Tribology International 89 (2015) 54–61

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Friction behaviour of hydrophilic lubricious coatings for medical device applications

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ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form
9 January 2015
Accepted 1 February 2015
Available online 11 February 2015

Keywords:
Friction coefficient
Chitosan coatings
Hydrogels
Catheter coatings

ABSTRACT

The friction behaviour of new chitosan derivative coatings obtained by chemical modification of chitosan with fatty acids (linoleic and dilinoleic acid) has been investigated in order to explore their potential as endovascular catheter coatings and to benchmark them against commercially available coatings used in endovascular catheter applications. An *in vitro* tribological system was developed that was intended to represent to a limited extent the *in vivo* tribological conditions of a typical endovascular catheterization procedure. Continuous reciprocating sliding tests were carried out with uncoated and coated polymer specimens. The results showed that all of the coatings tested decreased the coefficient of friction compared to the uncoated polymer. Compared to a neat chitosan coating, the chitosan derivative coatings showed a clear reduction in the coefficient of friction to levels similar to those of the commercially-available coatings. A comparison between the friction results and contact angle measurements carried out on the coatings indicated that a range of contact angle values exists for which the friction coefficient is at a minimum. The reason for this is unclear and further studies are required in order to confirm and investigate the trend, especially within the context of hydrophilic lubricious coating development.

1. Introduction

Rapid progress and increasing needs in the biomedical field have contributed to the extensive development of polymeric coatings. Many of the improvements of currently used devices and new solutions have been led by the variety and tailor-made properties of polymer coatings [1–5]. The application of hydrophilic-type coatings can provide advantages such as good wetting, inducement of capillary flow, good biocompatibility, low protein adsorption, and in contact with blood, reduction of the risk of thrombogenesis. In endovascular catheterisation procedures, friction against the luminal surface of a blood vessel along which the catheter passes is integral to the insertion, manipulation and removal of the catheter by the operator. A hydrophilic coating on the catheter can replace or supplement the lubricating action of the endothelial surface layer [6], facilitating catheterisation [7].

Existing hydrophilic coatings are formed by polymers with functional groups able to absorb water molecules, such as amino, hydroxyl or carboxyl groups. For this reason the most commonly used polymers are acrylic polymers, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polyethylene glycols (PEG)s, some natural polymers such as polysaccharides, and various derivatives and their copolymers [8]. The primary focus of commercially available hydrophilic coatings for endovascular catheters is on improving the lubricity, maintaining a low and stable friction for the relatively short distance that the catheter slides against the vessel wall during the catheterisation procedure. This distance is associated with inserting, positioning, and removing the catheter after the treatment has taken place. For such applications, provided the friction does not increase during sliding, the coating wear behaviour is of minor importance since the catheters are single-use devices, discarded after use.

However, while these coatings have proven effective at reducing the incidence of spasm and improving patient comfort, the use of hydrophilic sheaths does not appear to prevent the reduction in flow mediated dilation, an index of endothelial dysfunction [9], and did not markedly influence the incidence of radial occlusion [10,11]. Further, the use of certain hydrophilic coatings (for example, those manufactured by Cook [12,13]) has been associated with the formation of sterile granulomas and abscesses [14–18]. Clearly, there is substantial room for improvement in the field of lubricious coatings for endovascular catheter use and, in particular, biodegradability would be a marked advantage.

Chitosan is a natural hydrophilic polysaccharide, which can absorb water, due to the presence of amino groups in the structure, despite being insoluble in water. It is also non-toxic, biocompatible,

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http://dx.doi.org/10.1016/j.triboint.2015.02.003
0301-679X/

and, importantly, biodegradable, in addition to possessing some antimicrobial activity [19–21]. To improve the physical and biological properties, as well as widen the range of potential applications, versatile chitosan derivatives have been synthesised [22]. Amphiphilic derivatives are especially interesting, due to the presence of a hydrophobic molecules in the chitosan structure, which can modify the rheological behaviour, resulting in self-assembly ability [23–25]. There are also studies that show improvements in blood compatibility and antimicrobial activity [26]. Our prior work has explored the modification of chitosan with fatty acids (linoleic and dilinoleic acid) and examined the antimicrobial properties of these new materials [27,28]. Catheter related infections remain a serious problem in both intravascular applications [29] (indwelling catheters, in particular), as well as in urinary applications [30]. As a result, the combination of blood compatibility and antimicrobial properties, if combined with good lubricity, would make these chitosan derivatives of great interest as coatings for catheter applications.

The aim of our present work was to investigate the friction behaviour of the chitosan fatty acid derivative coatings, benchmarking them against commercially available coatings, in order to assess their potential for catheter coating applications. For this purpose an *in vitro* biotribology test system was developed. It was our goal to emulate the *in vivo* friction conditions of a typical endovascular catheterization procedure, whilst avoiding many of the experimental and regulatory issues associated with *ex* vivo and *in vivo* testing. The test system, which was necessarily limited in its ability to simulate the real conditions, consisted of synthetic materials instead of living tissues or blood to minimise variability resulting from the lack of reproducibility of living tissues and also to facilitate comparisons between the coatings.

2. Experimental

2.1. Tribological system

An *in vitro* tribological system was developed in order to compare the friction behaviour of hydrophilic coatings intended to be used on the outside of cardiovascular catheters. As far as possible, the individual elements of the system were matched to reflect the conditions of the catheterization process.

2.1.1. Tribological testing conditions

Reciprocating sliding friction tests were carried out using a CETR (Brüker) UMT Multi-Specimen Test System. The test set-up is shown schematically in Fig. 1. In line with the application, the value and stability of the friction coefficient were investigated for a total sliding distance of 0.9 m, this being a distance considered to be typical of a routine endovascular catheterisation procedure. Because it is the friction behaviour rather than the wear behaviour that determines the performance in this application, the actual wear of the coatings in terms of volumetric wear loss was not investigated here. The coatings to be tested were deposited on injection-moulded spherical poly(ether-b-amide)(PA) polymer probes (representing the catheter material) with a diameter of 3.95 mm and rubbed against flat pieces of soft poly(vinyl alcohol) (PVA) hydrogel which represented the blood vessel. During the test, the probes were partially immersed to a depth of approximately 3 mm in a glycerol–water mixture representing human blood. A specially-designed holder enabled the wet hydrogel to be fixed in place during the test, see Fig. 2. All friction tests were carried out at a load 0.1 N, velocity 0.5 mm/s and stroke 10 mm at room temperature and each test was repeated at least five times using fresh materials and coatings for each test to obtain the average and standard deviation values shown in the results section. Estimates of the contact radius (r) of the circular contact area and of the mean contact pressure (P_m) were made using a Hertzian contact model (see below) where R is the radius of the spherical probe, N is the normal force and E′ is the effective modulus of elasticity

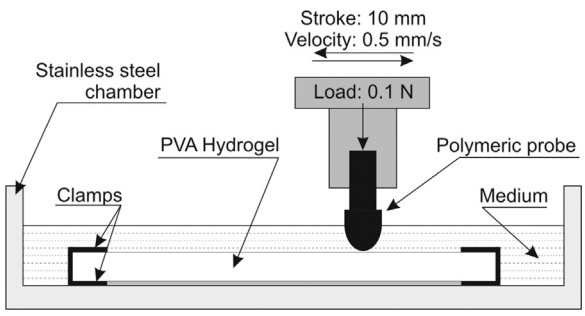

Fig. 1. Schematic diagram of the tribosystem.

$$\text{(Spherical) contact Radius } (r) = \left(3RN/2E'\right)^{1/3} \tag{1}$$

$$\text{Mean contact pressure } P_m = \frac{N}{\pi \times r^2} = \frac{1}{\pi} \times \left(\frac{2 \times E'}{3 \times R}\right)^{2/3} \times N^{1/3} \tag{2}$$

The effective elastic modulus is given by

$$\text{Effective elastic modulus } E'^{-1} = \frac{1}{2} \times \left(\frac{1-\nu_P}{E_P} + \frac{1-\nu_H}{E_H}\right) \tag{3}$$

where E_P, E_H, ν_P and ν_H are the elastic moduli and Poisson constants of the probe and hydrogel respectively.

Manufacturer's data (Arkema Group) was used for the elastic modulus of the PA33 material: 14.6 MPa. For the harder PA69 material the manufacturer's data (Arkema Group) on the flexural modulus was used as a first approximation of the elastic modulus: 510 MPa (ISO 178 test method). This is a reasonable assumption in view of the small expected deformation of the polymer in this case. For the PVA hydrogel the value of the compressive modulus at 0.1 N force was used as a first approximation of the elastic modulus: 16.8 kPa. A value of 0.4 was taken as the Poisson constant for the probe polymers PA33 and PA69 and a value of 0.44 was used for the PVA hydrogel [31]. Using the above equations and values, the estimated mean contact pressure in our experiments was 0.01 MPa for both the PA33 and PA69 material.

2.1.2. Blood vessel analogue (PVA hydrogel)

A key element of the tribological system developed here was the selection of contact partner of the coatings intended to simulate the blood vessel lumen. It is apparent from previous research into biomechanical modelling and the development of synthetic blood vessels for clinicians' training devices that PVA hydrogel can be used to simulate the interior of blood vessels [32–34]. In addition to having similar mechanical properties, PVA hydrogels have a high water content resulting in a low surface friction resistance and low interfacial energy with water or biological fluids [35], thus these materials can mimic human soft tissues.

An important advantage of PVA is the possibility to plan/design its properties by suitable selection of the ratio of hydrogel components, for example by changing the PVA and/or crosslinking agent concentration [36–38]. In this study, based on the work of Watler et al. [36], 10 wt% of PVA was chemically cross-linked using glutaraldehyde in the presence of magnesium chloride. The reaction of glutaraldehyde with hydroxyl groups of PVA results in a stable chemical network of acetal bridges.