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Assembly of Conductive Au Films on Poly(urethane urea) Elastomers Using a Solution-Based Approach

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Conductive Au films were successfully assembled on poly(urethane urea) (PUU) films using a solution-based approach. This method does not require prior surface functionalization before the Au attachment. Immersion of the PUU film in a colloidal Au solution immobilizes the Au particles on the surface, and the growth increases with time. This attachment occurs via strong interactions of Au with the amine and amide groups in the polymer. Three different PUUs with hard segment contents of 20%, 30%, and 35% were studied. Growth of the films was monitored using UV−vis spectroscopy and scanning electron microscopy. Immersion in the gold solution for long times, or for shorter times with subsequent seeding, forms very conductive films. The resistivity of the films was $(7 \pm 1) \times 10^{-5}$ Ω·cm. Using this approach, PUUs can be used as adhesives for the attachment of gold to different surfaces. Since the PUUs are highly elastic materials, the effect of strain on the resistance was also studied. It was seen that the resistance increased as a function of the strain. This change in resistance was reversible and was recovered when the material was relaxed. Higher strains of >50% cause the conductive film to become completely insulating. However, it becomes conducting again as the film is relaxed. Such a switching behavior in the resistance has potential applications in sensors and electromechanical switches.

Introduction

Metallic nanoparticles have emerged as an area of considerable research in recent years.[1,2] These materials have properties that are between those of the bulk and a single atom and hence can be utilized advantageously in many applications. Some of these applications include catalysts,[3] fabrication of single-electron transistor devices,[4,5] optical sensing and imaging materials,[6] and biological sensor materials,[7] among others. Many efforts are being directed toward the controlled synthesis of nanoparticles of different sizes and shapes[8−11] and tuning their properties.[12−16] Colloidal particles have been extensively studied in solution, and more recently their properties on surfaces have also been investigated. Doron et al.[3] have used Au monolayers on indium−tin oxide surfaces to form substrates for assembling redox-active species. Brust et al.[17,18] have assembled Au films using dithiol linkers and have investigated the electronic and optical properties these films. Electrochemical properties of Au−dithiol films have been investigated by Lu et al.[19]

Au and Ag colloidal films have received considerable attention, especially in their use as substrates for surface plasmon resonance (SPR)[20] and for surface-enhanced Raman spectroscopy (SERS).[21,22] Natan and co-workers have investigated the solution-based assembly of Au and Ag colloids on substrates such as glass and silicon.[23,24] They have used

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two approaches to deposit colloidal films on the substrates. One is a seeding approach,[25,26] in which Au is reduced onto the particles already attached to the surface to increase coverage. The other involves the use of a bifunctional linker molecule, and multilayer films are built up by alternate immersion in the colloid solution and linker molecule solution.[27] In another approach, Murray and co-workers have utilized Au particles stabilized with organic molecules (monolayer-protected clusters) to deposit metal films on glass substrates.[28] The films were either assembled using a layer-by-layer method or drop-cast onto glass slides. Thermolysis of the materials at ∼300 °C gave adherent metal films. In a recent report, Prevo et al.[29] have demonstrated the assembly of Au films on glass and polystyrene substrates using convective assembly, which does not require any prior surface modification.

The strong attachment of colloidal particles on surfaces usually requires the presence of functionalities on the surface that have an affinity for the particle, such as $-SH$, $-NH_2$, or $-CN$ for Au and Ag particles. This is achieved by the deposition of silanes with these terminal functional groups, which act as a molecular adhesive. On substrates such as glass and silicon, the deposition of silanes is facilitated by the hydroxyl groups present on the surface. These in the presence of a little moisture can react with the silanes to form a covalent siloxane linkage. In previous reports, we have described methods for the fabrication of conductive Au films on flexible polymeric substrates.[30] In this case, the polymer surfaces have to be functionalized prior to silane deposition, and this was achieved by a plasma treatment. The ability to fabricate metal films on flexible polymeric substrates using solution-based methods, as opposed to conventional techniques such as sputtering or vacuum deposition, has a number of advantages. Conventional methods use expensive equipment and controlled conditions, which lead to increased costs of fabrication. Nanometer-scale control over properties is difficult to achieve. They also require the deposition of adhesion promoters such as Ti or Cr in the case of Au deposition, leading to problems including grain-boundary diffusion.[31,32]

In a recent study, Mangeney et al.[33] have reported that hydrophilic polyacrylamides end-capped with disulfides may be covalently attached to Au particles in solution to form stabilized polymer-coated particles. In another study, the surface of polybutadiene was modified by the addition of different sulfur-containing functional groups.[34] Evaporated Au and Cu films adhered better to the modified polymer films compared to the unmodified films. Au films were reported to adsorb better onto poly(vinylpyridine) (PVP) films compared to polystyrene (PS) films.[35] This was attributed to the stronger interaction of Au with PVP compared to PS. A recent study by Tarazona-Vasquez and Balbuena[36] has characterized the complexation of the metal atoms and ions to poly(amidoamine) (PAMAM) dendrimers using ab initio techniques. The binding energies of different metal atoms and ions to the core, amine, and amide binding sites were determined. The results were high negative binding energies of Au(III) (−872.9 and −827.0 kcal/mol for the amine/core and amide, respectively) and Au atom (−8.3 and 3.3 kcal/mol for the core/amine and amide, respectively) to the amine/core and amide sites. The primary coordination is to the amine N with a secondary coordination to the amide N. Both of these interactions produce a cooperative effect in binding the atom or ion to the dendrimer. An experimental study reported that the adhesion of Au onto Si substrates was significantly enhanced when a thin film of PAMAM dendrimer was coated onto Si.[37] These results suggest that Au can bind to the amine and amide groups in the PUU polymers also in a similar manner, without any surface functionalization for Au attachment.

In our previous studies, the polymeric substrates used were commercially available Kapton and polyethylene. Segmented polyurethanes (PUs) and poly(urethane urea)s (PUUs) are a class of polymeric materials that are widely used as high-performance elastomers, fibers, coatings, adhesives, and biomaterials.[38,39] The chemical composition of thermoplastic PUs and PUUs that consists of alternating soft and hard blocks gives researchers the flexibility to tune the mechanical and thermal properties of PUUs.[40] For example, the high performance of PUU elastomers is attributed to the microphase separation between the hard and soft blocks and the strong hydrogen-bonding interactions within urethane or urea hard blocks. In such segmented copolymers, polyether, polyester, or poly(dimethylsiloxane) oligomers that have low glass transition temperatures form the soft segment.

To investigate the attachment of Au on flexible substrates further, experiments were conducted on PUU films. In this study, the attachment and properties of Au films on PUU substrates have been examined. Conductive films of Au were deposited using the seeding method. The films were characterized by UV−vis spectroscopy and scanning electron microscopy (SEM). A significant advantage over the fabrication of Au films on other substrates is the elimination of the silane deposition step. Urea and urethane segments in the

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Table 1. Chemical Compositions of Linear PUU Elastomers

	soft segment		hard segment		
sample	PTMO M_n	amt (g)	HMDI amt (g)	Dytek A amt (g)	[HS] (%)
PUU-35	2000	65.00	26.87	8.13	35
PUU-28	2000	72.00	22.30	5.70	28
PUU-20	2900	80.00	16.08	3.92	20

PUU backbone act as the attachment points for the Au particle. Hence, the PUU film can be directly immersed in the Au solution without the deposition of any other functionalities. The mechanical behavior of the Au-coated films has also been studied. The electrical properties of the Au film as a function of strain were investigated, and the resistance of the film was observed to be a strong function of the strain.

Experimental Methods

Materials. For the synthesis of the Au nanoparticles, gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), chlorotrimethylsilane, hydroxylamine hydrochloride, and sodium citrate dihydrate were purchased from Aldrich. All the chemicals were used without further purification. For the synthesis of PUUs, bis(4-isocyanatohexyl)methane (HMDI; 99.5+%) was kindly donated by Bayer. Poly(tetramethylene oxide) oligomers (Tetrathane) with number average molecular weights (M_n) of 2000 (PTMO-2K) and 2900 (PTMO-2.9K) and 2-methyl-1,5-diaminopentane (Dytek-A) were kindly donated by Du Pont. The solvents HPLC-grade isopropyl alcohol (IPA; EM Science) and tetrahydrofuran (THF; Aldrich) were used as received.

Synthesis of PUU. Linear PUU elastomers were synthesized with three different hard segment contents, 35%, 28%, and 20%, which are denoted as PUU-35, PUU-28, and PUU-20 (Table 1). The hard segment content is reported as the weight percentage of urethane and urea groups in the composition, [HS] (%) = 100([HMDI] + [Dytek A])/([HMDI] + [Dytek A] + [PTMO]). A two-step methodology, prepolymer synthesis and chain extension, was used to synthesize PUU elastomers. The prepolymer, which consists of isocyanate-terminated PTMO, was synthesized via the reaction of excess HMDI with PTMO (PTMO-2K or PTMO-2.9k) at 80 °C, in the presence of 50 ppm dibutyltin dilaurate as catalyst. The hard segment content governed the molar ratio of HMDI to PTMO in the prepolymer synthesis. For the synthesis of PUU-35 and PUU-28, PTMO-2K was used. To achieve a lower hard segment content and synthesize PUU-20, PTMO-2.9K was used in the first step. Upon the synthesis of prepolymer, the reaction was cooled to room temperature and dissolved in THF to 20 wt % solution. A solution (10 wt %) of Dytek A, the chain extender, was prepared in an addition funnel, using an equal stoichiometric amount of amine to residual isocyanate in the prepolymer. The second step, chain extension, was completed upon the dropwise addition of Dytek A solution into the prepolymer solution over 2 h. A highly viscous, clear solution of the final product was obtained. Both the first and the second step reactions were followed by FT-IR spectroscopy.

Fabrication of PUU Films. The PUU films were solvent cast from THF/IPA (1:3) on nylon-6 or Teflon molds. The films were kept at ambient conditions for about 6−8 h and then heated at 60 °C in an oven for ~12 h or until a constant weight was achieved. The films on Teflon were removed easily by peeling them off. However, for the films cast on nylon this was difficult. Hence, the films were immersed in water for about 3−4 h to facilitate removal of the film. All films were ultrasonicated in water prior to Au deposition.

Fabrication of Au Films. The Au particles were synthesized using previously described methods.[30] The size of the particles was ~18 nm as measured by transmission electron microscopy. After ultrasonication in water, the solvent-cast PUU films were immersed in the colloidal Au solution for 6−24 h and rinsed thoroughly in Nanopure water (18 MΩ from a Barnstead Nanopure water purifier). Further gold was reduced onto the attached gold by suspending the gold-coated samples in a 200 mL solution of 2.6 mg of hydroxylamine and 20 mg of $HAuCl_4 \cdot 3H_2O$ under constant agitation for 30 min. This procedure was repeated twice to achieve a continuous, conductive film.

Characterization of the Au Films. The surface of the PUU films was characterized by a Perkin-Elmer 5400 X-ray photoelectron spectrometer. The spectra were corrected with respect to the C 1s peak at 285.0 eV. The growth of the Au films was characterized by UV−vis spectroscopy using a Hitachi U-2001 spectrophotometer and by scanning electron microscopy using a Leo 1550 field emission scanning electron microscope (FE-SEM), operating at an accelerating voltage of 5 kV. The dc resistance of the films was measured using the two-point method by touching the leads of a digital multimeter (Sperry DM-350A) to two points on the film. The resistance and resistivity of the films were also measured using a four-point probe (Loresta MP MCP T-350). Current−voltage curves were obtained using a Keithley 236 source-measure unit; contacts were made by two leads attached to the films, by touching, about 1 cm apart.

Mechanical Tests. Stress−strain measurements were performed using the ASTM standard D638.[41] Dogbone samples of specified dimensions were cut from the cast PUU films and were coated with Au. All the tests were performed at a strain rate of 0.083 mm/s. The stress−strain and resistance−strain measurements were performed on a Stable Microsystems texture analyzer, model TAXT plus, with a 50 kg load cell and a resistance module that can measure up to 20 000 Ω. For measuring the resistance, two leads were attached to the sample either by using conductive Cu tape or by simply touching the sample, separated by a known distance. This was usually in the narrow region of the dogbone, and they were about 2 cm apart. Care was taken not to put extra stress on the sample while attaching the leads.

Results and Discussion

Synthesis of PUU Elastomers. PUU elastomers were synthesized using a conventional two-step methodology, prepolymer synthesis and chain extension. In PUU-type segmented copolymers, the hard segment content, which is described by the weight percent of the urea and urethane groups, is commonly used to describe the chemical composition. Urethane and urea groups are capable of forming monodentate (in the case of urethane) or bidentate (in the case of urea) type hydrogen bonding. As the hard segment content is increased, the hydrogen-bonding capability, and therefore the tensile strength, of PUU elastomers is expected to increase. In our synthesis, urethane and urea groups were spaced by short alkyl chains, forming the hard segment. On the other hand, a polyether oligomer, PTMO, formed the soft segment (Figure 1). To investigate the influence of the hard segment content on the Au adhesion and the mechanical performance of Au-coated PUU elastomers, the hard segment content was varied systematically from 35 to 20 wt %. The composition of the polymers is shown in Table 1.

Growth of Au Films. The attachment of Au colloidal particles to surfaces usually occurs via the strong interaction

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(41) ASTM D638-03, ASTM International, West Conshohocken, PA.

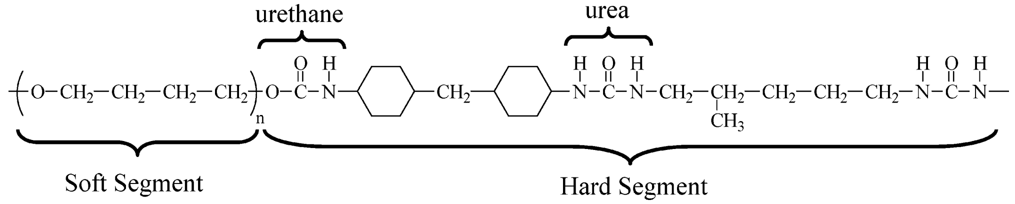

Figure 1. Chemical structure of linear PUU elastomers consisting of alternating soft and hard segments.

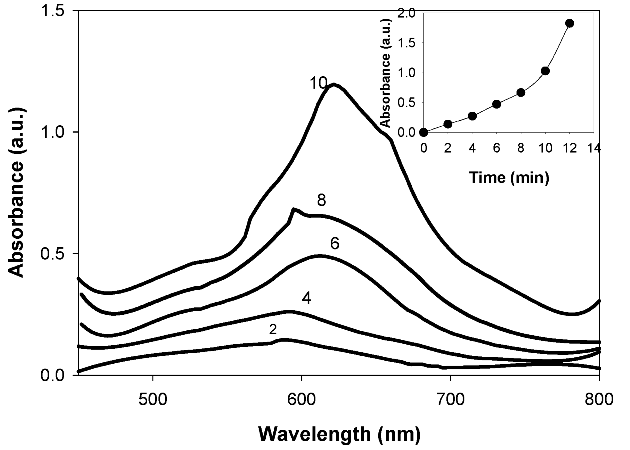

Figure 2. UV−vis absorbance spectra as a function of time for Au on PUU-35 (the numbers indicate time in minutes). Inset: Absorbance at 580 nm as a function of time.

of Au with functional groups such as −SH and $-NH_2$. On most surfaces these groups have to be introduced using different methods. One of the most common methods of performing this is by the attachment of silanes with these different terminal functional groups.[24] The silanes react with −OH groups on the surface to form siloxane linkages with the functional groups on the outside. The −OH groups are present on surfaces such as glass or silicon and can be introduced on polymeric surfaces using a plasma treatment.

In our study, linear amine-terminated PUU films were used. Films of the polymer were solvent cast on Teflon and nylon-6 molds from a solution of THF/IPA. The films cast on Teflon could be removed easily. However, the Au attachment was very poor. X-ray photoelectron spectroscopy (XPS) of the film revealed the presence of fluorine, which inhibits the attachment of Au. Hence, all the films used in the study were cast on nylon-6 molds, which were presumed to promote urethane and urea groups on the surface. The films were dried at ambient conditions and in an oven at 60 °C until constant weights were achieved. Due to the strong hydrogen-bonding interactions between the PUU film and the nylon mold, it was difficult to remove the film, so the films were immersed in water for 4−5 h, when the films could be easily removed. Subsequently, the films were sonicated in Nanopure water to remove any impurities or small molecules that might coagulate the Au solution. Omission of the sonication step resulted in the coagulation of the Au solution in all cases.

Linear PUUs with hard segment contents of 35, 28, and 20 wt % were studied. For all three compositions, there was a good attachment of Au and no significant difference was observed. The growth of Au was characterized using UV−vis spectroscopy and SEM. Figure 2 shows the absorbance spectra of Au on PUU-35 as a function of time. The absorbance increases rapidly with time, and there is a slight red shift of the absorbance peaks, indicating aggregation of the particles. The inset depicts a plot of the absorbance at 580 nm as a function of time. The increase in the absorbance is linear up to about 10 min, after which it increases much more rapidly. After 12 min, the absorbance was so high that it was beyond the range of our instrument. Figure 3 depicts the SEM images of the Au on PUU-35 taken after different times of immersion in the Au solution. After 10 min, the surface is decorated with the Au particles. These are mostly individual, and there is very little clustering. After 30 min, there is increased surface coverage and more aggregation. Immersion for 1 h produces increased surface coverage, and some areas of 3-dimensional coverage also begin to appear. The surface after immersion for 2 h shows a porous 3-dimensional film with very good surface coverage. Increased times of immersion did not significantly change the surface. In the absence of any external stimulus, the movement of Au particles to the polymer surface is entirely by diffusion. Grabar et al. studied the adsorption kinetics of Au colloids on amine- and thiol-terminated organosilane-coated surfaces.[42] Similarly, Kunz et al. have investigated the adsorption of colloidal Au to PVP surfaces.[43] Both studies assumed that the initial coverage of Au on the surface was limited by diffusion:

$$\Gamma = pC(Dt/2)^{1/2}$$

where Γ is the surface coverage of Au particles, p is the probability that a particle reaching the surface will adsorb, C is the solution colloid concentration (number of particles/cm^3), D is the diffusion coefficient, and t is the time in seconds.[44]

Experiments performed confirmed a linear dependence of the coverage on $t^{1/2}$, confirming the diffusion-limited model. Other studies have reported similar observations for the attachment of various colloidal particles to different surfaces.[16,45] Hence, a similar mechanism may be assumed to be occurring in this system also. Other studies by Sastry and co-workers on the kinetics of adsorption of Au to amine-terminated self-assembled monolayers depict two distinct regions: first a linear increase in the mass of adsorbed particles with time and subsequently a plateau where there is no increase in mass with time.[46,47] This corresponds to

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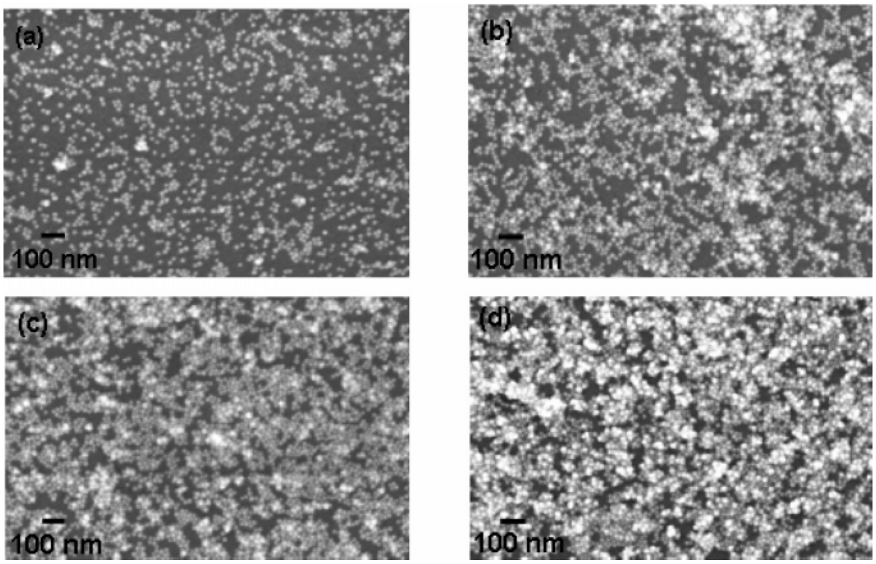

Figure 3. SEM images of Au attached on PUU-35 after immersion in Au solution for (a) 10 min, (b) 30 min, (c) 1 h, and (d) 2 h.

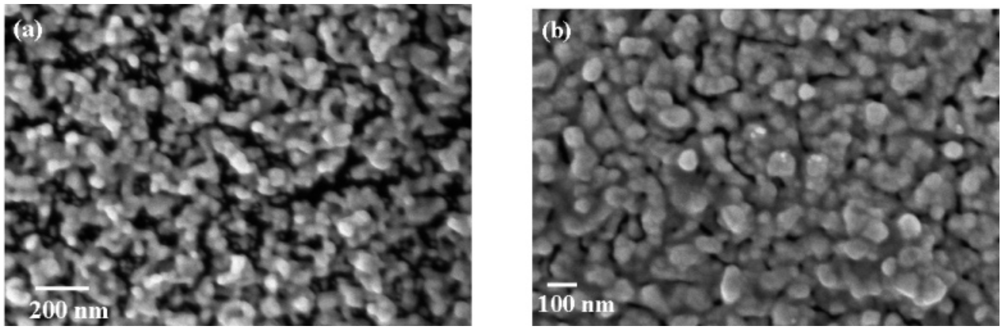

Figure 4. SEM images of Au on PUU-35 seeded (a) once and (b) twice.

our observations that the morphology of the surface did not change significantly with longer immersion times.

Seeding. Although the Au films formed by immersion had good surface coverage, longer immersion times of more than 2 days were required to achieve good conductivity. Another approach to obtain good conductivity at shorter immersion times is the "seeding" method. This involves the reduction of more gold onto the gold already attached to the surface. Figure 4 shows the SEM images of the Au film after seeding once and twice. After seeding, the particles lose their spherical shape and become more irregular in shape and there is increased surface coverage. Seeding the film two times transforms the porous films to an almost continuous film with very little porosity. This process increases the number of conducting pathways and improves the electrical properties of the film dramatically. Elimination of the silane deposition step is an important advantage over the previous methods of solution-based Au film fabrication. This method is extremely simple, requires no sophisticated equipment or controlled conditions, and can be performed on a laboratory benchtop. The good attachment of Au to PUU suggests that PUU can be used as an adhesive for gold. We have utilized this in the fabrication of Au electrodes for Nafion-based polymeric transducers.[48]

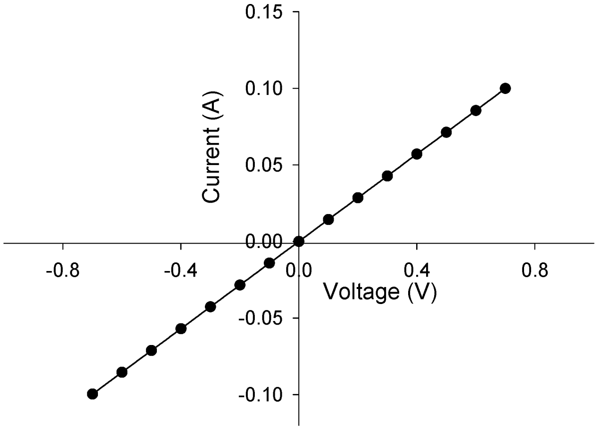

Figure 5. Representative *I*−*V* curve for Au on PUU-35.

The resistivities of the Au films on linear PUU-20, PUU-28, and PUU-35 are $(8 \pm 1) \times 10^{-5}$, $(7.3 \pm 1) \times 10^{-5}$, and $(2.2 \pm 2) \times 10^{-3}$ Ω·cm, respectively, after seeding once. For the PUU-20 and PUU-28 extremely low resistivities were obtained only after seeding once. For the PUU-35 low values were obtained after seeding twice ($(7 \pm 1) \times 10^{-5}$ Ω·cm). The lowest resistivities obtained are only about 30 times that of bulk Au (2.4×10^{-6} Ω·cm). The resistance of the films was also measured using *I*−*V* curves (Figure 5), which are linear in the voltage range measured, indicating that the resistance is ohmic. The resistance is calculated as the reciprocal of the slope of the curve.

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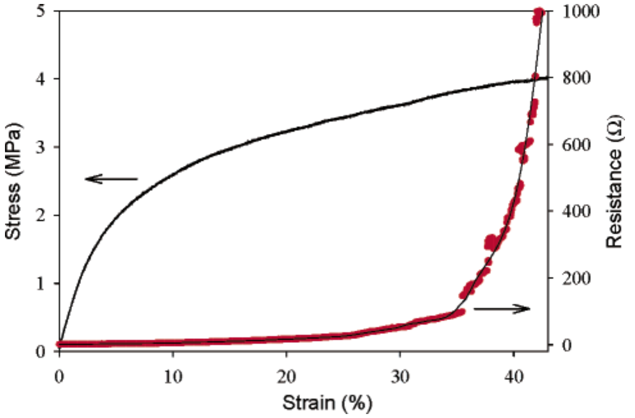

Figure 6. Stress of a Au−PUU film and resistance of Au on PUU-35 as a function of strain. The line for the resistance plot is just an aid to the eye.

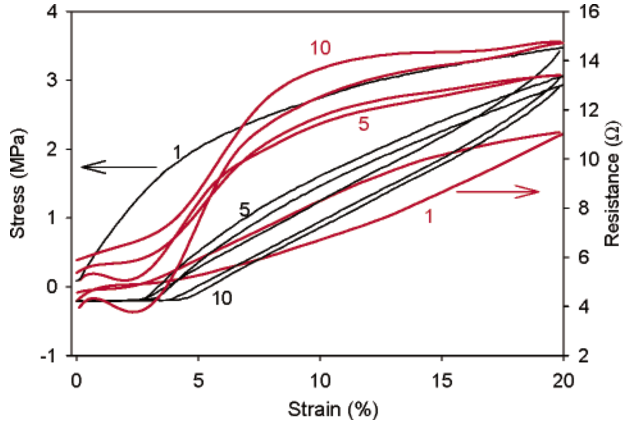

Figure 7. Hysteresis curves for stress−strain and resistance−strain measurements (the numbers indicate the number of cycles).

Adhesion. The Au films had extremely good adhesion to the polymer substrates. Rubbing the film manually, twisting, bending, or rinsing the film in water or other solvents did not remove the film. The adhesion strength of the films was also determined qualitatively using the tape-peel test. An adhesive tape (Scotch, 3M) was pressed firmly onto the film and was slowly removed. The amount of Au attached to the tape gives an indication of the adhesion strength of the film. For all the polymer substrates, a negligible amount of Au was transferred onto the tape for Au before or after seeding, indicating good adhesion of Au to the substrates. This good adhesion of the Au particles to the substrates is attributed to the high binding energy of Au to the amine or amide groups, as discussed before. The adhesion of these films is comparatively better than for the Au films deposited on other polymers using silane surface functionalization reported earlier.[30] Previous studies by Schull et al.[43] on the attachment of Au on poly(vinylpyridine) surfaces have reported that the Au particles are partially embedded into the polymer matrix. It is possible that a similar phenomenon is occurring here also as the polymer is above its T_g at room temperature and the chains are mobile, permitting the Au particles to partially penetrate the surface. This could contribute to the enhanced adhesion.

Mechanical Tests. The resistance of any material varies linearly with its length if the cross-sectional area remains a constant. This concept is used in some types of strain gauges to determine strain by measuring a change in the resistance, where the area is minimized compared to the length. For all materials, the Poisson ratio governs the change in cross-sectional area as a function of the change in the length. For elastomeric materials such as PUU, the Poisson ratio is ∼0.5, indicating that the change in the longitudinal direction (the length in this case) will be more than the change in the transverse direction (the cross-sectional area). Hence, there will be an increase in the resistance as the material is stretched. PUU elastomers generally display 1000−1200% elongation. To understand the behavior of the Au film under strain, mechanical tests were performed.

It was observed that, as there is an increase in the strain of the sample, there is an increase in the resistance of the Au film also (Figure 6). This resistance increase is almost linear up to about 20% strain. After that it becomes more exponential, and after about 50% strain there is no conductivity in the film. As the sample is relaxed the film starts conducting again. The resistance of the film at the beginning is about 0.8 ± 0.2 Ω. After it was stretched to the point where there is no conductivity and was allowed to relax, the resistance measured immediately was about 11 ± 1 Ω. After the sample was allowed to relax for about 5 min, the test was performed again. After this stretch, the resistance immediately after it was allowed to relax was about 20 ± 1 Ω. The resistance measured after the sample was allowed to relax for about 7 h was 10 ± 2 Ω. These results suggest that there is hysteresis in the resistance behavior similar to the hysteresis in the stress−strain behavior.

Figure 7 depicts the hysteresis curves for stress−strain and resistance−strain measurements. The sample was repeatedly stretched and relaxed for 10 cycles, up to 20% strain, which is just above the elastic region of the PUU material. The curves shown are for cycles 1, 5, and 10. Similar to the hysteresis in the stress−strain curves, there is a hysteresis in the resistance−strain curves also. Just as the material never comes back completely to its original length, the resistance also never comes back completely to its starting value. The area under the first hysteresis curves for both the stress−strain and resistance−strain are largest. Subsequent curves have smaller areas. This suggests that with increasing number of cycles, the hysteresis in both the stress−strain and resistance−strain curves will become smaller and smaller until they reach a steady value.

As the polymer substrate is stretched, the Au particles that were initially touching are pulled further apart because Au is not as elastic as the polymer (Figure 8). This breaks the conducting pathways, where some particles are still touching and some are not, leading to an increase in resistance. However, the film is still conducting even though the particles may not be touching, probably by mechanisms such as electron hopping or tunneling.[5,18] After stretching for 50−60% the original length, the particles are so far apart that the film becomes insulating. When the film is relaxed, the particles start coming closer and touching, leading to the recovery of electrical conduction.

After the film is stretched above 50% strain, there is visible cracking of the Au film. Figure 9 depicts the SEM images of the Au film after it has been stretched and allowed to relax. Cracks are visible in the film, and the direction of the

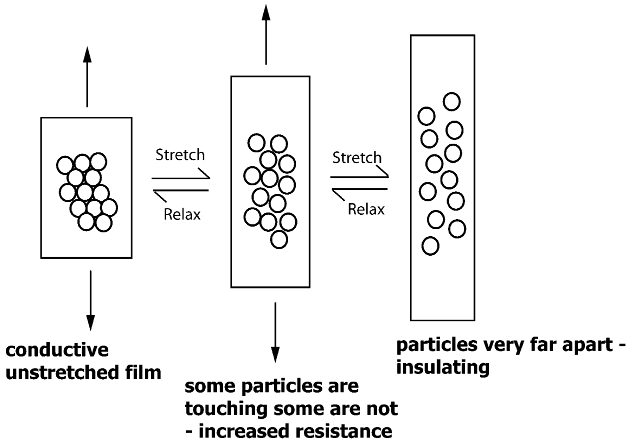

Figure 8. Schematic illustrating the change in the film structure causing a change in resistance upon stretching and relaxing (the film is actually comprised of irregularly shaped Au particles; the circles shown here are merely illustrative).

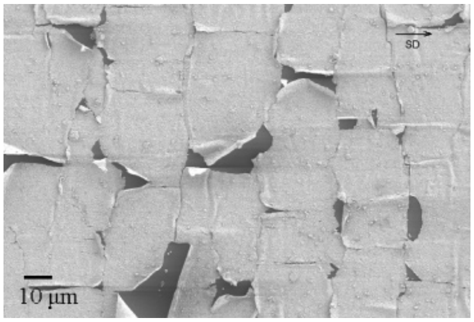

Figure 9. SEM image of Au on PUU-35 after stretching to 50% and relaxing. SD indicates the stretch direction.

cracks is both in the stretch direction and in the perpendicular direction. Volynskii et al.[49,50] have studied the effect of stretching metal films coated on polymer substrates. A similar cracking of the films was observed. When the film is stretched, there is a lateral contraction. Since the Au film is not elastic, cracks are formed in the direction of the stretch to relieve the stress. When the film is allowed to relax, there is a lateral expansion, causing the film to crack in the direction perpendicular to the stretch. In some areas the film starts peeling off starting at the cracks.

The increase in resistance, which is gradual at low strains, becomes exponential at higher strains, and after a certain value there is a sharp reversible transition from conductive to insulating film. This suggests that the Au-coated PUU films can be used as switches that go on or off depending upon the strain. Figure 10 depicts the stress−strain and resistance−strain curves of a film that was prestrained to 45%. Then it was stretched between 50% and 75% strain for five cycles. For the first cycle the material became insulating at about 70% strain and regained conductivity at about 57% strain. For subsequent cycles, the on−off behavior was between 50% and 60%. The large difference in the first cycle is due to the big hysteresis curve. As the number of cycles increases, the smaller hysteresis loops cause a smaller difference in the on and off positions. After a sufficient number of cycles, the on and off positions of the film will reach steady values, as the hysteresis curves also will. This is a very interesting behavior observed in this type of conductive film, which to our knowledge has not been reported before. Applications of this phenomenon are envisioned in the fields of sensors and switches for flexible mechanical devices and other such areas.

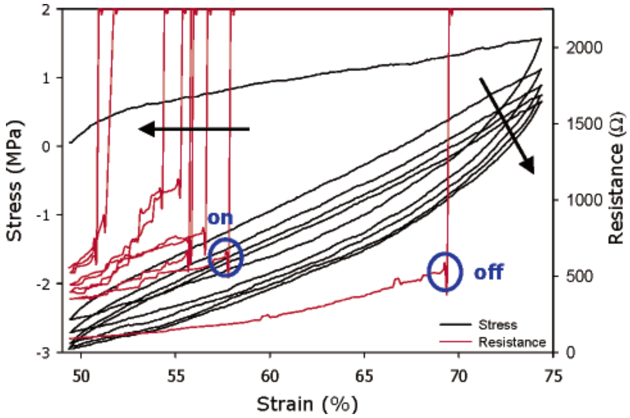

Figure 10. Stress−strain and resistance−strain curves for Au on PUU-35 showing the switching behavior in resistance. The off and on positions are marked for the first cycle (arrows indicate increasing number of cycles).

Conclusions

The deposition of a conductive Au film on flexible PUU using a solution-based method has been successfully demonstrated. This eliminates the polymer surface functionalization by silanes to promote the attachment of Au, which is the standard method used to attach Au particles on surfaces. This is possible due to the high affinity of Au to the urea−urethane groups in the polymer backbone. The Au is attached to the surface simply by immersion in the colloidal gold solution for a few hours. This provides a very simple and inexpensive method of formation of conductive films on polymer surfaces with extremely good adhesion. This method can also be used on other polymers that have −SH, $-NH_2$, or other groups with affinity for Au, either in their backbone or as end groups. The formation of conductive films on elastomeric materials has the advantage of studying the properties of the film at different mechanical strains. This led to some interesting observations. The electrical resistance of the film increased as a function of strain, the increase being linear up to about 20% strain and rising exponentially after that, until it becomes completely insulating. However, this change is reversed upon relaxing the film, and it becomes conducting again. The transition of the film from conducting to insulating and vice versa is sharp. Potential applications of this on−off switching behavior are in the fields of sensors and flexible switches.

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