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New tensiographic studies on protein cleaning of polymer surfaces

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Abstract

Presently, only indirect methods exist to monitor protein contamination of polymeric contact lens surfaces. This study, based on a fiber optic sensor, proposes a new quantitative and dynamic measurement technique to address this problem. Comparative contamination studies on three representative proteins: γ globulin, bovine serum albumin (BSA) and ovalbumin (molecular weight 240,000, 60,000 and 45,000), using a new tensiographic method, have been developed for a polymethylmethacrylate (PMMA) substrate.

Keywords: Tensiograph; Protein adsorption; Polymer surface; Surface contamination; Cleaning

1. Introduction

The monitoring of protein/lipid and other biomolecular contamination of the surfaces of contact lenses can only be assessed with indirect methods. Perhaps the most relevant work developed to date on the contamination of surfaces by proteins is that of Matsumura et al. [1]. Work by Chandry and Scully [2] and co-workers found that hydrophobic polymer surfaces on their optical-sensor were easily contaminated and those of hydrophilic glass were not. Most polymeric materials such as, polyethylene, polypropylene, polystyrene, acrylic nylon and biomedical polymers are strongly hydrophobic. McMillan et al. [3] found that acrylic nylon was very easily contaminated by biomolecules in beers whilst nylon 66 was not easily contaminated.

Polymers generally present surfaces that have a very high site density and which interact strongly with proteins. The highest molecular weight polymers are generally the ones that adsorb protein more readily [4]. It is common to consider that many segments of a protein molecule being attracted by a surface site interacting with hydrophobic domains, or alternatively, an interaction that arises from a surface site interacting strongly with patches on a protein. Moreover, ionic interaction can bind protein molecules to solid surfaces very strongly. Air–water studies have shown that proteins only need to get sufficient foothold on the surface to minimise the probability of desorption. Once attached to the surface, the protein being surface active moves towards the interface. It is clear that the binding to a surface increase with increasing hydrophobicity of the surface and with increasing hydrophobicity of the protein. Norde [5] reported in a classic study that desorption from hydrophobic surfaces under normal circumstances does not usually occur but exposure to extreme pH, high ionic strength, or extensive rinsing can remove the proteins. Recent work has shown that proteins can be replaced by suitable surfactants from liquid interfaces [6,7].

The present work is indeed a very close analogue of Norde's work [5], however, Norde's sensitivity throws some doubt on the validity of the conclusions drawn and the efficacy of standard procedures for cleaning surfaces. Studies on serum albumin molecules on glass surfaces show that the adsorption is considerable. Given that micron thick layers have been reported and the size of this molecule is only of the order of 5 nm multilayer structures must be formed. Terashima and Tsuji [8] studied the adsorption of bovine serum albumin (BSA) onto mica surfaces

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by a direct weighing technique to determine the thickness of the adsorbed layer and contact angle measurements to determine the degree of surface covering. They found that over time the thickness of the adsorbed layer was increasing after the mica surface had been completely covered. They concluded, "The excess of adsorbance can be attributed to an adsorption of BSA molecules onto the adsorbed BSA layer because the mica surface has been confirmed to be completely covered at earlier stages of adsorption. Accordingly, it is safe to say that a multilayer adsorption of BSA molecules takes place if the adsorption is continued for a long period." Silberberg found importantly that the forward reaction of adsorption, is limited, and reproducibly so, by concentration [4]. Clearly, a precise concentration dependent factor is at work. These findings are highly relevant to the experimental work reported here.

2. Apparatus

The multianalyser tensiograph [9] was developed on the principles of stalagmometric instruments. It is a fiber optic instrument based on some simple principles of physics. An infra red or visible beam reflects light through a drop while it is forming. The instrument monitors the optical coupling between source and collector fibers placed in the drop-head and the opto-electronic signal produced is known as a tensiotrace. Every liquid has a unique drop shape and hence a unique tensiotrace, which leads to the fingerprinting capability of the instrument. Therefore, the instrument is fundamentally a development of surface and interfacial science because it is based on the analysis of an optical signal determined fundamentally by the shape of the liquid on the drop-head.

The present study is concerned only with the analysis of protein solutions, but the technique has been used in a number of other application areas [10–12]. From current work it is clear that there are a wide range of other potential application areas for the multianalyser such as adhesive manufacture, in food analysis where it can be used to analyse oils and other liquid products and in pharmaceutical fingerprinting for the forensic identification of drugs.

The drop-head used in this work is of a concave design. A drawing of the head is shown in Fig. 1. The design employs 1 mm polymethylmethacrylate (PMMA) fibers. The fibres are down polished to 0.3 μm using lapping film before gluing them into the drop-head. The drop-head is made from poly-ethyl-ethyl-ketone (PEEK). The diameter of the head is 9 mm with the fibers separated by 6 mm.

The fibers are positioned with a jig to give a standard tensiotrace and just protrude a small distance from the concave base. A HPLC capillary, glued into the centre of the head is used to deliver the liquid. The head is designed such that it wets (i.e. the suspended liquid covers the entire lower surface of the drop-head) when liquid is delivered. Light from an LED source is injected into the drop-head through the source fiber and the signal is picked up by the collector fiber and goes to the photodiode, which then produces the trace. Water is taken as the reference liquid for most applications. The principal features of the tensiotrace (rainbow peak, the tensiograph peak and the drop period)

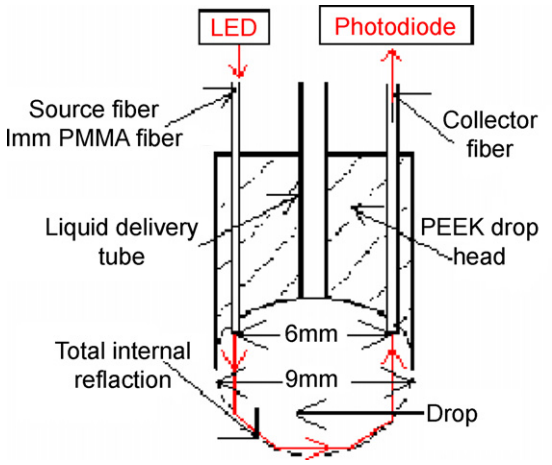

Fig. 1. Drop-head design for PMMA fibers cylindrical head showing the light trace from the source to the detector.

obtained for a water sample are illustrated in Fig. 2. A number of peaks essentially arising from total internal-reflection have been observed in various drop-head designs with different fiber spacings. This is due to the light coupling by different types of reflections from the source to the collector fiber on the far side of the drop-head. In this drop-head second and third order reflection deliver two peaks at different sizes of drop.

The Multianalyser operates by recording just one single tensiotrace. The tensiotrace is scissored from the incoming A/D detector signal, which is produced from the light collected from the collector fiber. The trace is obtained by recording the opto-electronic signal between the fall of two drops from the head. To achieve this scissoring a "trigger drop" is formed and falls from the drop-head. First, the data acquisition is triggered by the control signal of optical eyes situated below the drop-head. The recording of the signal from the detector on the end of the collector fiber then proceeds until the second drop, the measurement drop, falls. The data for this measurement drop is then stored in the archival system of the computer after conversion to a digital form by the A/D card. The trace recorded for a single drop is known as the tensiotrace and is a unique fingerprint of the liquid.

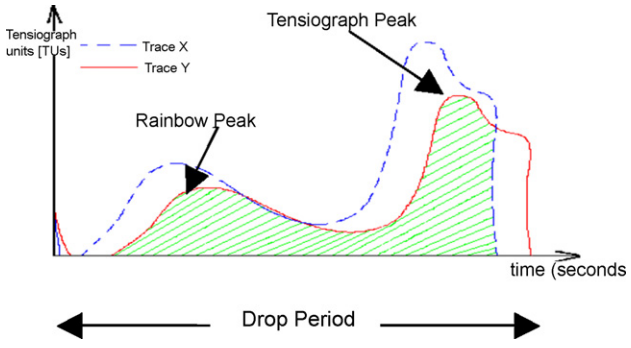

Fig. 2. Typical water tensiotrace showing the characteristic features and the overlap area between two traces.