples were shown to maintain a large majority of their adhesive capabilities at doses as high as 750kGy. Doses within the 750-1500kGy range cause the adhesives to begin to lose their ability to generate directional adhesion. Eventually, at a dose of 1500kGy, the adhesives lose all ability to generate directional adhesion and behave like a pressure sensitive adhesive. At this point, adhesion generation ability has saturated to a value of around 1kPa. SEM examination of the surface morphology of the adhesives showed significant embrittlement and cracking at and above the 2MGy dose. Water droplet contact angle testing suggests that irradiation has altered the surface chemistry enough to produce changes in surface energy, a likely cause of adhesive performance degradation. Given the robustness shown by the material and predicted long service life, these adhesives present a promising opportunity for new applications in high radiation environments.

Additional investigation is necessary to determine the effects of different types of ionizing radiation on polymer based adhesives. Future work will involve determining the effects of high-energy photons (in the X- and gamma ray spectrum) on adhesion for applications with different types of special nuclear material as well as space applications.

Acknowledgement 1 *The authors would like to thank the staff at the Ion Beam Materials Laboratory at Los Alamos National Laboratories, New Mex-*

ico, USA, and the Stanford Nanofabrication Facility, California, USA, for the use of their facilities.

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