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PDMS/Kapton Interface Plasma Treatment Effects on the Polymeric Package for a Wearable Thermoelectric Generator

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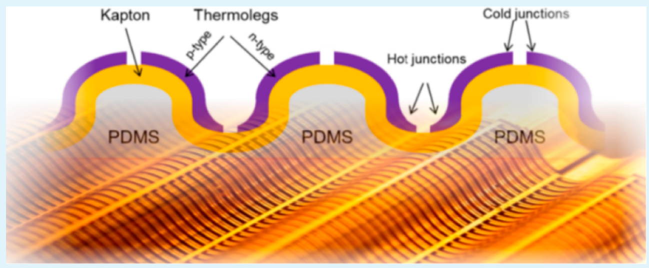
ABSTRACT: The present work highlights the progress in the field of polymeric package reliability engineering for a flexible thermoelectric generator realized by thin-film technology on a Kapton substrate. The effects of different plasma treatments on the mechanical performance at the interface of a poly(dimethylsiloxane) (PDMS)/Kapton assembly were investigated. To increase the package mechanical stability of the realized wearable power source, the Kapton surface wettability after plasma exposure was investigated by static contact-angle measurements using deionized water and PDMS as test liquids. In fact, the well-known weak adhesion between PDMS and Kapton can lead to a delamination of the package with an unrecoverable damage of the generator. The plasma effect on the adhesion performances was evaluated by the scratch-test method. The best result was obtained by performing a nitrogen plasma treatment at a radio-frequency power of 20 W and a gas flow of 20 sccm, with a measured critical load of 1.45 N, which is 2.6 times greater than the value measured on an untreated Kapton substrate and 1.9 times greater than the one measured using a commercial primer.



KEYWORDS: *PDMS/Kapton adhesion, high-performance package, surface free energy, contact-angle measurements, scratch test, flexible thermoelectric generator*

INTRODUCTION

In the actual context of the development of renewable energies and of the research of new sources of green energy, thermoelectric energy generation represents an attractive and promising alternative. To this aim, in the last years many efforts of the industrial and scientific community have been devoted to the development of integrated and portable energy-harvesting systems able to efficiently recover and manage energy from the heat dispersed into the environment.[1−5] In Ambient Assisted Living applications, an increasing interest was manifested by the scientific community and caregivers toward low-cost solutions for energy autonomous and wearable biometric monitoring sensors for elderly assistance. In order to extend the lifetime of the traditional batteries, intensive research is currently focused on the development of portable power generators able to harvest energy from different environmental sources and convert it into electricity. To this aim, the technological transfer of such microsystems on flexible substrates is a key point for the development of unobtrusive, low-cost, wearable, and ubiquitous integrated devices for healthcare and biometric parameter monitoring.

In a previous work,[6] the authors presented the initial results on the design, fabrication, and characterization of the first prototype of a microthermoelectric generator (μTEG) realized on a flexible Kapton substrate. Kapton is a tough, aromatic polyimide film that exhibits an excellent balance of physical, chemical, and electrical properties over a wide temperature range, particularly at unusually high temperatures, as reported in the producer datasheet. Contrary to a conventional rigid substrate, like glass or silicon, a flexible one adds to the device lighter weight, increased robustness, freedom of shape, compactness, and low cost. The second prototype was designed with scaled-down dimensions compared to the first one. The fabrication process requires only two photolithographic steps to complete the thermopile because the single thermocouple consists of a direct p−n junction. A Kapton substrate is parallel to the deposition plane and contains both cold and hot thermocouples junctions; when it is placed in contact with a heated surface, the heat is uniformly transferred to the entire substrate and no thermal gradient useful for the thermoelectric effect can be recovered. Such a problem was solved by designing an appropriate package (Figure 1), which was optimized by the finite-element method (FEM). The temperature distribution and thermal energy flux inside the device as a function of a few design choices were studied using FEM analysis in order to prevent and improve the TEG performances in the operating conditions of interest. The proposed package, fully compatible with the standard clean room facilities, was optimized by coupling the thermoelectric module realized onto Kapton foil to a poly(dimethylsiloxane) (PDMS)

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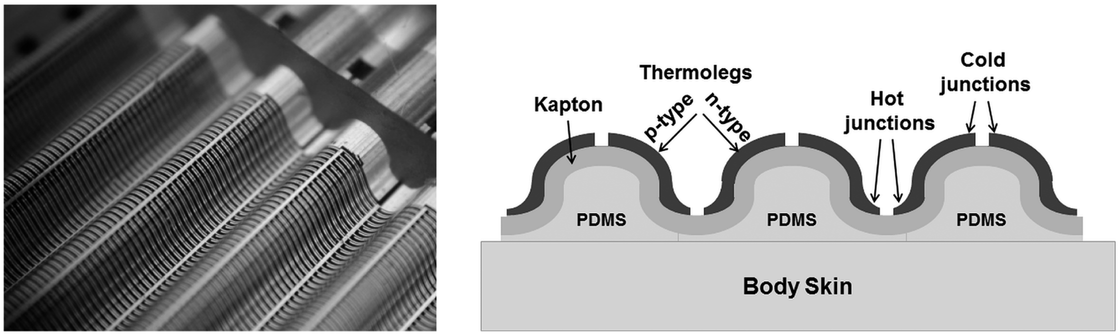

Figure 1. Fabricated flexible thermoelectric generator (left) and a cross section of the proposed package (right), with a typical application on the body skin.

layer opportunely molded in order to thermally insulate the thermocouple cold junctions, enhancing the thermal gradient useful for energy scavenging. Figure 1 shows the fabricated flexible thermoelectric generator (left) and a cross section of the proposed package (right) where the Kapton/PDMS assembly is reported. A uniform and thin PDMS layer (about 200 μm thick) was also deposited underneath the thermocouple hot junctions in order to give greater mechanical stability to the package and avoid the presence of any sort of discontinuity that could compromise the adhesion between Kapton and PDMS. Heat transfer by conduction and natural convection was considered in FEM analysis; simulation results indicated that the designed package is able to recover about 5 K between hot and cold thermocouple junctions, with a thermal difference of 17 K initially available between the body skin and environment. This result was experimentally validated by a thermal IR camera used to evaluate the real performance of the designed package. The relatively small curvature radius of about 2 mm required a stable and mechanically resistant adhesion of the substrate (Kapton) to the structural package (PDMS). In order to overcome the problem of the polyimide foil peel-off experienced during the handling of the fabricated device and obtain a more enduring interfacial bond, which can increase the mechanical reliability of the wearable generator, the authors attempted to enhance the structural adhesion between PDMS and Kapton by performing a surface modification of the polyimide substrate before the bonding. The well-known poor adhesion of the polyimide film to other materials, such as metals and other polymers, is a critical factor that remains to be resolved for reliable microsystem fabrication. In the last years, different methods of surface modification of the polyimide film have been reported, such as wet chemical treatments,[7,8] plasma treatment,[9−11] laser irradiation,[12,13] and the use of ion beams,[14] with the aim of improving the adhesion to other materials. Few works have been published about the bonding improvement between PDMS and Kapton foil. Cai and Neyer[15] achieved good adhesion between PDMS and Kapton by modifying the PDMS prepolymer with a surface adhesion promoter and activating the Kapton surface by $KMnO_4$ wet etching. Tang and Lee[16] used a chemical gluing strategy based on a silane coupling reaction, followed by an amine−epoxy bond formation at the PDMS/polyimide interface. In this work, an experimental study on the effect of different plasma treatments on the Kapton substrate is presented, and the obtained results on the adhesion improvement of the PDMS silicone onto the polyimide Kapton HN foil are discussed. Among the possible surface treatments of polymers, plasma processing was chosen because it is a very fast process having a very low specific consumption of chemicals and energy, making use of environmentally friendly or inert gases like nitrogen. The treatment effects only the surface and not the bulk material and modifies the polymer surface, creating chemically active functional groups that are able to enhance the wettability and surface energy of the polymer. In this work, the plasma treatment proved particularly effective in the improvement of the Kapton interfacial adhesion to the PDMS.

■ EXPERIMENTAL SECTION

Typically, the application of discharges in air, nitrogen, or O_2 on the polymer surfaces transforms initially hydrophobic surfaces into hydrophilic surfaces, while fluorine-containing plasmas provide enhancement of the hydrophobic properties. The increase in the gas pressure, discharge current, and treatment time leads to a reduction of the contact angle and to enhancement of the wettability. However, the major enhancement of the hydrophilic properties occurs during the initial treatment time of 30−120 s.[17] In our experiments, the duration of the plasma treatments was set to 30 s. The Kapton substrate wettability before and after different plasma surface treatments and its adhesion performances to the PDMS were investigated using the contact- angle analysis and scratch-test method. A 25-μm-thick Kapton foil (100HN, from DuPont) was used for the experiments. Prior to the plasma treatment, the polyimide substrates were ultrasonically cleaned for 5 min in acetone, washed in deionized water, N_2 flow dried, and baked at 125 °C for 10 min on a hot plate. All plasma treatments were performed at room temperature and a working pressure of 1 mTorr using a low-pressure radio-frequency (RF) plasma chamber (Femto, Diener Electronic, Germany). Different process gases (O_2, dry air, and N_2), gas flows (from 5 to 20 sccm), and plasma RF powers (from 20 to 60 W) were used for the treatments.

The Young−Dupre equation was used to evaluate the work of adhesion of PDMS on untreated and plasma-treated Kapton substrates. The work of adhesion is defined as the reversible thermodynamic work that is needed to separate the interface from the equilibrium state of the two phases to a separation distance of infinity.[18] The work of adhesion (W_a) between the solid and liquid is defined in Dupre's equation as

$$W_a = \gamma_l + \gamma_s - \gamma_{sl} \quad (1)$$

where γ_l is the surface energy of the liquid phase, γ_s is the surface energy of the solid phase, and γ_{sl} is the interfacial surface tension. The interfacial equilibrium condition for a liquid droplet on a smooth solid surface is described by Young's equation:

$$\gamma_{sl} = \gamma_s - \gamma_l \cos\theta \quad (2)$$

where θ is the contact angle between the solid and liquid. By combining eqs 1 and 2, Young−Dupre's equation can be derived:

$$W_a = (1 + \cos\theta)\gamma_l \quad (3)$$

The solid surface free energy (SFE) γ_s and its polar and nonpolar components, indicated with γ_s^p and γ_s^d, respectively, were estimated using Owens–Wendt's equation:[19]

$$(1 + \cos\theta)\gamma_l = 2\sqrt{\gamma_s^d \gamma_l^d} + 2\sqrt{\gamma_s^p \gamma_l^p} \quad (4)$$

The polar component of the surface energy describes the polar interaction between the solid and liquid phases due to polar groups, electric charges, and free radicals on the surface. The dispersive component is related to the London force; it takes into account nonpolar interactions between the material and dispensed liquid, and it is determined by the roughness, unevenness, and branching level of the surface. Because two unknown parameters, γ_s^p and γ_s^d, appear in eq 4, the contact angle has to be measured using two measuring liquids in order to determine the SFE of a polymer. In this study, static contact-angle measurements were performed at room temperature and analyzed by a drop-shape analysis program,[20] using deionized water and PDMS as test liquids: the former has a dominant polar component, and the latter was used as a dispersive liquid. The SFEs for the wetting liquids and their polar and nonpolar components are listed in Table 1.[21] Water surface tension components were easily found in the literature, and the polar and dispersive components of tested PDMS were experimentally determined using the Owens–Wendt method by measuring the PDMS contact angles on test surfaces whose surface energy is known.

Table 1. Surface Energy Components of Water and PDMS, Measured at 20 °C

testing liquids	γ_l (mJ/m^2)	γ_l^d (mJ/m^2)	γ_l^p (mJ/m^2)
water	72.8	21.8	51
PDMS	37.0	36.0	1.0

A quantitative evaluation of the adhesion performances of the polyimide before and after the plasma treatments was performed by the scratch-test method. In a scratch testing, a diamond stylus of defined geometry is drawn at constant speed across the specimen surface with a normal force, which can be set as constant, progressive, or incremental. In this work, scratch tests were done with a CSM microscratch test using a 200-μm-diameter Rockwell C diamond tip. Each test was performed with an increasing load in the range of 0.05–2 N over a length of 5 mm. The scratches were subsequently examined by optical microscopy.

For scratch-test specimen preparation, the Sylgard184 elastomer kit (Dow Corning) was used by mixing and degassing the base and curing agent in a 10:1 weight ratio. In order to prevent PDMS from sticking to the wafer, trimethylchlorosilane was vapor-deposited onto the silicon substrate, and then a uniform 50-μm-thick PDMS was spin-coated onto the silicon wafer. The plasma-treated Kapton substrates were immediately put on the spin-coated film of uncured PDMS to form an initial bond at room temperature. Then a thermal curing was carried out in an oven at 80 °C for 90 min.

The efficacy of the plasma treatments was evaluated by variation of the measured critical load with the treatment conditions and compared with the adhesion performance obtained using a commercial silicone primer (ELCH PRO P819). The primer was spread on the Kapton surface before being put in contact with liquid PDMS. The subsequent thermal treatment has completed the polymerization process.

RESULTS AND DISCUSSION

Static contact-angle measurements were performed at room temperature using deionized water and PDMS as test liquids. Milli-Q-grade water drops of 2 μL were deposited on the plasma-treated Kapton substrates using a flat-ended needle micropipet. The volume of the PDMS drops was approximately 8.9 ± 0.3 μL, as calculated mean volume on 18 drops consecutively dripped. The data reported in Tables 2–4 indicate the mean value of four contact angles experimentally measured on different parts of the polyimide surface and the calculated standard deviation. The untreated Kapton showed contact angles of 74° and 22° with water and PDMS as test liquids, respectively.

Table 2. Water and PDMS Contact Angles Measured after the Air Plasma Treatments at a RF Power of 30 W and with Increasing Gas Flows

gas flow (sccm)	water contact angle (deg)	PDMS contact angle (deg)
5	18 ± 1	32 ± 3
10	14 ± 2	30 ± 7
20	18 ± 1	36 ± 1

Table 3. Water and PDMS contact angles measured after the O_2 plasma treatments

RF power (W)	gas flow (sccm)	water contact angle (deg)	PDMS contact angle (deg)
30	5	15 ± 1	26 ± 5
	10	17 ± 2	25 ± 4
	20	21 ± 2	30 ± 3
50	5	15 ± 1	26 ± 5
60	5	15 ± 1	26 ± 5

Table 4. Water and PDMS Contact Angles Measured after the Nitrogen Plasma Treatments

RF power (W)	N_2 gas flow (sccm)	water contact angle (deg)	PDMS contact angle (deg)
20	5	19 ± 3	20 ± 2
	10	24 ± 1	21 ± 4
	20	22 ± 3	16 ± 2
30	5	16 ± 1	23 ± 5
	10	20 ± 1	27 ± 4
	20	21 ± 2	22 ± 2
50	5	16 ± 3	22 ± 2
	10	16 ± 3	22 ± 2
	20	12 ± 3	21 ± 2
60	5	15 ± 3	24 ± 2
	10	15 ± 4	24 ± 3
	20	16 ± 2	25 ± 2

As a first investigation, the effect of 30% relative humidity air plasma at 30 W with increasing gas flows was considered. As shown in Table 2, such a treatment effected a marked decrease of the water contact angle and an increase of the PDMS one.

Similar results were obtained on samples treated in increasing O_2 flows (Table 3).

The contact-angle results listed in Table 4 reveal the interesting contribution of nitrogen plasma to the improvement of the Kapton/PDMS interaction. The lower PDMS contact angle of 16° was measured after a plasma treatment performed with a RF power of 20 W and a gas flow of 20 sccm. At higher powers, N_2 gas flow seems to have a poor effect on the PDMS contact angle, which does not vary appreciably. Figures 2 and 3 report variation of the PDMS and water contact angles measured after different treatments performed by applying a RF power of 30 W, increasing flows, and using different gases: the results highlight the scarce influence of the gas flow during treatment and the lack of any kind of loading effects.

Figure 3 shows variation of the water and PDMS contact angles measured by applying a nitrogen plasma with increasing powers. The nitrogen plasma treatment at reduced power (20 W) is proven be the more effective treatment in the reduction

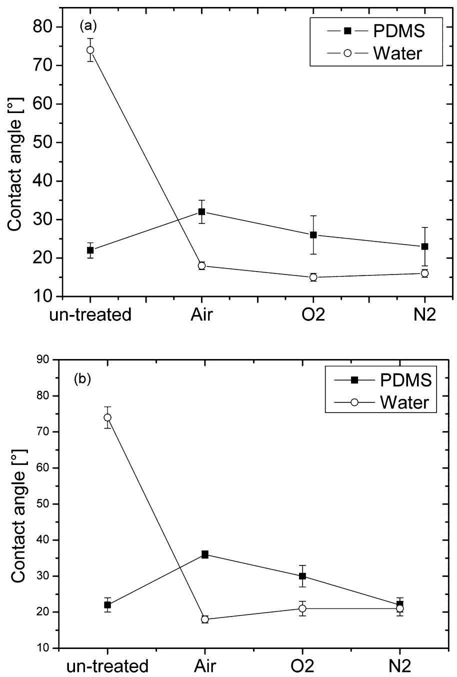

Figure 2. Effect of different gases on the wettability of the Kapton surface, with a plasma power of (a) 30 W and a gas flow of 5 sccm and (b) 30 W and a gas flow of 20 sccm.

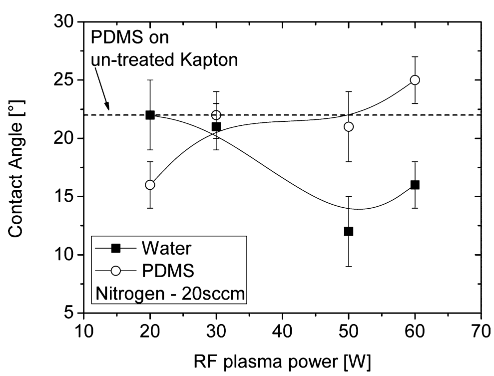

Figure 3. Water and PDMS contact angles measured after a nitrogen treatment at different plasma powers.

of the PDMS contact angle. When higher powers were applied, the Kapton hydrophilicity improved, but a worsening in the PDMS wettability was obtained: the nitrogen plasma treatment at a power of 60 W proved even counterproductive because a PDMS contact angle greater than the one measured on the untreated polyimide was obtained after treatment. This effect was also observed in different experiments on the Kapton surface and was clearly imputed to a physical damage of the surface,[22] also observed in our samples by optical microscopy.

All plasma treatments raised the Kapton SFE, with an increase of the polar component and a decrease of the dispersive one. Table 5 shows that the work of adhesion between PDMS/Kapton and the Kapton SFE of the more effective plasma treatments, which were selected for the scratch-test investigation.

The scratch-test results are shown in Figure 4, with indication of the dispersive-to-polar ratio variation with the plasma treatments.

As can be seen in Table 5, a clear effect of the plasma treatments on the polyimide surface is denoted by the increased

Table 5. Work of Adhesion and SFE Components of the More Effective Plasma Treatments Selected for Scratch-Test Measurements

plasma treatment	θ_{PDMS}	W_a^{PDMS} (mJ/m^2)	γ_s (mJ/m^2)	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)
untreated Kapton	22 ± 3	71.30	38.36	29.73	8.63
20 sccm N_2, 20 W	**16 ± 2**	**72.57**	**67.88**	**24.5**	**43.39**
20 sccm N_2, 60 W	25 ± 2	70.53	70.04	22.34	47.70
5 sccm N_2, 30 W	23 ± 5	71.06	70.06	22.81	47.25
5 sccm air, 30 W	32 ± 3	68.38	69.28	20.56	48.72

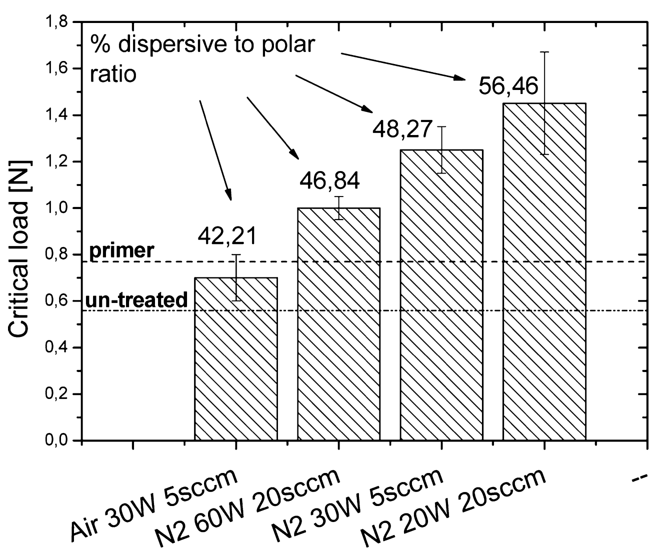

Figure 4. Results of the scratch test performed on untreated and plasma-treated Kapton surfaces.

dispersive contribution to the SFE instead of the polar one. The interaction between PDMS and untreated Kapton has a clear dispersive nature characterized by a low energetic content, which determines the poor adhesion of PDMS/Kapton also confirmed by the relatively low critical load of 0.56 N.

The nitrogen plasma treatments are able to activate the Kapton surface, improving the interaction between the polyimide surface and the active components present in PDMS, as indicated by the strong increase of the polar component. This effect leads to an increase of the PDMS/Kapton adhesion, as is clearly indicated by the high value of the critical load estimated by the scratch test for all plasma-treated surfaces (Figure 4). Moreover, for all of the plasma-treated surfaces, there is a correlation between the percentages of the dispersive component of the surface (related to the London force) and the critical load. This indicates that the adhesion between the treated Kapton surface and PDMS is partially related to dispersive adhesion (gecko-like adhesion). In fact, the sample with the best mechanical performance is characterized by the highest dispersive-to-polar ratio but the lowest polar component among the treated samples. Therefore, even if the dispersive adhesion is relatively weak, it can clearly help the adhesion between PDMS and Kapton.

As shown in Figure 4, the best adhesion result was obtained with the nitrogen plasma treatment at a RF power of 20 W and a gas flow of 20 sccm (this is the same treatment that minimized the PDMS contact angle), with a measured critical load of 1.45 N, which is 2.6 times greater than the value measured on an untreated Kapton substrate and 1.9 times greater than the one measured using a commercial primer.

■ CONCLUSIONS

A study on the wettability enhancement of plasma-treated Kapton substrates and on the improvement of the adhesion of the polyimide to PDMS was proposed. Different process gases, gas flows, and plasma RF powers were investigated; variations of the Kapton surface wettability were measured by contact-angle measurements, while the scratch-test method was used to quantify the adhesion of the plasma-treated Kapton foil to PDMS. The best adhesion performances were measured on samples treated with N_2 plasma at 20 W RF power and 20 sccm gas flow, with a value of critical load 2.6 times greater than that of the untreated Kapton substrate. Further measurements are ongoing in order to monitor the time decay of the plasma-induced effects and to evaluate the possible influence of the environment humidity and the mechanical deformations of the package on the determined critical load values.

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Notes

The authors declare no competing financial interest.

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