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Short communication

Substituting Plastic Casings with Hydrophobic (Perfluorosilane treated) paper improves Biodegradability of Low-Cost Diagnostic Devices

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ABSTRACT

The demand for rapid diagnostic in developing countries has recently increased, in part due to growing populations, emerging diseases, and rise in healthcare cost. Use of low-cost lateral flow/dipstick devices, especially paper-based ones, has increased. In most of the developing world, however, biomedical waste management systems either do not exist or are poor, as such, used devices either get incinerated or dumped alongside household trash. The plastic casing that is often used to hold the test strip, while useful before the test, also slows the biodegradation of the used contaminated devices. We demonstrate that by replacing the plastic casing with paper encasements, we promote biodegradation of these devices while reducing its total weight, making their transport and packaging more compact and more environmentally friendly—hence qualifying this simple modification as green engineering. The ability to use paper casing has the added advantage that devices can be readily assembled locally with ease and without need for sophisticated manufacturing tools as needed with the plastic casings.

1. Introduction

Interest in low-cost diagnostic devices has gained attention in the recent past, in part due to rising healthcare cost, growing population, environmental concerns, opening (emerging) markets in developing countries, and also due to an increased level of research funding in this area. For this reason, low-cost rapid diagnostic devices (LC-RDT) for common maladies in the developing world (e.g malaria, HIV, and typhoid) have been commercialized, with mixed successes. These point of care (POC) devices introduce prompt result on biological testing. The rapid increase in tools and materials that can be used for the fabrication of LC-RDTs has also gained impetus, in part due to involvement of multi-disciplinary teams in their development. Although the development in low-cost diagnostics has been well received, little effort has been put into understanding the fate of the subsequent biomedical waste especially in developing countries like Kenya. In countries without proper solid-waste disposal and/or recycling systems, used diagnostic devices often end up in dumpsites where the poorest of the population (often homeless women and children) manually scavenge for recyclables as a way of life. (Abdelmouleh et al., 2004) Unfortunately, these 'manual recyclers' do not have access to proper protection or medical services and as such are least likely to get treatment once exposed to pathogens from contaminated medical devices. Disease

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pathogens, like viruses, are resilient to many harsh conditions especially in cases where the containers holding the medical waste abet their survival.

The use of LC-RDTs continues to increase not only among the medical practitioners but to the patient, without concomitant increase in the required biomedical waste management systems or public awareness as to the dangers associated with their disposal. This challenge puts communities at risk of spreading diseases or re-introduction of more resilient bugs (superbugs) that are more resistant against available treatments. One of the main concern with current LC-RDTs is their poor degradability, in part due to the way they are packaged. A typical commercially-available lateral-flow LC-RDT is made of the active test strip – the basis of the test and two plastic casing (Fig. 1a). The latter, made of plastic, constitutes the bulk of the device and is not readily biodegradable. To illustrate the challenge with plastic waste, polystyrene alone accounts for 20% of the global waste. (Huang et al., 1990; Shah et al., 2008; Webb et al., 2012; Zheng et al., 2005)

To avert the waste-management crisis associated with persistent biomedical waste generated by the use of LC-RDTs, we hypothesized that the casing can be substituted with a greener, sustainable and biodegradable material, allowing for the contaminated portion of the test to be readily exposed and therefore rapidly decompose. A challenge with most available materials is low rigidity, wettability, and availability. Paper, although commercially available in thin sheets, can be modified to increase mechanical strength and/or control wettability. We hypothesized that we can replace the plastic casing with paper without compromising the mechanical integrity or the protective role of the casing on the active test strip. Cellulosic materials are generally hydrophilic, making them unusable for low-cost diagnostic device due to their high water absorption. This aspect may however be mitigated by rendering the surface hydrophobic. (Oyola-Reynoso et al., 2015a,b,d) There are two main processes commonly used to create hydrophobic paper surfaces *viz;* i) physi-sorbed – in which the paper is considered as a porous structure (Fig. 1c) and infused with a hydrophobic wax or polymer, and ii) chemi-sorbed – where the chemical structure of the paper (Fig. 1c) is exploited to covalently graft hydrophobic units on the surface rendering the material hydrophobic. (Oyola-Reynoso et al., 2015d) Our approach, entails considering paper both as a biodegradable polymeric and structurally complex material. We hypothesized that mechanical strength can be increased by stacking while hydrophobicity can be achieved via chemical modification of the cellulosic surface hydroxyls.

2. Materials and Methods

2.1. Materials

Cardstock paper (Georgia-Pacific®, purchased in Staples™); trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (97%, Sigma Aldrich) used as received; Scotch ® permanent Glue Stick (0.28oz, 3 M ™, purchased from Staples™); Chromatography dipstick reader pad was used as received from Malaria Dipstick devices (Biocan® Diagnostic Inc., Coquitlam, Canada); Silhouette craft cutter (Silhouette® America Lehi, Utah).

2.2. Device Fabrication

2.2.1. Paper based Casings

Cardstock paper was aligned along the dimensions of the Silhouette cutter mat and fed into the cutter. Dipstick shape patterns were sketched in the provided user inteface and the cutting was initiated using the corresponding modes of cardstock paper and blade setting. Once the cutting was finished, the shaped paper was detached from the mat and set aside for treatment.

2.2.2. Paper Treatment and Assembly

Paper surface treatment was performed by transferring 100 μL of trichloro (octyl) silane into a 10 mL vial. The pre-cut paper casing were placed in a warm desiccator along with the vial containing silane. The system was then sealed and vacuumed (~ 100 mmHg) for 5 minutes then placed in oven at 95 °C for 24 hours. The paper patterns were then removed from the desiccator and used to assemble the device.

2.2.3. Device Fabrication

Device assembly was performed by bonding the three pieces of hydrophobic paper patterns using permanent glue or wood glue as shown in Fig. 2. The absorbent pad was placed in the corresponding position and secured with a top layer of hydrophobic paper on which sample inlet, buffer inlet and an observation window had been precut (Fig. 2 (iii)). An exact replica (in terms of dimensions) of the Biocan® malaria Ag test was also made by stacking pre-cut papers (Fig. 2d).

3. Results and Discussion

The use of plastic casing allows the flow of biological fluids without any interference from the casing. With a new casing, capillary flow of biological fluids (artificial urine and blood) were evaluated with the fabricated devices and flow rates compared to the commercially available tests. We observed that changing the casing to a paper-based one did not significantly interfere with the test, and as such, we could evaluate the efficiency of the paper-based casing in promoting degradation. We, therefore, focus the remaining discussion on the treatment and biodegradation of the devices, considering that the most obvious form of promoting biodegradation in developing countries will entail burying the devices.

3.1. Surface Modification

Silanes are widely used to control wetting on surfaces bearing reactive moieties like hydroxyls and amines. (Abdelmouleh et al., 2004; Abdelmouleh et al., 2002; Andriot et al., 2007; Bel-Hassen et al., 2008; Hair and Hertl, 1969; James, 2000) We recently showed that when paper is treated with trichlorosilanes the surface texture changes with concomitant change in wetting properties. (Oyola-Reynoso et al., 2015c) This evolution of surface texture is expected based on the Flory-Stockmayer theory (Eq. (1))(Klemperer and Ramamurthi, 1990), which predicts the formation of gel, due to an increase in crosslinking probability of the monomers, as shown in Eq. (2). The Flory-Stockmayer equation takes into consideration the probability of monomer B reacting with monomer A on a unit of branch A $p_B^2\rho$ and the molar ratio (r) of the reactive group in each of the monomers in the reaction. We demonstrated that treatment of paper with trichloro octylsilanes leads to formation of polymeric particle on the surface of the fibers when the reaction conditions and ensuing kinetics are well controlled. Unlike the physisorbed coatings, this type of paper modification gives biphillic surfaces and we hypothesized that the spacing between the formed gel particle would allow for biodegradation agents to eventually diffuse into the paper fibers and cause degradation.

$$\alpha = \frac{p_B^2\rho}{\frac{1-(p^2B)}{r(1-\rho)}} \qquad \ldots\ldots\ldots\ldots(1)$$

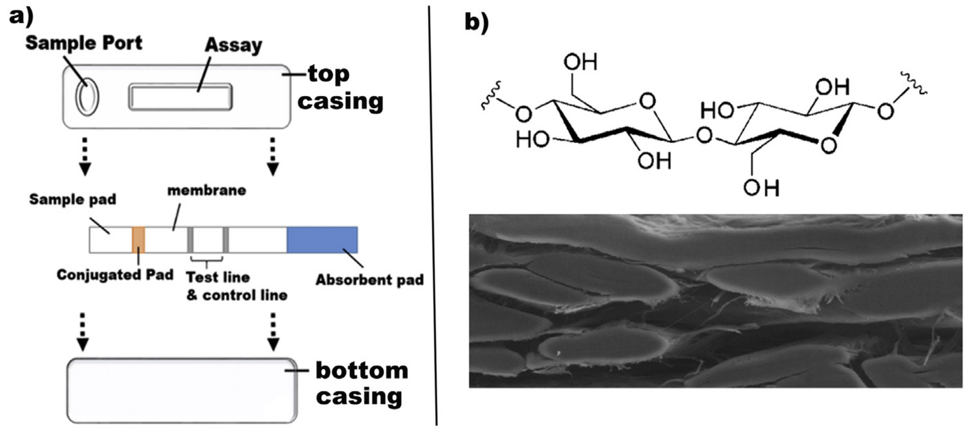

Fig. 1. Key components making up a lateral flow rapid diagnostic test; a) the top cover through which the results are visualized and sample introduced. The active test strip on which the assay is executed and fluid movement/separation achieved. The top and bottom covers make up the casing and is the bulk of the device (both in size and weight). b) Key properties of paper; the organic polymeric materials – cellulose, illustrated by the chemical structure showing different reactive moieties, the basis of chemisorbed hydrophobic barriers. A scanning electron microscope image showing the physical structure of paper, the basis of physisorbed hydrophobic barriers.

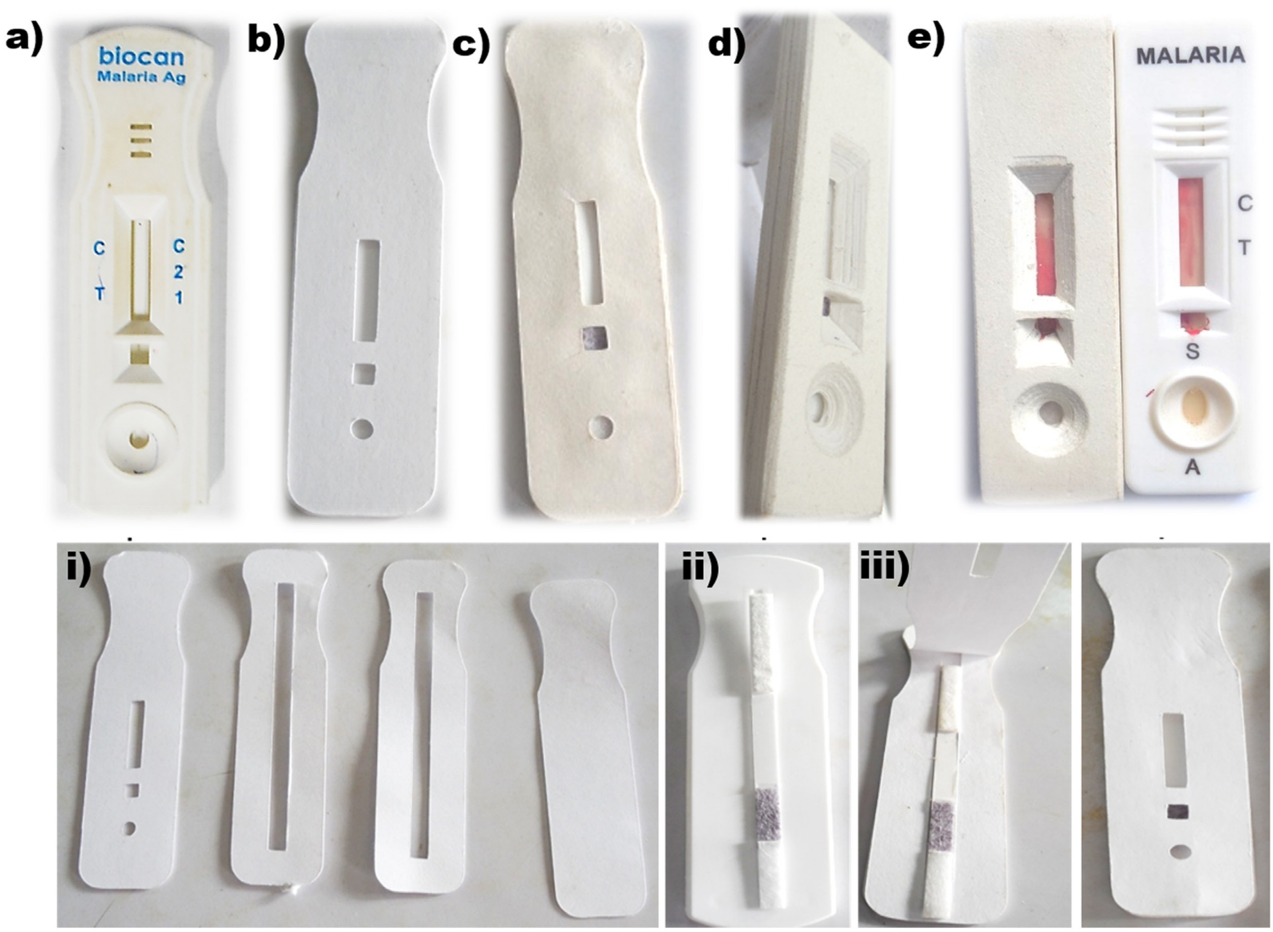

Fig. 2. Commercially available plastic casings dipstick devices (a), alongside paper based dipstick devices assembled in Kenya (b) and the USA (c). An exact size-replica of the commercial device with paper casing (d) illustrates the bulkiness – due to use of multiple layers of paper. A step-by-step guide to the assembly of the devices. Step (i): precut the papers and chemically treat them to make them hydrophobic. (ii) Stack the back cover and two papers with a precut groove for the test-strip, (iii) install the top cover and the device is ready to use.

3.2. Evaluating hydrophobicity

Hydrophobicity is required for the application of paper in fabricating casing for LC-RDTs. Surface wettability of the treated papers was evaluated by measuring the static contact angle. As expected, untreated paper was hydrophilic but became hydrophobic when treated with the silane with a contact angle $\theta_s = 119.8 \pm 2$.

3.3. Mechanical testing

The effect of surface modification on mechanical property of paper was determined by comparing tensile strengths of treated and untreated paper. 2 × 5 cm paper strips were evaluated using an Instron® 5569 Universal Testing Machine with 100 kN load cells. The results showed that there was a slight decline in the tensile strengths with surface silanization compared to untreated paper samples (24.34 vs 58.15 MPa respectively) as inferred from the stress-strain curve (see supporting information Fig. S1). We infer that the decrease in tensile strength could be due to a partial decrease in hydrogen bonds as surface hydroxyls are recruited for the silanization.

3.4. Biodegradation

Many hydrophobic coatings on paper are physisorbed polymers and these coatings, like the plastic casing, limit the biodegradation of the paper. Recent approaches to creating hydrophobic barriers on paper offer no advantages to the biodegradation of the material over plastics. Physisorbed barriers that are widely used in paper-based devices include thermosets like SU-8 (Martinez et al., 2008a; Martinez et al., 2008b) or infusion with wax via wax printing (Carrilho et al., 2009; Dungchai et al., 2011; Lu et al., 2009; Yadav et al., 2014). These barrriers lead to a significant amount of material being deposited on the paper which significantly interferes with the mechanical and chemical properties of the paper. Chemical surface modification – especially in chemical vapor deposition, however, allows for small size coatings, sometimes as thin as a molecular monolayer, and as such has little to no significant effect on the mechanical properties of the material albeit with drastic changes in the surface properties. By retaining structural integrity of the bulk of the material, one can envision faster biodegradation through mechanical and/or chemical bleaching of the thin surface coating. In our case, this is expected to occur even faster since there is only partial coverage of the paper surface, and therefore a direct access to the non treated cellulosic fibers.

We hypothesized that the fabricated paper based casings are expected to fully degrade when compared to plastic casings in composting environments. Both the plastic and paper based casings were randomly buried on campus (Kenyatta University, Nairobi, Kenya) in 4 separate sites in the open field. Observations were made for a period of 12 months at 2 month intervals when samples were dug up gently dusted (manually and with a stream of blowing air) and weighed. The mass loss (%) were used to assess and compare the biodegradability of the paper based casings versus the conventional plastic casings. We exercise caution in interpreting the absolute values as the weight loss parameter carriers with it a systematic errors. By subjecting the devices to the same conditions, however, we can confidently interpret the relative comparisons which clearly show that the paper-based casings degrade better than the plastic analogs (Fig. 3 and Supporting information Table S1). We observe that the paper based casings were mostly decomposed in a year, while the plastic casings showed no significant mass loss (Fig. 3). The rate of mass loss follows an exponential decay (p<0.1), which is expected for a normal decay process. We observe that when an exact replica was made, as expected, the degradation was slower as more layers of paper were needed to achieve similar dimensions. On the other hand, when only few layers (4) of paper were used, the overall degradation was rapid with about 80% total degradation in about 8 months. Under our experimental conditions, an initial lag in the degradation process was observed which could be associated with the need to break through the hydrophobic barrier before the paper fibers can start degrading. In fact, the mass of the paper casings increased marginally during this period, presumably due to slight moisture intake. Despite the surface modification of paper casings, the material was degradable although much slowly compared to the untreated paper which complete decomposes within the 2 month experimental intervals. Thus, the application of ultra-hydrophobic paper produced by silane treatment provides a greener alternative for making diagnostic devices casing. Although perfluorinated reagents are used, the reduced weight (hence transport cost), biodegradability and ease of fabrication enables us to qualify these casings as a greener alertenative (based on 12 principles of green chemistry and green engineering) to conventional plastic casings.

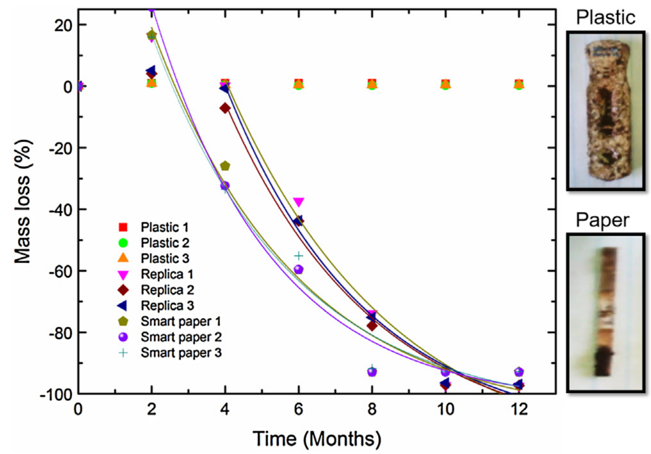

Fig. 3. Change in mass of plastic and paper based casings over a period of 12 months buried underground. An exponential decay in the mass of the device was observed for the paper-based devices but not for the plastic ones. Alongside are the remainings of both plastic and paper based casings after 12-month soil study. As shown in the images, paper based casing has degraded substantially leaving behind only the plastic support of the active strip, while the plastic casings had no sign of degradation.

We demonstrate that even under prolonged treatment (24 hrs) with a perfluorinated silane, the paper can degrade and therefore avert accumulation of contaminated biomedical waste. In an actual dumpsite where heat and moisture is high, we anticipate that the degradation process will be much faster and it would take less that 8 months to achieve 75% total degradation. Due to the presence of a plastic support on the active strip, total degradation of the device was much slower and seems to asymptot below 80% mass loss.

4. Conclusions

This paper demonstrate that a simple substitution of plastic with hydrophobic paper allows for greener, more adaptable, and affordable alternative to conventional casings for low-cost diagnostic devices. The new device design allows us to reduce on the overall bulk size while promoting degradation albeit, as expected, slower than an analogous one derived from untreated paper. A major role of the casing is to provide mechanical integrity of the device.

Conflicts of Interest

The authors declare no conflict of interest.;1;

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.indcrop.2016.08.051.

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