SILICONE-COATINGOF NITINOL STENT WIRES BY ELECTROSPINNING: CATHETER DEPLOYMENT TEST

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In this study, we investigated the effect of silicone-coating of individual wires on the deployment force of a non-vascular stent. As a new strategy, we utilized an electrospinning technique to selectively coat the wires of the stent, not including the spaces between the intersecting stent wires. We characterized the stent coating and wires with various characterization techniques. The tensile properties of the silicone film at different drying temperatures were measured and catheter deployment test was carried out. Fully silicone film-encapsulated Nitinolwires were obtained after drying at 150 and 200^{o}C. The silicone-coated stent showed lower deployment force compared to the bare stent. This is attributed to the smoother surface provided by the silicone coating. Furthermore, the coating enhances the bending ability of the stent. The facile coating technique could provide improve catheter stent deployment as well as improve the biocompatibility of the stent.

(Received October 1, 2013; Accepted December 12, 2013)

Keywords: Electrospinning; silicone; stent; Nitinol; deployment test

1. Introduction

A non-vascular stent is a man-made wire mesh biomedical implant scaffold that is used to open up obstructed non-vascular passageways such as esophagus, bile duct, etc, in a human body[1]. It is usually inserted via a catheter. The stent is crimped and inserted into a small-diameter catheter, and it is then deployed into the targeted area in the body through expansion of the crimped stent. There are many issues associated with the use of stent such as migration of stent, positioning difficulties, fracture of stent, and restenosis[2]. The easy insertion and deployment of stent is also an important issue. A stent with rough surfaces would make it difficult for easy deployment due to friction between the stent wire and the inner wall of the catheter. However, if the surface of the stent is too smooth, though it would make the insertion and deployment easier, it has a tendency for stent migration to occur due to lower attachment surface area for the surrounding tissues[3]. Thus, an optimum roughness is required for ease in insertion and deployment, as well as for preventing stent migration. Several studies have utilized surface modification techniques to smoothen the surfaces of stent. In our previous studies, we utilized laser and magnetic polishing[4] to improve the surface finish of stent. Improved surface finish and consequently better stent deployment was obtained for the magnetically-polished stent.

Another way of improving the surface finish is by coating the stent with a polymeric

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matrix. It could be done by completely covering the whole stent or by just coating the individual wires. Some studies have covered the stent with polyurethane or silicone films by dip-coating or by electrospinning methods[5]. Though, stents are successfully covered, there is still an issue of possible migration of the cover from the stent due to not-fully attached cover on stents during insertion, deployment, or after-deployment. Another issue is the durability of the cover when exposed to constant pressure inside the body. In the present study, our approach is to just cover the individual wire of the stent with silicone film to induce smoother surface. This approach is also an initial step for possible inclusion of drugs in the coating for targeted-drug delivery applications. Though dip-coating technique is the usual method of coating, we utilized electrospinning technique in this study. In dip-coating, usually the inter-wire spaces are also covered with film, thus covering the whole stent. Electrospinning is a versatile way of producing ultrafine fibers onto a targeted substrate by the application of high voltage electric fields. We utilized silicone material as it is one of the most common polymers used as cover for stents[6]. However, electrospinning of silicone to produce nanofibers is a difficult task, thus we only utilized electrospinning to produce liquid droplets/films directly on the wires of the stent, and subjected the coated stent to heating/curing at different temperatures. We expected that silicone can fully cover the whole wire and attached strongly to the wires. The thin film-like silicone coating on stent wire can make the surface smooth and could add flexibility and strength to the whole stent mesh.

The objective of the present study was to investigate the effect of silicone coating of individual wires of a titanium-nickel (TiNi or Nitinol) stent on the deployment force of the stent. We utilized an electrospinning technique as our coating method using a laboratory-made automatedelectrospinning system. Ourmain goal was to reduce the frictional coefficient at the stent interface by producing a uniform surface roughness of TiNi stents by means of silicone film coating.

2. Experimental

Electrospinning was carried out using the electrospinning system (Fig. 1a) used in our previous study[7]. Silicone solution (17 wt%) was prepared by dissolving silicone mixture (Nusil Silicone Technology) in acetone/ xylene (1:1) solvent by magnetic stirring. The silicone solution was electrospun for 1 h at 20 kV for a tip-to-collector distance of 70 mm and a feed rate of 80μl/min. Nitinol stents (from MITech., Korea, length = 8 cm; inner diameter = 10 mm) were used directly as collector, placed on a rotating mandrel.After electrospinning, the coated stent was heated at either 150 or 200^{o}C in an oven. Then, characterization and tests followed.

The morphological properties and thickness of coating were observed using scanning electron microscopy (SEM, Hitachi X-650, Japan). Energy dispersive spectroscopy (EDS) was utilized to check the elemental composition of the samples. The tensile properties of the silicone films only (without the stent) were obtained using an Instron Bench-type Tensile Tester (LR5K Plus, Lloyd Instruments, 100 N loadlimit). We used a dog-bone specimen based from ASTM D882-10. The specimens were fixed on a paper frame by taping both ends of the specimen. The crosshead speed was 10 mm/min and 5-10 specimens were tested for each sample. The thickness of the specimens were measured using a digital microcaliper (Mitutoyo Absolute, Mitutoyo Corp., Japan) with an accuracy of ±0.5 μm by getting the average value of at least 3 measurements.Deployment (push-out) tests were carried out using a bench-type tensile test machine (1000 N load cell, LRX Plus, Lloyd Instruments) at a crosshead speed of 50 mm/min. The catheter had an inner diameter of 2.38 mm and a length of 1800 mm.

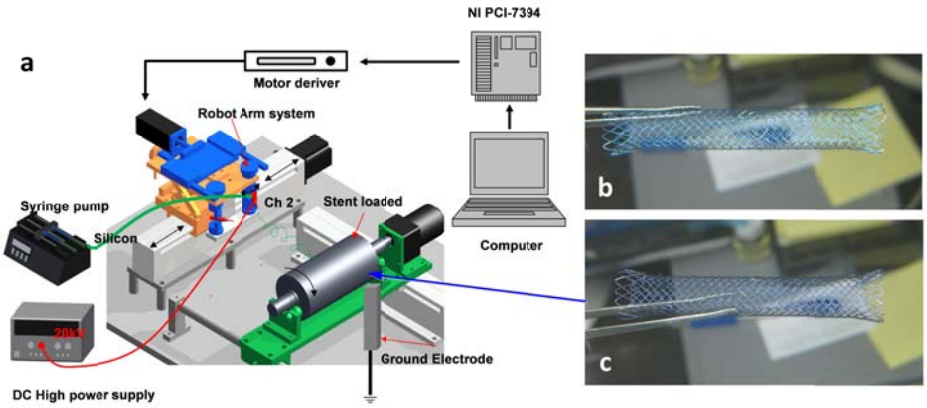

Fig. 1.(a) Electrospinning set-up, (b) bare (uncoated) Nitinol stent, and (c) Silicone-coated silicone Nitinolstent.

3. Results and discussion

It is important for stents to have optimal surface roughness so as to enable easy deployment from the catheter/introducer during insertion and to allow good tissue bonding once the stent is placed in the target area[8]. This will lessen the chances of stent migration inside the body, which could pose danger to human health. In this study, we utilize electrospinning to selectively coat the individual wires of a Nitinol stent. Instead of a stream of nanofibers being fabricated on the stent, a jet of ultrafine liquid solution is ejected from the nozzle tip towards the Nitinol stent that served as direct collector. It is very hard to produce nanofibers with silicone. This presents a facile and one-step way for directly coating the wires without film formation in the spaces between the intersecting wires. Figures 1c show a more dull colored stent after being coated with silicone film as compared to the brighter-colored bare stent (Fig. 1b).

A closer look at the bare stent (Fig. 2a) showed uneven surface roughness. EDS spectra of Fig. 1 confirmed the presence of Ti and Ni on the metallic stent. When silicone was coated (Fig. 2b), the surface shows uniform coating around the wire.EDS spectra confirmed that the coating was indeed silicone from the high intensity Si peak observed. It is very interesting to note that the whole stent wire was coated with silicone (Fig. 2c and 2d), not only partially at the electrospinning side. The wire was fully-enveloped with silicone coating thereby making sure the uniformity of coating throughout the stent.Silicone is a common material used for biomedical application especially as cover for stents because of its good biocompatibility properties[9]. As silicone is normally dried/cured after fabrication, we checked the effect of curing temperature at the silicone film tensile properties.

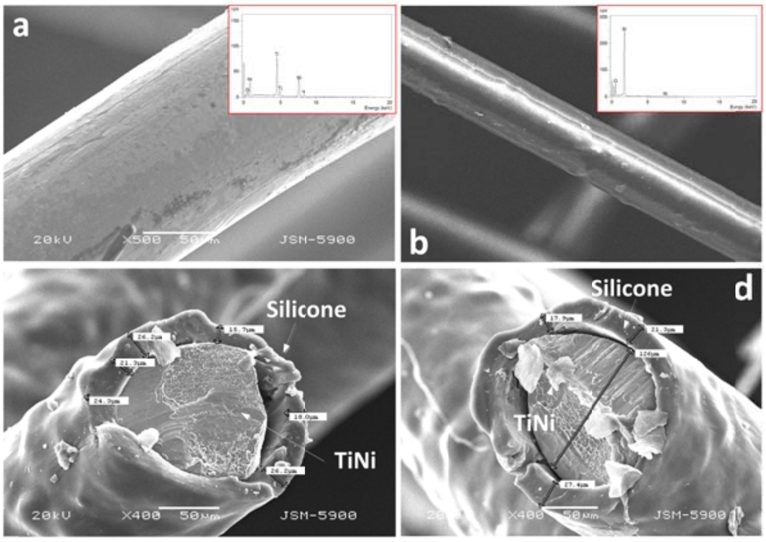

Fig. 2.SEM and photographic images of bare and silicone-coated stents: (a) bare Nitinolstent (inset: EDS spectra); (b) silicone-coated Nitinolstent wire; cross-section of silicone-coated Nitinolstent wires cured at (c) 150^oC, and (d) 200^oC.

Figure 3 shows the tensile properties of silicone film only after drying/curing at 150 and 200^{o}C. The stress-strain curves showed similar trend for both heat-treatment temperatures. Curing at 200^{o}C showed better tensile strength and strain compared to heating at 150^{o}C. Heating at 200^{o}C showed a tensile strength and strain of 9.75 MPa and 3900% strain, respectively, while heating at 150^{o}C showed lower tensile strength (8.5 MPa) and strain (3250%). The heat treatment has improved the properties of silicone when compared to silicone film dried at room temperature, with tensile strength of 3.9 MPa and strain of 2063% as reported in our previous study[10]. As shown in Fig. 2c, smoother silicone coating was also achieved at 200^{o}C heating. This tensile property improvement could provide beneficial effects on using silicone and its curing for stent coating. The thickness of the silicone was around 77 μm.

Figure 4a shows the deployment test through pull-out of Nitinol stent from catheter. This is important for the administering person to enable to have a smooth deployment of stent to the targeted area. As can be seen, the bare (uncoated) stent required much higher force during deployment at a maximum force of 2.66 N. This is attributed to the rougher surfaces of the bare stent. On the other hand, coated stent showed a lower maximum force of 2.35 N. This confirms the positive effect of selective silicone wire-coating of stents. Silicone has provided smoother surface and a better biocompatible condition. It was reported that a smoother stent surface has low thrombogenic tendency and neointimal hyperplasia compared to rougher surface [11]. Additionally, the silicone coating which has high tensile strain has provided flexibility to the whole stent. As can be seen in Fig. 4c, silicone-coated stent showed round corners upon bending compared to diamond-shaped corner of the bare stent. This could help in increasing the durability of stents when exposed to constant pressure when inserted inside the body. The coated stent showed an increased returning force of 23-25 gf compared to 21 gf of the bare stent. Furthermore, the radial force was also found to improve from 15-160 gf of bare stent to 170-180 gf after coating (results not shown).

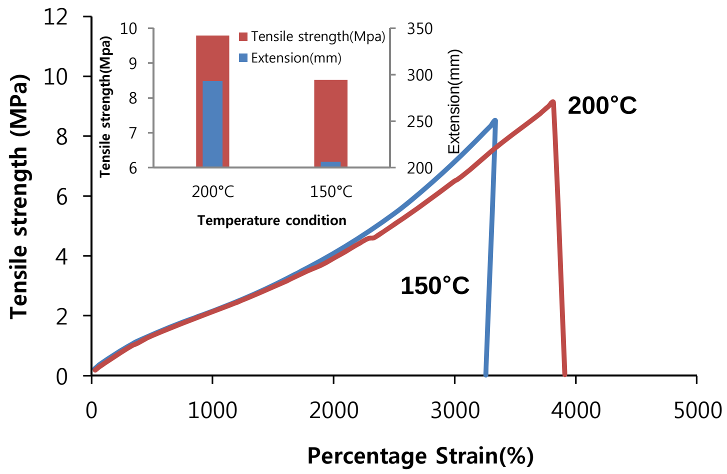

Fig 3.Stress-strain curves of the silicone film (without wire) cured at different temperatures.

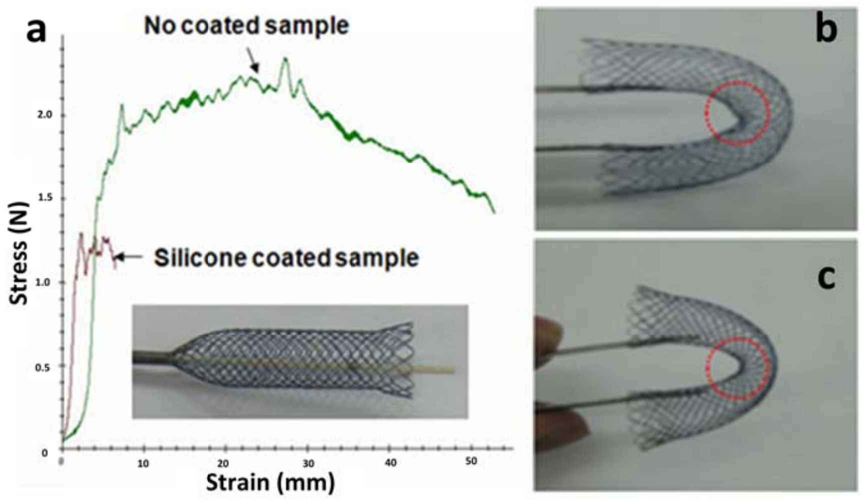

Fig. 4.(a) Depolyment/pull-out test graph of coated and bare stents; photographic images of (b) bare and (c) silicone-coated Nitinol stents after simple bending.

4. Conclusions

We present here for the first time the coating of individual wires of Nitinol stent by an electrospinning technique. Our results showed improved tensile properties of the silicone film when heated/cured at 200°C. By simple electrospinning of silicone, film-type coating fully-encapsulated each stent wire providing smooth surface and improved bending ability. Lesser force was needed for the catheter deployment of silicone-coated stent compared to the bare stent. This gives good advantage during the insertion of stent in operation. Our present study has shown the potential of electrospinning and heat treatment in improving the deployment ability of a coated stent. This approach also presents an initial step for possible inclusion of drugs in the coating for targeted-drug delivery applications.

Acknowledgements

This research was supported by grants from the Mid-Career Research Program of the National Research Foundation (NRF) of Korea (Project no. NRF-2013R1A2A2A04015484) and from the Business for Greening the Manufacturing Environment Technology Development Project funded by the Korean Small and Medium Business Administration (Project no. S2025435). Partial funding was provided by the Ministry of Education, Science and Technology (MEST) through the Leaders in Industry-University Cooperation (LinC) Project (Project no. 2012-C-0043-010111) and also from theBasic Science Research Program of NRF (Project no. 1201000217).

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