Two-Dimensional NMR Relaxation Study of the Pore Structure in Silicone Hydrogel Contact Lenses

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Received 15 July 2008; revised 3 September 2008 © Springer-Verlag 2009

Abstract. A combination of two-dimensional nuclear magnetic resonance (NMR) proton relaxometry and differential interference contrast optical microscopy is used to compare the pore structures of hydroxyethyl methacrylate-based hydrogels used in conventional contact lenses with three silicone hydrogels primarily developed for continuous-wear contact lenses. It is shown that both types of hydrogel have a connected network of nanopores but that, in addition, the silicone hydrogels contain pores on the micrometer scale that enhances their permeability. The potential of other two-dimensional NMR relaxation and diffusion methods for detailed characterization of hydrogels is discussed.

1 Introduction

In recent years two-dimensional (2-D) nuclear magnetic resonance (NMR) relaxometry has emerged as a powerful new tool for probing the microscopic distribution of water in porous materials. Following pioneering studies on porous rocks [1, 2], 2-D relaxometry has been applied to many diverse materials including complex foods [3, 4], cellular tissues [5, 6] and cement [7, 8]. In this paper we report, for the first time, its application to novel synthetic silicone hydrogels that have been primarily developed for use in continuous-wear contact lenses. Conventional, noncontinuous-wear lenses are based on hydroxyethyl methacrylate (HEMA) which because of its hydroxyl groups is hydrophilic, having an equilibrium water content of about 38 wt%. To maintain material stability and transparency, the polymer chains are usually cross-linked with 1% ethylene glycol dimethacrylate. A number of flow studies have been undertaken to investigate the average diameters of the pores in HEMA-based hydrogels and these suggest that the water, ions and oxygen diffuse through a connected aqueous network of nanopores [9].

To satisfy the demand for continuous-wear contact lenses, several novel silicone hydrogels have been developed. For continuous wear the contact lenses need
to have not only water and ion permeabilities at least as high as conventional HEMA-based contact lenses but also much higher oxygen permeability to obviate adverse corneal hypoxic complications. This is the case with silicone hydrogels because oxygen can now diffuse not just through the aqueous phase as in HEMA-based lenses but also through the silicone-based polymer phase. However, the water and ion permeability is still controlled by the aqueous pore network, and determining the pore structure in silicone hydrogels has been problematic because of their biphasic nature. This biphasic structure arises because they are manufactured using mesophase polymerization and phase inversion. Mesophase polymerization involves preassembly of intermediate polymer groups (blocks) as described in several patents [10–12]. Phase inversion is the innovative polymerization process that causes phases within a system to interchange so a dispersed phase becomes the ordered continuous phase and vice versa [13]. Typically this approach has controlled the phase separation expected when mixing a hydrophilic phase with, for example, hydrophobic silicone to ensure lens transparency in low-water-content silicone hydrogels and phase continuity [12].

In this paper we therefore use a combination of optical microscopy and 2-D NMR proton relaxometry to try to compare the pore structure of conventional HEMA-based hydrogels with that of three commercial silicone hydrogels. As we shall see, our results suggest that the silicone hydrogels not only have a connected nanopore structure similar to that found in HEMA-based materials but also contain pores on the much larger micrometer distance scale and this gives them their unique permeability properties.

2 Materials and Methods

Four different hydrogels were studied, comprising a conventional HEMA-based material (Contaflex) and three novel silicone hydrogels being developed for continuous-wear contact lens applications (Air Optix Night and Day, PureVision and Acuvue Advance). The hydrogels were received either as dried samples or hydrated in physiological saline. Those in saline were repeatedly purged in purified water and checked for salt concentration by impedance spectroscopy. Other samples were fully dehydrated by heating to 80 °C in a vacuum, until constant weight was obtained, and then hydrated again to constant weight with purified water. The equilibrium water content (EWC) of the samples was obtained from the relationship: EWC (wt%) = [(hydrated wt − dry wt)/hydrated wt] · 100%.

An Oxford Instruments DRX spectrometer operating at a proton frequency of 23.4 MHz was used for all NMR measurements using a NMR sample tube with a diameter of 10 mm. To minimize dehydration a polytetrafluoroethylene (PTFE) piston was placed against the sample and the holder was then sealed. This arrangement was then weighed on a high-precision balance before and after pulse sequence investigations to confirm the level of dehydration, minimal differences were observed typically less than 1%. The temperature of the samples was stabilized at 298±0.5 K. 90-degree pulse lengths were typically between 2–5 μs. 1-D relaxation data was deconvoluted as a continuous distribution of relaxation times with