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Characterization of network morphology in anion binding hydrogels used for wastewater remediation

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Abstract

This work reports on morphological features of hydrogels, which have been used for the ultimate removal and recovery of nutrient and toxic anions from wastewater effluents. The sorbent used was crosslinked polyamine (PAA·HCl) polymeric hydrogels. The surface topography and morphology of these hydrogels were characterized by tapping mode atomic force microscopy. The change of the gel surface in response to the degree of crosslinking was observed via phase imaging. The crosslinker amount affects both the crosslink density and uniformity. Phase images were recorded at moderate to hard tapping conditions ($A_{sp}/A_0 = 0.3–0.6$) and related to surface stiffness variations associated with Young's modulus (E) change. Bright ellipse and sponge-like domains of submicrometer scale were found on irregularly crosslinked gels, while the gel topography was uniform in gels that were prepared with a more regular distribution of crosslinks. The observed AFM domain size was strongly affected by the gel's degree of crosslinking.

Keywords: Hydrogel; Atomic force microscopy; Wastewater

1. Introduction

It has been recognized that properties of polymer networks, such as mechanical strength, thermal, viscoelasticity, kinetics of deswelling, ion binding, diffusion, and transparency, depend on their spatial inhomogeneities [1–8]. In every case, hydrogel performance in applications depends upon the details of the network structure. Often a single numerical value, a swelling ratio, or an effective crosslink density is employed to characterize the network structure [1]. More detailed and quantitative characterization of crosslinked polymer networks remains a frontier problem despite advances that have been achieved in the elucidation of the structure of linear (soluble) polymers. The insolubility of networks and their spatial/topological complexity are the principle reasons for the difficulty in characterization.

Although the swelling behavior of gels and the elasticity of such systems appears to be understood quite well [4], there are many questions concerning the structure of real polymer networks and the structure development during the sol–gel transition process. In contrast to model networks, which have a constant length of network chains between crosslinks, real networks display a large variation in chain lengths between network crosslinks. In addition, a number of network defects, such as dangling ends, crosslink agglomerations, concentration fluctuations, and elastically ineffective crosslink loops [1,4] are known to occur. These inhomogeneities have been shown to influence the elastic, swelling, and ion binding properties by changing the effective crosslink density of gel networks.

Weiss et al. [9] first reported the presence of network inhomogeneities. Network inhomogeneities can be thought of as strongly crosslinked areas within a less densely crosslinked environment. The higher the crosslink density of a polymer network, the lower is its swelling capacity. Thus, inhomogeneously crosslinked gels consist of regions with relatively high polymer concentration, or crosslinker agglomerations, and more swollen or diluted regions with lower polymer concentration. On the basis of light scattering experiments Tanaka et al. [10] stated that gel network inhomogeneities were arising from two origins. The first is due to the formation of the inhomogeneities fixed or frozen in

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the gel during the gelation process. As the sol–gel reaction proceeds under certain conditions, the resultant linear and branched polymers exhibit critical concentration fluctuations or undergo domain formation due to phase separation. The fluctuations or domains are subsequently fixed by crosslinking, producing static (or frozen) inhomogeneities within the gel network. They may form a kind of internal structure, or microgels, permanently trapped in the resulting gel. Therefore, the degree of spatial inhomogeneities increases with increasing crosslinker concentration in the gel [5]. The second origin is due to the dynamic inhomogeneities. These are the dynamic thermal concentration fluctuations of the gel network whose amplitudes and relaxation times depend on the position in the phase diagram of the gel.

A number of techniques have been used for quantitative characterization of polymer gel networks. A convenient way to probe concentration fluctuations in a system is by light scattering methods. Light scattering investigations on gels have been performed in order to obtain information about inhomogeneities [4]. Shibayama et al. [5,6] have shown that the presence of spatial inhomogeneities in chemical and physical gels could be simply monitored by static/dynamic light scattering as speckles, i.e. random fluctuations in the scattered intensity as a function of sampling points. Schosseler et al. [11] carried out scattering studies on weakly charged acrylic acid gels and observed a scattering maximum, which they attributed to frozen-in inhomogeneities existing in the weakly charged gels due to the inhomogeneous distribution of crosslinks. Kofinas et al. [1] employed wide angle X-ray scattering and dielectric spectroscopy to elucidate crosslinking reaction condition variations on poly(allyl amine) gel structure. Hirokawa et al. [8] applied laser scanning confocal microscopy to translucent poly(*N*-isopropylacrylamide) gels and observed internal structures caused by the static inhomogeneities (or concentration fluctuations).

The objective of this work was to observing internal structures in epichlorohydrin (EPI) crosslinked poly(allyl amine) hydrochloride (PAA·HCl) gels caused by static inhomogeneities. The ionic polyamine gels have been demonstrated to be appropriate materials for treating various types of wastewaters in either the batch or continuous modes. Pollutant anion concentrations were reduced to levels suitable for discharge into natural surface waters. Phase imaging in tapping mode atomic force microscopy (TMAFM), a relatively non-traditional technique, was employed to satisfactorily characterize the topography and obtain a stiffness mapping of the PAA·HCl gel surfaces. This 'fingerprinting' technique aided in the understanding of the effects of various processing parameters (e.g. amounts of NaOH and EPI) on the gel morphology, and provided information on the network topography.

Variations in the conditions of the EPI crosslinking reaction led to reproducible changes in the swelling response, and anion binding capacity [2,3,12,13] of these materials, thereby leading to some sense of how the detailed network topology varies from sample to sample. A detailed understanding of a gel's morphology and the parameters influencing the gel formation will help the commercial manufacturer of these nutrient and toxic anion binding hydrogels create a reproducible material on a batch-to-batch basis, having control over its morphology and properties.

2. Materials and methods

The details of the gel synthesis an preparation can be found in Ref. [14]. Tapping mode atomic force microscopy (TMAFM) was performed with a multimode scanning probe microscope (SPM) and a nanoscope IIIa control system (Digital Instruments Santa Barbara, CA, USA). Topographic (height) and phase images were recorded simultaneously at ambient conditions. Commercial silicon cantilever probes, each with a nominal tip radius of 5–10 nm and spring constant in the range of 20–100 N/m were oscillated at their fundamental frequencies, which ranged between 150 and 200 kHz. The level of tapping force used during imaging is related to the ratio of the setpoint amplitude to the free-oscillation amplitude, hereafter called the set-point ratio (r_{sp}). As the set-point ratio decreases from 1 to 0, the tapping forces increase as the sample further restricts the oscillatory motion of the scanning probe.

Depending on the operating conditions, different levels of tapping force were required to produce accurate, reproducible images on different samples. The amount of tapping force used often affected the phase image, especially with regard to whether local tip–sample interactions are attractive or repulsive. For consistency two force levels corresponding to r_{sp} of 0.5 (moderated tapping) and 0.35–0.25 (hard tapping) were investigated. All images were recorded using a free-oscillation amplitude of 2.5–8.0 V. Imaging at higher tapping amplitudes has been shown to result in more repulsive tip–sample interactions than imaging at lower amplitudes [17]. Since the focus here was to investigate changes in phase contrast based on changes in stiffness, a relatively high oscillation amplitude was chosen. Scan sizes of 1 and 15 μm at scan rates of 0.5–1.0 Hz were obtained.

Flat circular hydrogel slabs were prepared for the experimental purposes, by the aqueous reaction of 5 mL of 25% w/v PAA·HCl (15,000 g/mol) solutions and EPI. The sol–gel mixture was poured into 5 cm petri dishes prior to the sol–gel transition point (which varied depending on the chemical composition of the gel) and were left to cure for 48 h in covered petri dishes. Upon curing, the gel slabs were placed in 100 mL beakers and washed in portions of deionized water to purge NaCl and any unreacted reactants from the network. Subsequently, the gels were air dried at 40 °C in covered petri dishes for 2–3 weeks.

The final microstructure of the PAA·HCl gel is influenced by the relative amounts of reactants used in