Polymer 118 (2017) 150–162

Contents lists available at ScienceDirect

Polymer

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

Influence of silicone distribution and mobility on the oxygen permeability of model silicone hydrogels

Michelle E. Seitz [a, *], Meredith E. Wiseman [a], Iris Hilker [a], Joachim Loos [b], Mingwen Tian [b], Junyu Li [b], Mithun Goswami [b], Victor M. Litvinov [b], Scott Curtin [c], Markus Bulters [a]

[a] DSM Ahead – Material Sciences R&D, P.O. Box 1066, 6160 BB Geleen, The Netherlands
[b] DSM Resolve, P.O. Box 18, 6160 MD Geleen, The Netherlands
[c] DSM Biomedical, 2810 Seventh Street, Berkeley, CA 94710, USA

ARTICLE INFO

Article history:
Received 13 March 2017
Received in revised form
23 April 2017
Accepted 24 April 2017
Available online 27 April 2017

Keywords:
Silicone hydrogel
Contact lens
Morphology

ABSTRACT

In order to understand the influence of composition on oxygen permeability, the morphology of model silicone hydrogels in both the dry and hydrated states was characterized using a variety of techniques (AFM, HAADF-STEM, solid-state NMR, and X-ray scattering). The model system studied is heterogeneous on length scales below 20 nm and consists of globular silicone-rich domains that rearrange in response to changes in hydration. In contrast to the well-defined morphologies of block copolymer systems, these radically cured amphiphilic networks are less ordered, showing gradual composition fluctuations. Comprehensive morphology characterization rationalizes the transport behavior of these heterogeneous hydrogels: the non-linear permeability increase with increasing silicone monomer content is not only related to changes in the spatial arrangement of silicone-rich domains but also to their mobility. This understanding is needed for further optimizing soft contact lens materials where oxygen transport and optical clarity are critical features.

1. Introduction and motivation

The morphology of well-defined block copolymer systems is well understood due to the extensive experimental and theoretical frameworks that have been developed in the past decades. In contrast, characterization and morphological understanding is lacking for radically cured amphiphilic networks, where the chain structure and monomer distribution is less well-defined. One difficulty is in accessing detailed information about the monomer distribution as it is influenced by copolymerization ratios, mobility constraints created due to cross-linking, and possible kinetic trapping. Despite their complexity, such systems are ubiquitous in a variety of applications from coatings to batteries to contact lenses. Performance properties such as stain resistance of paints, oxygen transmissibility of contact lenses, and lithium ion conductivity in polymer electrolytes for batteries are related to transport within the material. This in turn is strongly influenced by the details of the morphology. In this paper, we demonstrate a multifaceted characterization approach in order to gain a detailed understanding of the morphology of model silicone hydrogels to better rationalize their oxygen permeability.

The oxygen permeability of contact lenses is relevant because clinical complications can result if lenses too severely restrict the supply of oxygen to the cornea [1]. Oxygen permeability is the product of oxygen diffusivity and solubility. It is commonly referred to as 'Dk' in contact lens literature and is reported in units of Barrers, equivalent to 10^{-11} [(cm^3 O_2 STP)·cm^2/(cm^3·s· mmHg)]. For traditional hydrogels, the oxygen permeability is well described by an empirical exponential relationship between equilibrium water content (EWC) and Dk as shown in Fig. 1 [2]. Handling and dehydration concerns at high water contents limit the Dk values for traditional hydrogel contact lenses. To reach higher permeability, silicones were incorporated because of their high intrinsic gas permeablility [1,3]. For example, the Dk of polydimethylsiloxane (PDMS) is ~800 Barrer [4]. Commercial silicone hydrogel lenses have Dk's between ~50 and ~150 Barrer (see Fig. 1), exceeding that of pure water (~90 Barrer) [5]. Unlike traditional hydrogels, the permeability of silicone hydrogels is not dominated by water content. One key difference between traditional hydrogels and silicone hydrogels is the possibility of a complex morphology due to the

* Corresponding author.
E-mail address: michelle.seitz@dsm.com (M.E. Seitz).

http://dx.doi.org/10.1016/j.polymer.2017.04.061
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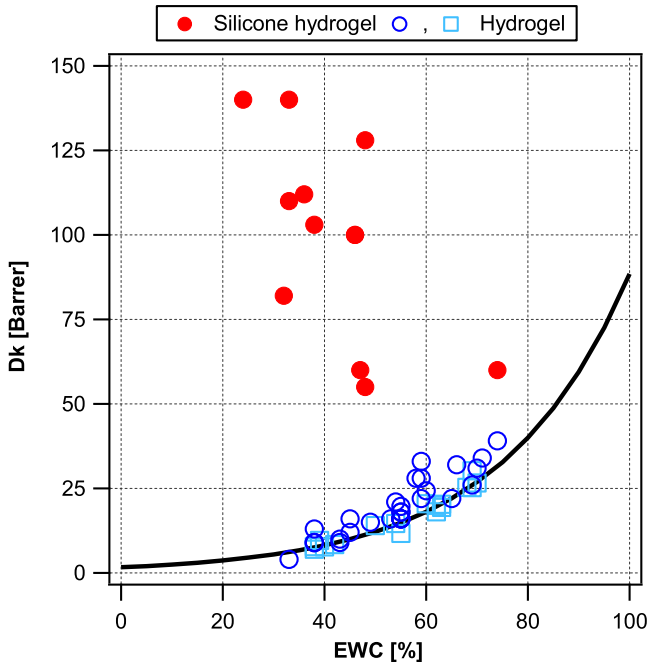

Fig. 1. Oxygen permeability (Dk) versus equilibrium water content (EWC) for commercial contact lens materials. Silicone hydrogels are shown as filled red circles and traditional hydrogels as open blue symbols. Circles are data on commercial contact lens materials reported in Ref. [6] and squares are reported in Ref. [2]. The line corresponds to the empirical relationship $Dk = 1.67e^{(0.0397*EWC)}$ proposed by Morgan and Efron for traditional hydrogels [2]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

incompatibility between silicones and water.

Nicolson and Vogt proposed that silicone hydrogels can be considered as composites of sharply distinguished hydrogel and silicone phases, each with fixed properties [1]. In this case, the overall permeability depends on the amount of silicone, its intrinsic permeability, and how it is spatially distributed. Fig. 2 shows how the Dk would theoretically depend on silicone content and distribution as well as illustrating possible morphologies for silicone hydrogels. The permeability of the silicone phase may be lower than that of pure silicone rubber because confinement could reduce the siloxane mobility and lower diffusivity. Confinement could arise from a domain boundary or a network constraint. If the silicone were distributed as non-connected inclusions, the overall permeability would be limited by that of the hydrogel phase. Only if the silicone percolated throughout the sample would there be a significant benefit for Dk and the level would be dependent on the path tortuosity. In the alternative limit, these materials could be well-mixed even at short lengthscales. In this picture, the spatial distribution of silicone is homogeneous and the permeability should increase linearly with the silicone content.

A few studies have experimentally investigated the influence of silicone monomer content on permeability. Lai observed that the oxygen permeability first decreases with silicone monomer addition before increasing at higher content for several different silicone hydrogel systems but did not perform morphological characterization [7,8]. Zhao et al. reported similar behavior for two silicone hydrogel systems and additionally showed that at a fixed silicone content the degree of hydration also influences the permeability [9]. Supported by some TEM analysis, they argue that complex relationship between silicone monomer content, water content and permeability is related to whether the hydrated or silicone phase forms the continuous phase. Tao et al. studied the

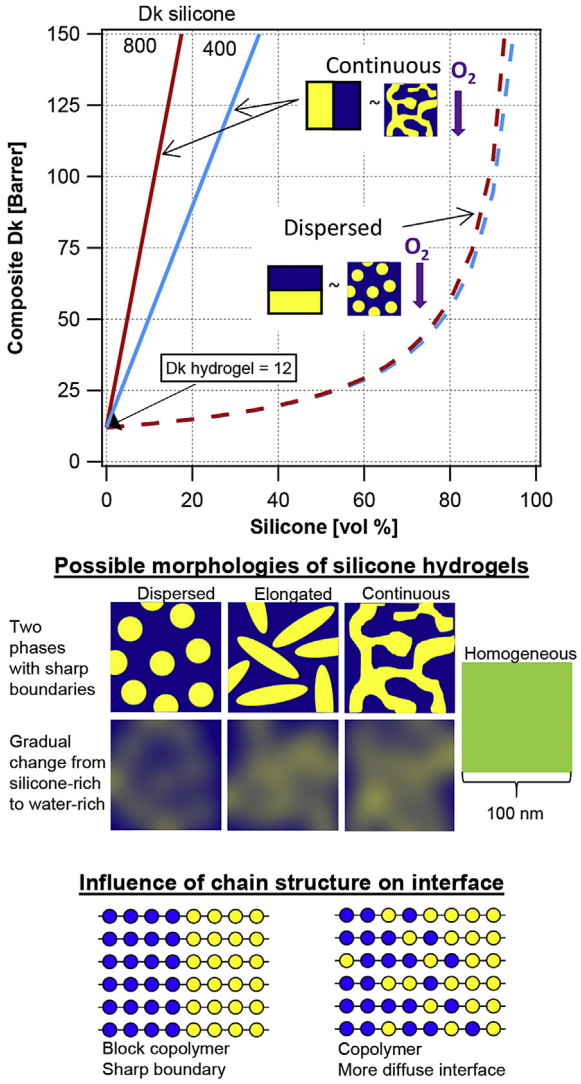

Fig. 2. Dk values versus silicone volume percent for a binary composite with fixed properties. Parallel or series arrangements of silicone (yellow) and hydrogel (blue) model bounds are plotted as solid or dashed lines, respectively. Model assumes silicone Dk = 800 (red line) or 400 Barrer (blue line) and hydrogel Dk = 12 Barrer (equivalent to hydrogel with EWC = 50%). Simple possible morphologies for well-defined domains as well as gradual composition variations and a completely homogeneous material are schematically drawn below. Also drawn is how monomer distribution could influence boundary sharpness between domains. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

influence of molecular weight for difunctional siloxane macromers on oxygen permeability, mechanics, and optical clarity for model silicone hydrogels [10]. From TEM analysis, they argue the morphology transitions from discrete domains to continuous to macroscopically phase separated as the silicone length increases from 1 to 10 kg/mol at a fixed silicone concentration.

While these studies indicate that morphology influences the oxygen permeation of silicone hydrogels, open questions remain as no study has combined permeability data with systematic morphology determination over a range of compositions due to difficulties in characterizing soft, hydrated networks. Additionally, the diversity of chemistries and processing methods found in commercial silicone hydrogel lenses and the academic literature makes it difficult to draw conclusions about the relative contributions of morphology and silicone content and structure. For information on chemistries used in silicone contact lenses and an